Supporting information

Unravelling the Effect of Side Chain on RAFT Depolymerization; Identifying the Rate Determining Step

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Methods

General materials

All chemicals were purchased from Sigma Aldrich, Alfa Chemistry or Fischer Scientific and used without any further purification. Distilled water was used for all experiments. NMR Spectroscopy. ^{1}H NMR spectra were recorded on a Bruker Avance-300 spectrometer in or $CDCl_3$. All the monomers were purified passing through a column of basic alumina before synthesis.

Computational methods

Standard density functional theory calculations were performed using Gaussian16.[1] Geometry optimizations and frequency calculations were performed at the M062X[2]/6-31G(d)[3-6] level of theory, using SMD[7] to model the 1,4-dioxane solvent environment. Intrinsic reaction coordinate (IRC)[8] calculations were performed to verify the connectivities of the optimized transition structures with the respective products and reactants. For the reactions of MMA, thorough conformational searches, with resolutions of 120° around sp^3-sp^3 bonds and 180° around sp^2-sp^3 bonds, were performed to locate the global minimum conformers of all species. For the reactions of HexMA, all equilibrium structures were also thoroughly searched to locate global minima. However, owing to their size, the build-up method was used to locate global minimum conformations of the transition structures. In this approach, minimum energy conformers of the reactants and products were first used to build conformers of the corresponding fragments in the transition structures, which were then subjected to additional conformational sampling around the relevant forming/breaking bonds. In order to obtain more accurate energies for all thus optimized equilibrium structures and transition structures, single point energies were calculated at the SMD[7]-(1,4-dioxane)-wB97X-D[9]/aug-cc-pVTZ[10, 11] level of theory. Gibbs free energies in solution were obtained using the "direct method[12] in which ideal gas partition functions are applied directly to solution-phase geometries and frequencies; a correction for the change of state from 1 atm to 1 M was included.[13] Noncovalent interactions (NCI) analyses[14] were performed using Multiwfn[15] and corresponding NCI plots were generated using VMD 1.9.4[16].

Size-exclusion chromatography (SEC).

Theoretical molar masses were calculated based on the target degree of polymerization and the amount of conversion achieved. SEC was measured on Shimadzu equipment comprising a CBM-20A system controller, LC-20AD pump, SIL-20A automatic injector, 10.0 μm bead-size guard column (50 x 7.5 mm) followed by three KF-805L columns (300 x 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), SPD-20A ultraviolet detector, and an RID-20A differential refractive index detector. The column temperature was maintained at 40 °C using a CTO-20A oven. The flow rate was set to 1 ml/min and with N, N-dimethylacetamide (DMAc, Acros, HPLC grade, with 0.03 w/v LiBr) as the eluent. The UV wavelength was set to 310 nm. Molar masses were determined relative poly(methyl methacrylate) standards with molar masses ranging from 5,000 to 1.5 x 106 g/mol (Agilent Technologies). All SEC samples were dissolved in DMAc and passed through 0.45 μm PTFE filters prior to analysis.

Polymer synthesis

PMMA will be used as the model example to describe a typical synthesis procedure. Into a 15 mL vial, 207 mg (RAFT agent 2-cyanoprop-2-yl dithiobenzoate (1 equiv.) was dissolved in 3 mL toluene. A stock solution of AIBN (20 mg) was prepared in 2 mL toluene, and 1.57 mL of this solution (0.1 equiv.) was transferred to the flask. Subsequently, the 4 mL monomer (40 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 79 % conversion by removing the reaction from the oil bath and removing the septum. (see Table S 1 for individual cases)

Table S 1: Characterization of the synthesized polymers by ^{1}H NMR and SEC.

Entry	Polymer	Target DP	Conv. (%)	DP_{theo}	$M_{n,theo}$	$M_{n,SEC}$	$Đ$	Precipitation solvent
1	PMMA	40	79	31.6	3300	3700	1.10	Methanol
2	PEtMA	40	74	29.6	3600	3600	1.13	Hexane
3	PBuMA	40	64	25.6	3900	3700	1.12	Methanol
4	PHexMA	40	68	27.2	4900	3400	1.11	Methanol
5	PLauMA	40	66	26.4	7000	--	--	Methanol
6	PEGMA	40	77	30.4	4600	5300	1.10	Pentane
7	PTEGMA	40	72	28.8	6900	6900	1.18	DET/Pentane
8	PPEGMA	40	77	30.8	14900	14800	1.14	DET/Pentane

Purification of polymers

PMMA will be used as the model example to describe a typical purification procedure. Polymers were precipitated twice times in methanol and filtered through a filter paper. The precipitates were dried in a vacuum oven for at least 12 h before use. (see Table S 1 for the individual cases). All the polymers were characterized by ^{1}H NMR and SEC.

Synthesis of block copolymers

The synthesis of PHexMA-b-PMMA will be used as a representative example for the synthesis of block copolymers. Into a 5 mL vial, 0.300 g of purified PHexMA-DTB (4830 g/mol, 61 µmol, 1 equiv.), 79 µL of MMA (7.42 µmol, 12 equiv.), 100 µmol of AIBN stock solution (61 mM, 6.19 µmol, 0.1 eq.), and 2 mL toluene were added. A stir bar was added prior to sealing the vial with a septum and stirred until completely homogeneous and subsequently bubbled with N_2 for 15 min. The reaction was lowered into a 70 °C oil bath and left to react till it reached more than 60%. The resulting block copolymer was precipitated three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Depolymerization kinetics

PMMA will be used as the model example to describe a typical depolymerization procedure. In a 15 ml test tube, 13 mg of PMMA was dissolved in 10 ml 1,4-dioxane (20 mM of MMA repeat unit). Poly(ethylene glycol) (350 g mol^{-1}) MW was added as an internal standard for NMR analysis. The test tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The glass tube was then put into a 120 °C oil bath to start the reaction. The tube was submerged into the oil bath until the surface of the solution inside was submerged ~3 cm below the surface of the oil bath. The reaction was periodically removed from the oil bath to take samples and quickly added to a water bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For NMR samples 0.5 mL of the sample solution was blow-dried and dissolved in deuterated chloroform.

Depolymerization procedure in presence of initiator

PMMA will be used as the model example to describe a typical depolymerization procedure in presence of ABCN. In a round bottomed flask of PMMA (13 mg, 0.024 mmol, 1 eq.) was dissolved in 10 ml 1,4-dioxane (20 mM of MMA repeat unit) along with 1,1′-Azobis(cyclohexanecarbonitrile) ABCN (11.89 mg, 0.048

mmol, 2eq.). 2 mL of the solution were divided between 5 glass tubes (5 mL), which were sealed with rubber septa. The solutions were degassed for 15 min and the glass tubes were put into a 120°C oil bath. The test tubes were taken out one by one at different time points, cooled and analyzed. For NMR samples 0.5 mL of the sample solution was blow-dried and dissolved in deuterated chloroform.

Depolymerization procedure of the block copolymers

A $[RU]_0$ = 20 mM depolymerization of PHexMA-*b*-PMMA will be used as a representative example. In a 20 ml glass tube, 35.23 mg of PHexMA-*b*-PMMA was dissolved in 11 ml 1,4-dioxane. 2 mg of 350 g/mol poly(ethylene glycol) monomethyl ether was added as an internal standard for NMR analysis. The tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 °C oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For NMR sample which ~500 μL of the reaction was blowdried with air before dissolving in $CDCl_3$.

Determination of depolymerization conversion

An internal standard is added in each reaction to ensure accurate conversion calculation through an alternative way. Specifically, a typical NMR sample was prepared by re-dissolving the dried reaction mixture (blowing the solvent with air). Conversions were then calculated by comparing the intensity of the backbone $–CH_3$ signals before and after depolymerization against a non-volatile internal standard (polyethylene glycol monomethyl ether). For non-volatile polymers (PPEGMA, PLauMA) depolymerization conversion was calculated by comparing the vinyl signals to the polymer backbone.

Additional data

^{1}H NMR and SEC characterization of the polymers

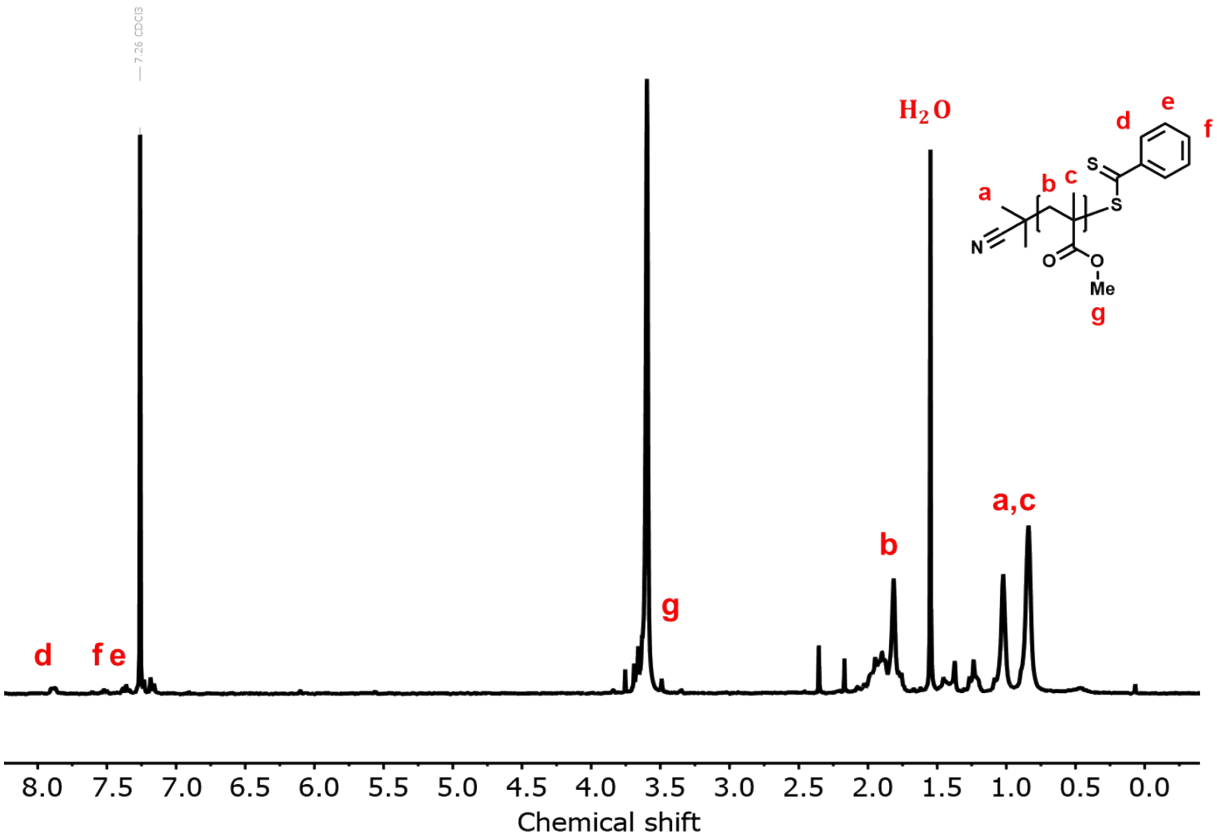


Figure S 1: ^{1}H NMR spectrum of purified PMMA prior to depolymerization.

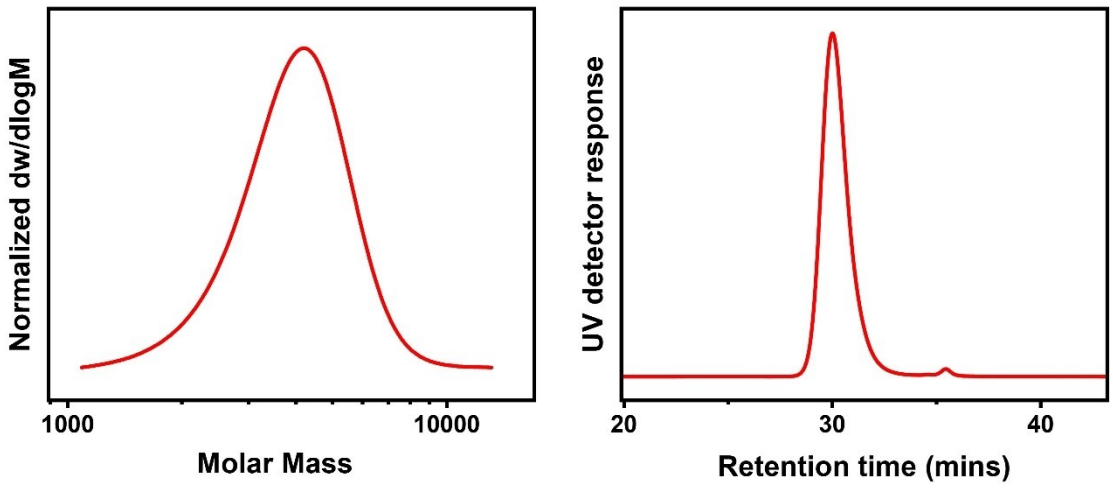


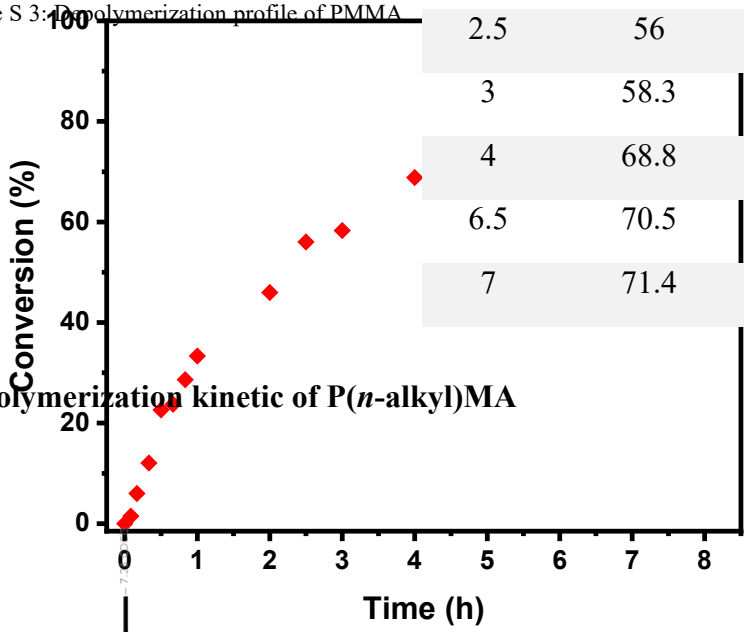
Figure S 2: SEC trace of purified PMMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion = 76%, $M_{n,SEC}$ = 3700 g/mol, $Đ$ = 1.11.

Depolymerization kinetics of PMMA

Table S 2: Depolymerization kinetic of PMMA in 1,4-dioxane at 120 °C, 20 mM RUC.

Time (h)	Conversion (%)
1	33.3
2	46
2.5	56
3	58.3
4	68.8
6.5	70.5
7	71.4

Figure S 3: Depolymerization profile of PMMA in 1,4-dioxane at 120 °C, 20 mM RUC.



Depolymerization kinetic of P(*n*-alkyl)MA

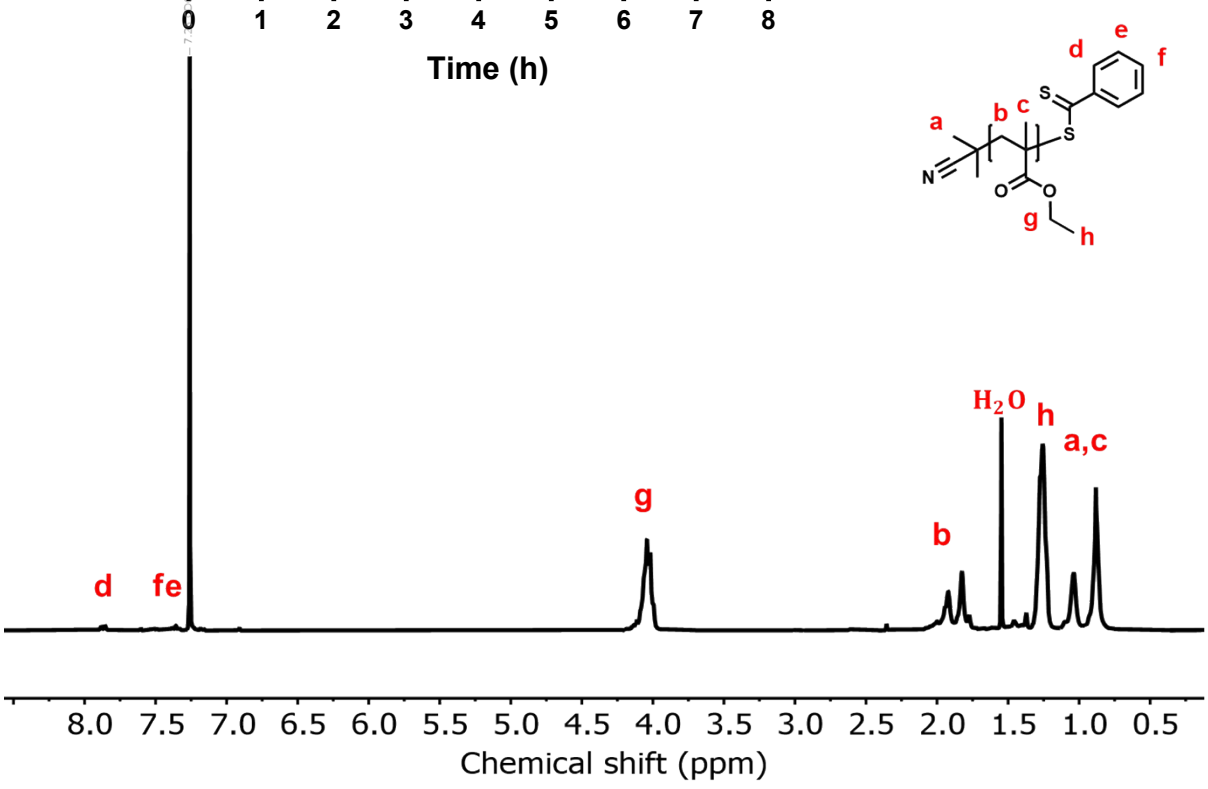


Figure S 4: ^{1}H NMR spectrum of purified PEtMA prior to depolymerization.

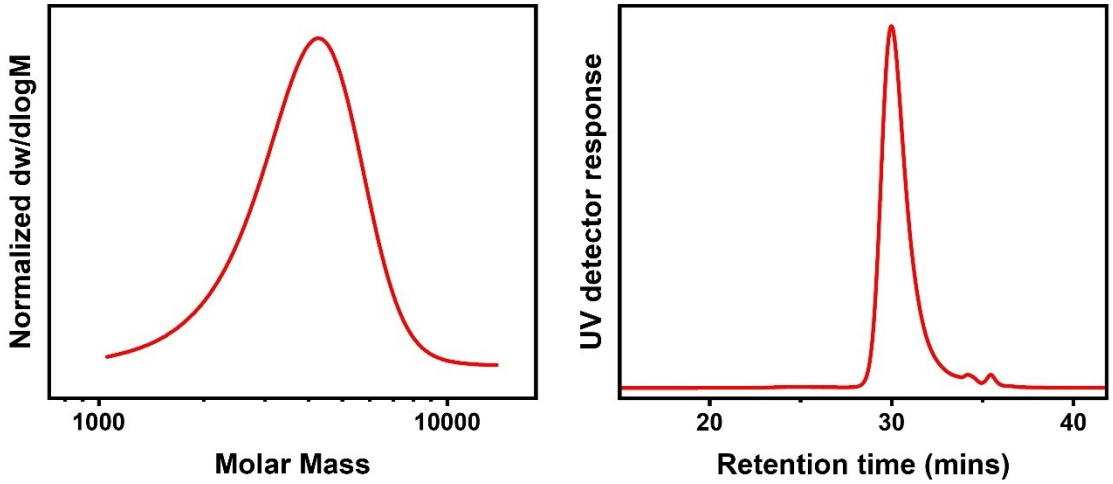


Figure S 5: SEC trace of purified PEtMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion = 74%, $M_{n,SEC}$ = 3600 g/mol, $Đ$ = 1.13.

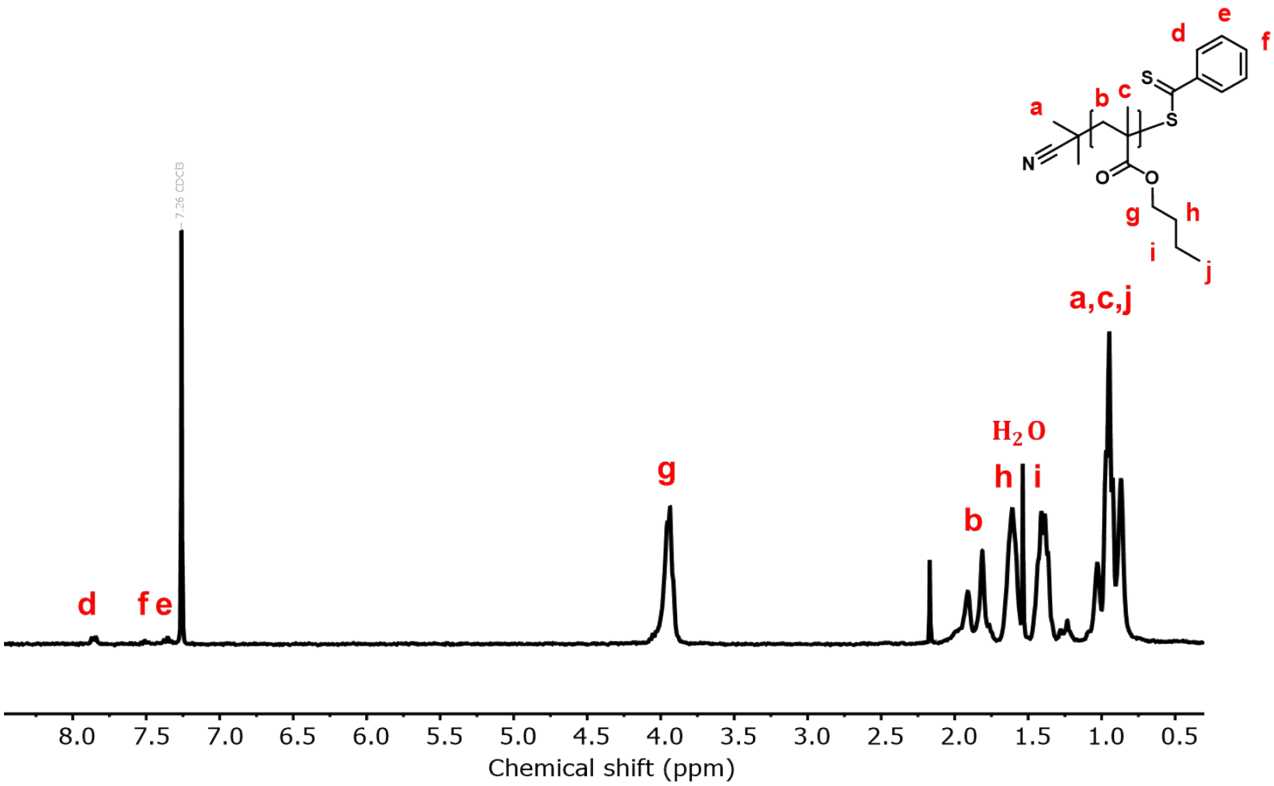


Figure S 6: ^{1}H NMR spectrum of purified PBuMA prior to depolymerization.

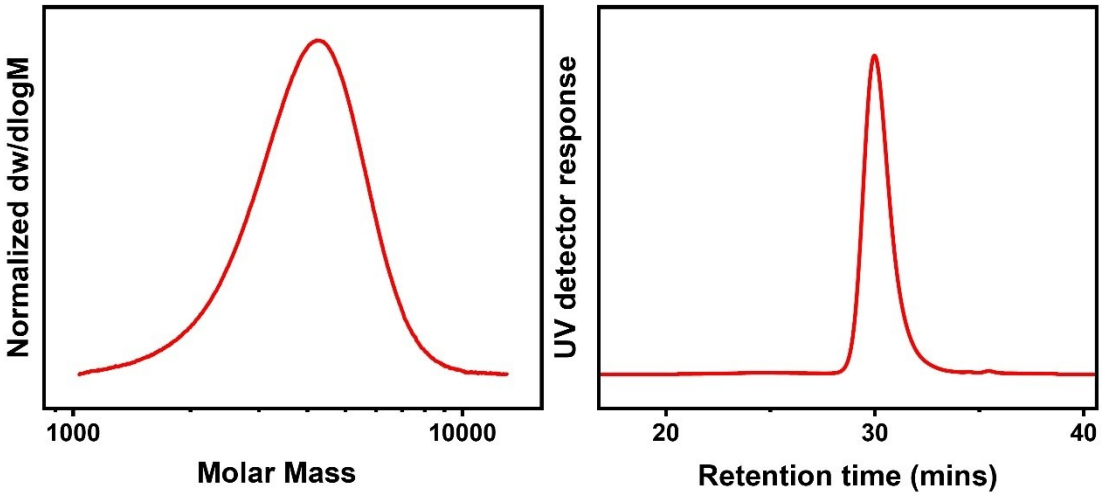


Figure S 7: SEC trace of purified PBuMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 65%, $M_{n,SEC}$ = 3700 g/mol, $Đ$ = 1.12.

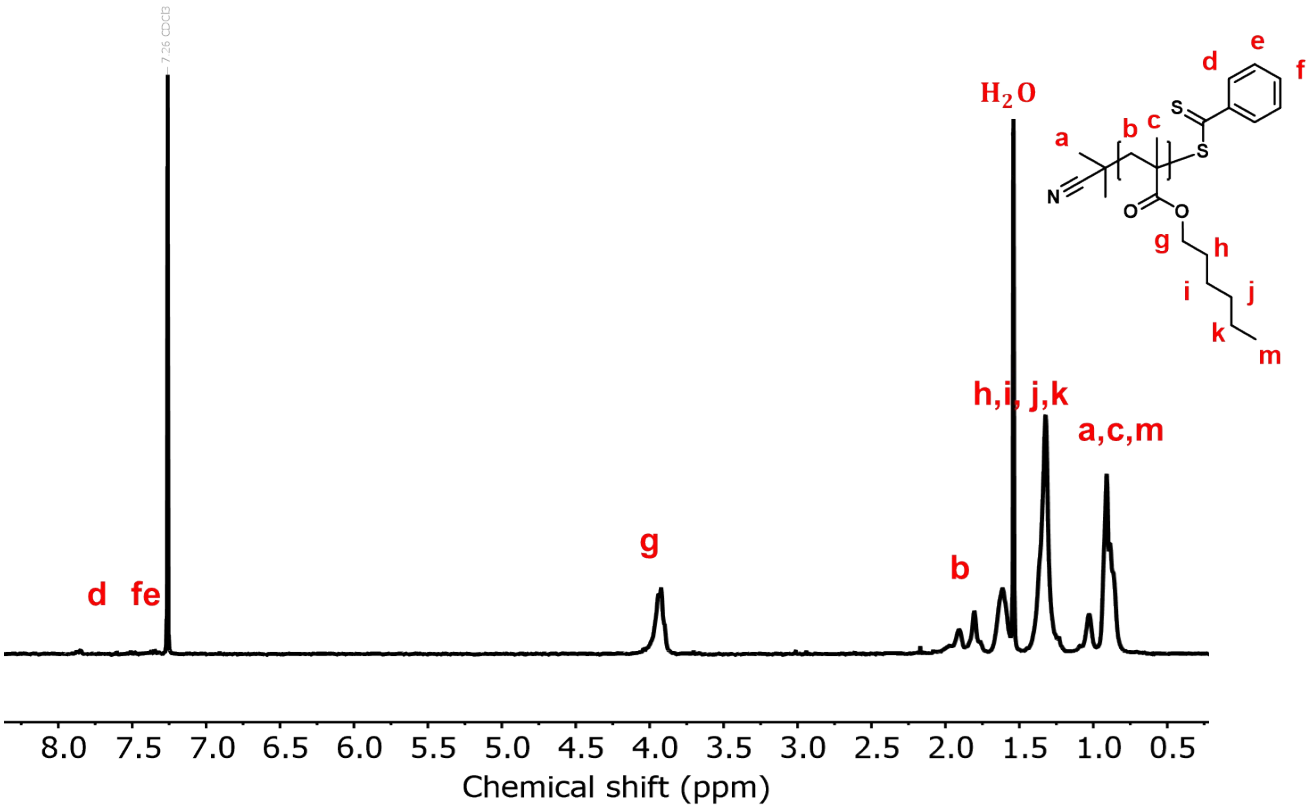


Figure S 8: ^{1}H NMR spectrum of purified PHexMA prior to depolymerization.

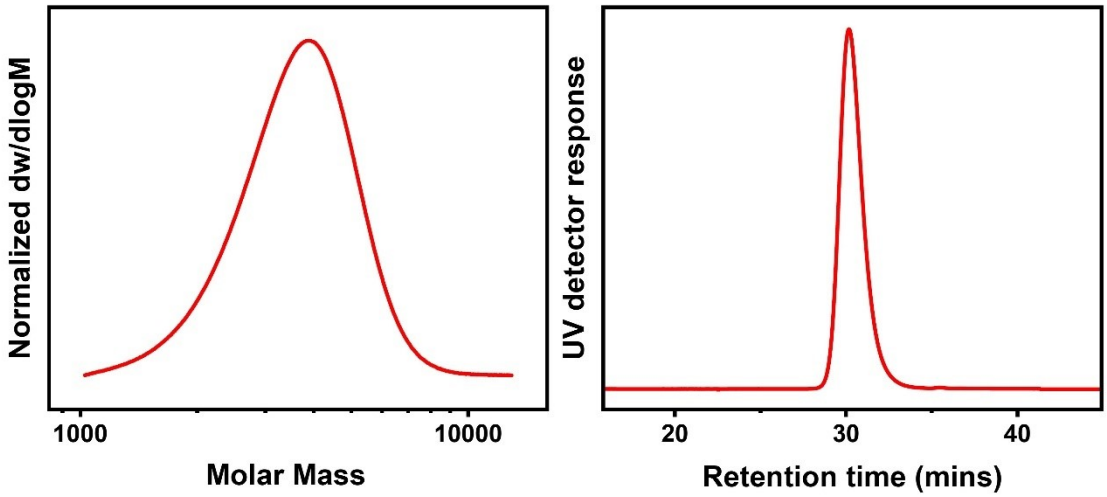


Figure S 9: SEC trace of purified PHexMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion =68%, $M_{n,SEC}$ = 3400 g/mol, $Đ$ = 1.11.

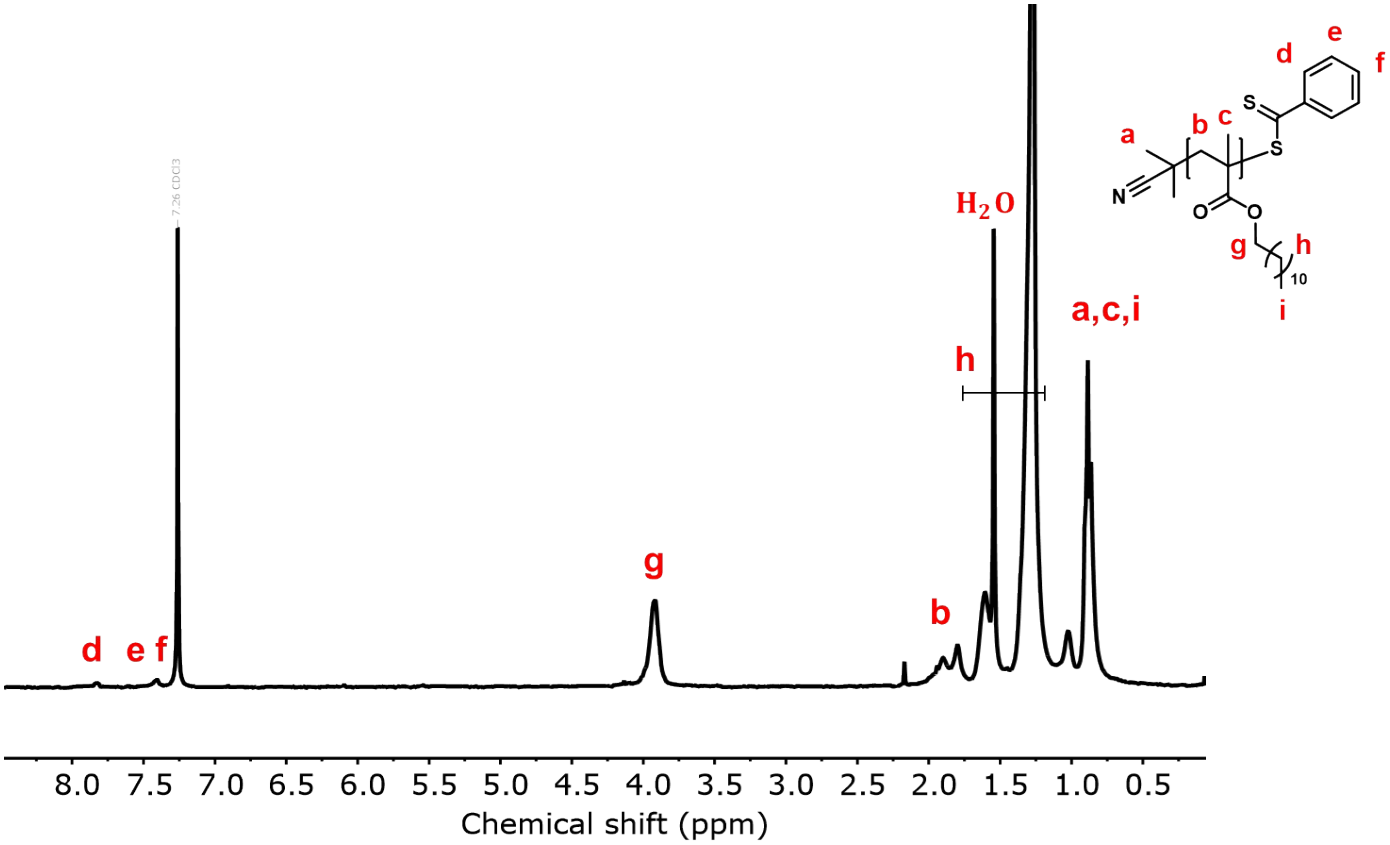


Figure S 10: ^{1}H-NMR spectrum of purified PLauMA prior to depolymerization.

Table S 3: Depolymerization kinetics (by ^{1}H NMR) of n-alkyl polymethacrylates (20 mM RU concentration).

	Depolymerization conversion (%)

	PMMA	PEtMA	PBuMA	PHexMA	PLauMA
5	1.5	6	6	7.2	8.0
10	6.0	13.2	7.9	11.4	15.0
20	12.1	16.3	17.5	25.5	19.0
30	22.6	20.8	25.7	31.5	33.0
40	23.7	27.5	30.6	35.4	40.0
50	28.6	32.4	38.5	41.8	45.5
60	33.3	40.4	40.8	50.2	52.0
$k_{dp,app}$	0.41	0.48	0.55	0.66	0.73
Pearson's R^2	0.98	0.98	0.99	0.98	0.99

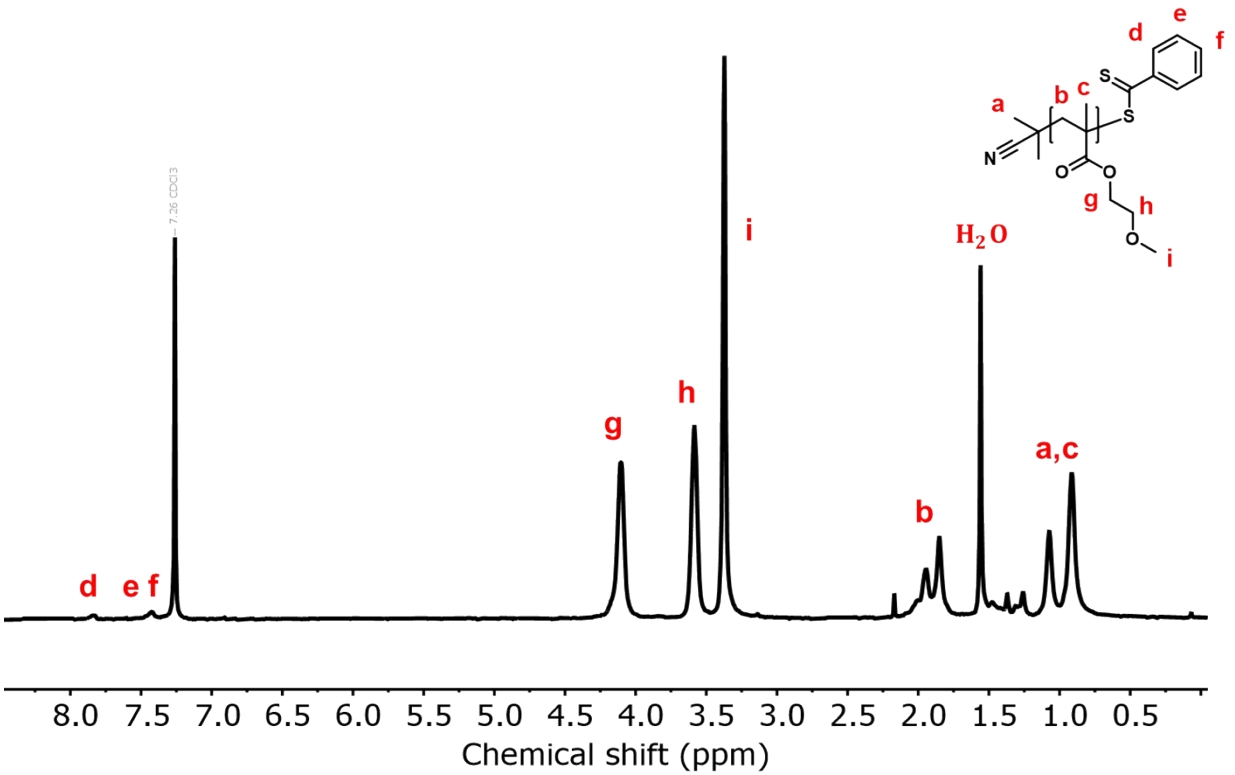


Figure S 11: ^{1}H-NMR spectrum of purified PEGMA prior to depolymerization.

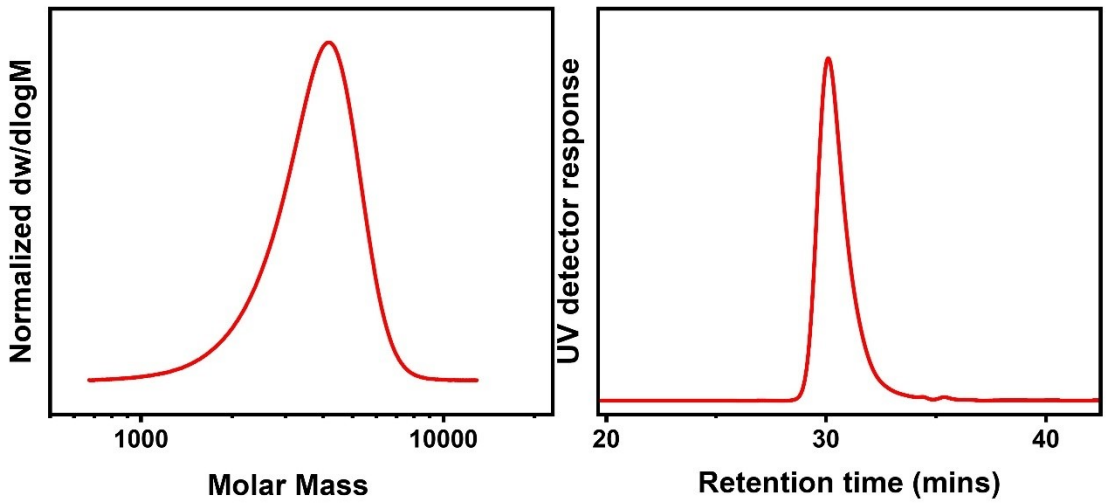


Figure S 12: SEC trace of purified PEGMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion =77%, $M_{n,SEC}$ = 5300 g/mol, $Đ$ = 1.18.

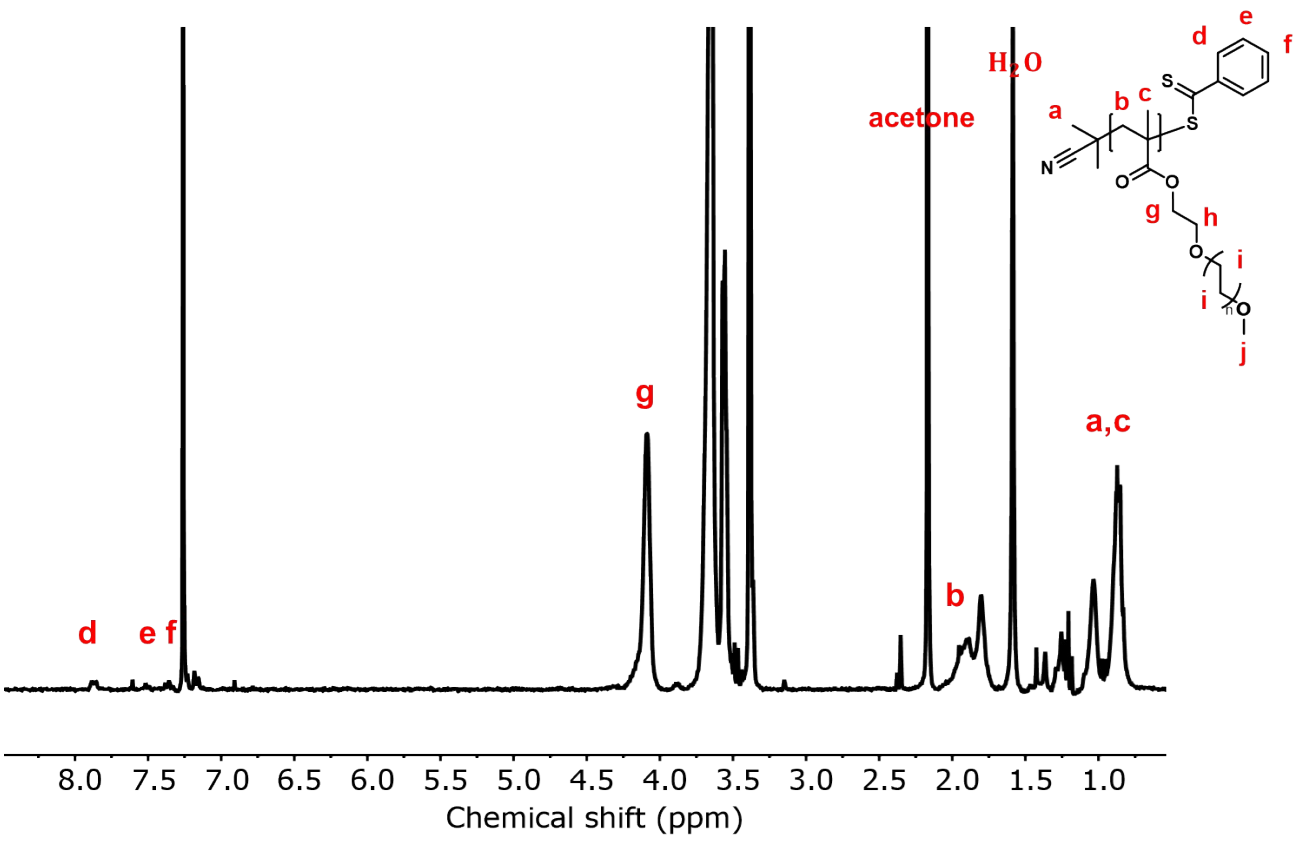


Figure S 13: ^{1}H-NMR spectrum of purified PTEGMA prior to depolymerization.

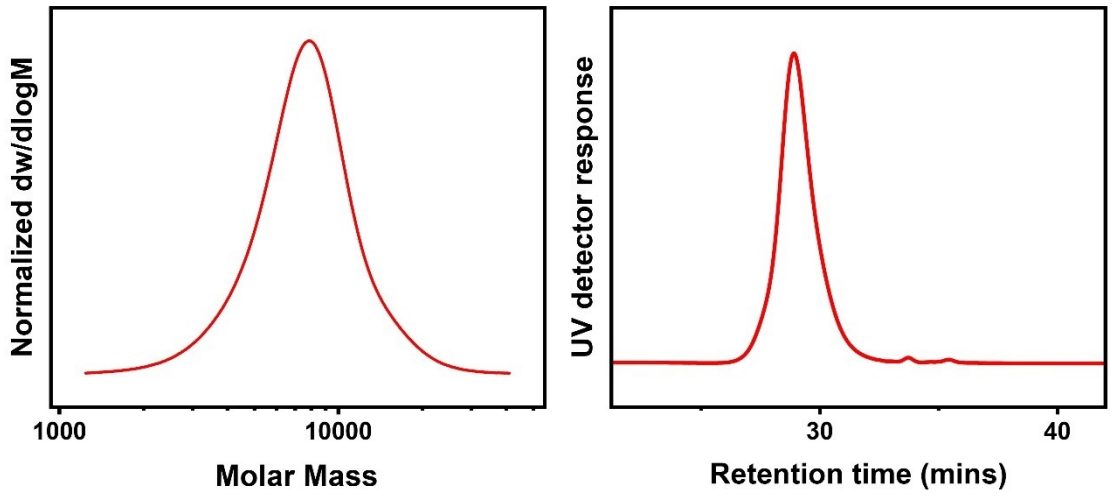


Figure S 14: SEC trace of purified PTEGMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion = 72%, $M_{n,SEC}$ = 6900 g/mol, $Đ$ = 1.19.

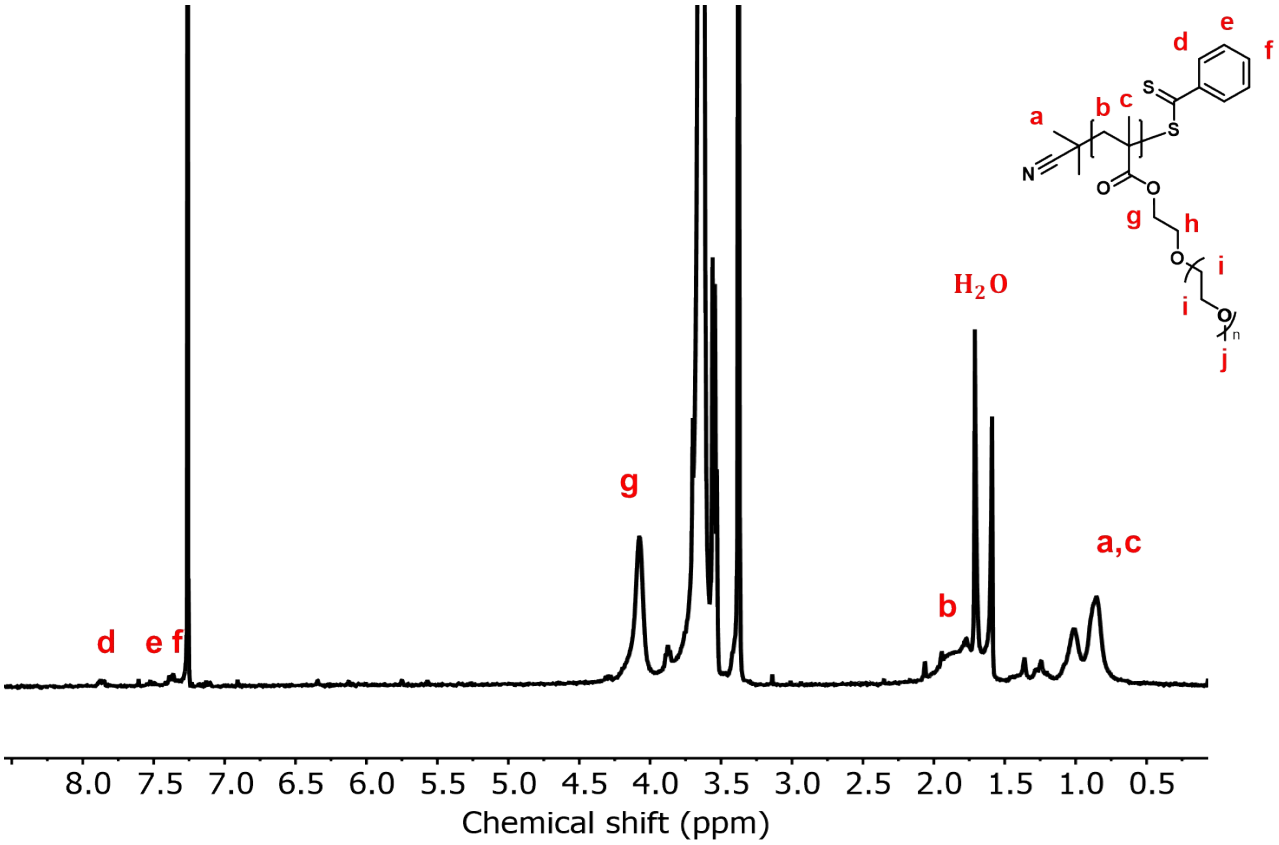


Figure S 15: ^{1}H NMR spectrum of purified PPEGMA prior to depolymerization.

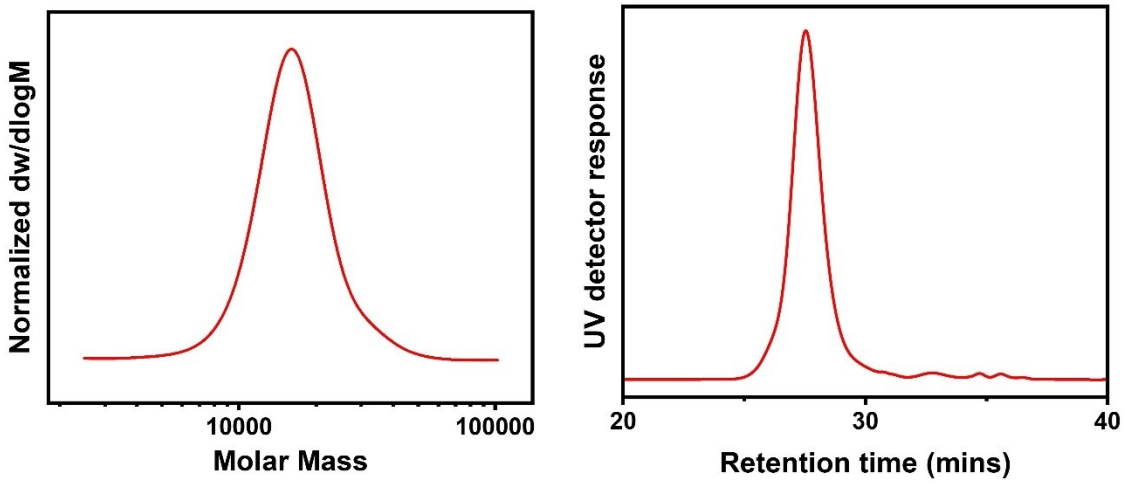


Figure S 16: SEC trace of purified PPEGMA synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate of the CTA. Conversion = 77%, $M_{n,SEC}$ = 14900 g/mol, $Đ$ = 1.14.

Table S 4: Depolymerization kinetics by ^{1}H NMR of PEGMA, PTEGMA, PPEGMA (20 mM RU concentration).

Time (min)	Depolymerization conversion (%)		
	PEGMA	**PTEGMA**	**PPEGMA**
5	6	0	0
10	11.7	7	12
20	19	9.5	15.5
30	25.6	19	27.5
40	34.2	31	35
50	38.1	36	40
60	44	44	48
$k_{dp,app}$	0.56	0.64	0.74
Pearson's R^2	0.99	0.98	0.99

Depolymerization kinetics of PMMA and PHexMA in presence of radical initiator

Table S 5: Kinetic data of depolymerization of PMMA and PHexMA in presence of radical initiator.

	Depolymerization conversion (%)		
Time (min)	**PMMA+2eq. ABCN**	**PHexMA+2eq. ABCN**	**Difference |x|**
1	1	0.3	0.7
2.5	19.6	18.4	1.2
3	28.1	29.8	1.7
4	47.1	49.1	2
5	54.5	57.7	3.2
6	58.9	62.4	3.5
8	63	62.4	0.6
10	63.9	63.7	0.2
$k_{dp,app}$ (1-6 min)	11.38	12.69	

Pearson's R^2	0.97	0.97

Calculation of the end-group fidelity of di-block copolymers

Harrisson and coworkers set guidelines to calculate minimum block lengths to ensure that most chains have at least one unit of each block assuming Poisson-distributed blocks of equal average length and absence of termination.[17] Defective chains were calculated by the equation:

$$Defective\ chains = 1 - \left(1 - e^{l}\right)^{N} \quad (1)$$

Where N is the number of blocks, with an average length of l.

The fidelity is:

$$a = \left(1 - e^{l}\right)^{N} \quad (2)$$

In this work, the synthesized diblock copolymers had different lengths, and the equation was modified to:

$$Defective\ chains = 1 - [(1 - e^{l_1}) \cdot \left(1 - e^{l_2}\right) \cdot \ \ldots \ \cdot (1 - e^{l_n})] \quad (3)$$

Where l_i is the length of each block and the fidelity:

$$a = [(1 - e^{l_1}) \cdot \left(1 - e^{l_2}\right) \cdot \ \ldots \ \cdot (1 - e^{l_n})] \quad (4)$$

Using eq. (4) the fidelity in diblock copolymers was calculated as shown in Table S 6.

Table S 6: Calculation of fidelity in chains for diblock copolymers PMMA-*b*-PHexMA and PHexMA-*b*-PMMA.

	PMMA-*b*-PHexMA		**PHexMA-*b*-PMMA**	
B1	DP_{real}	30.4	DP_{real}	27.2
	Đ	1.11	*Đ*	1.12
B2	DP_{real}	7.68	DP_{real}	8.16
	Đ	1.08	*Đ*	1.07
Fidelity in Chains	**99.95%**		**99.97%**	

^{1}H NMR and SEC characterization of the blockpolymers PMMA-*b*-PHexMA and PHexMA-*b*-PMMA

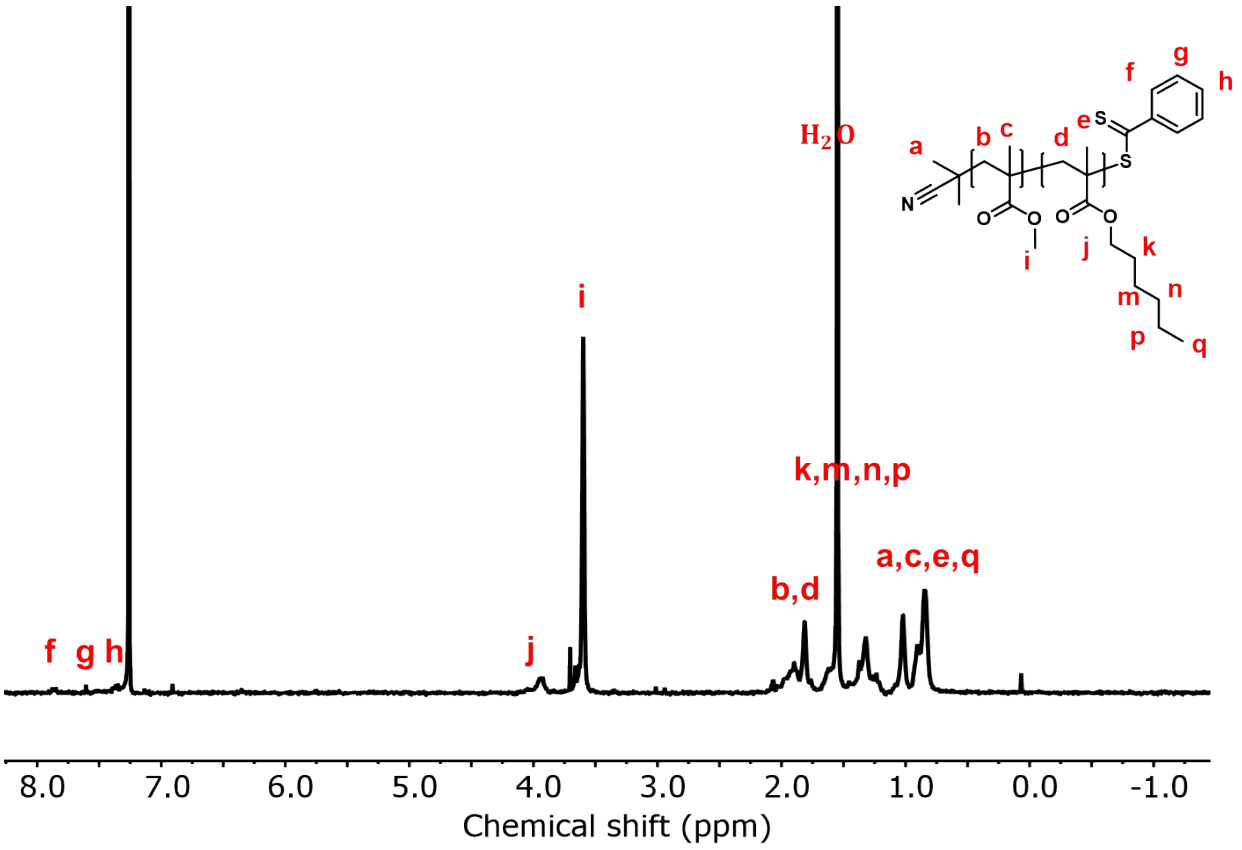


Figure S 17: ^{1}H NMR spectrum of purified PMMA-*b*-PHexMA prior to depolymerization.

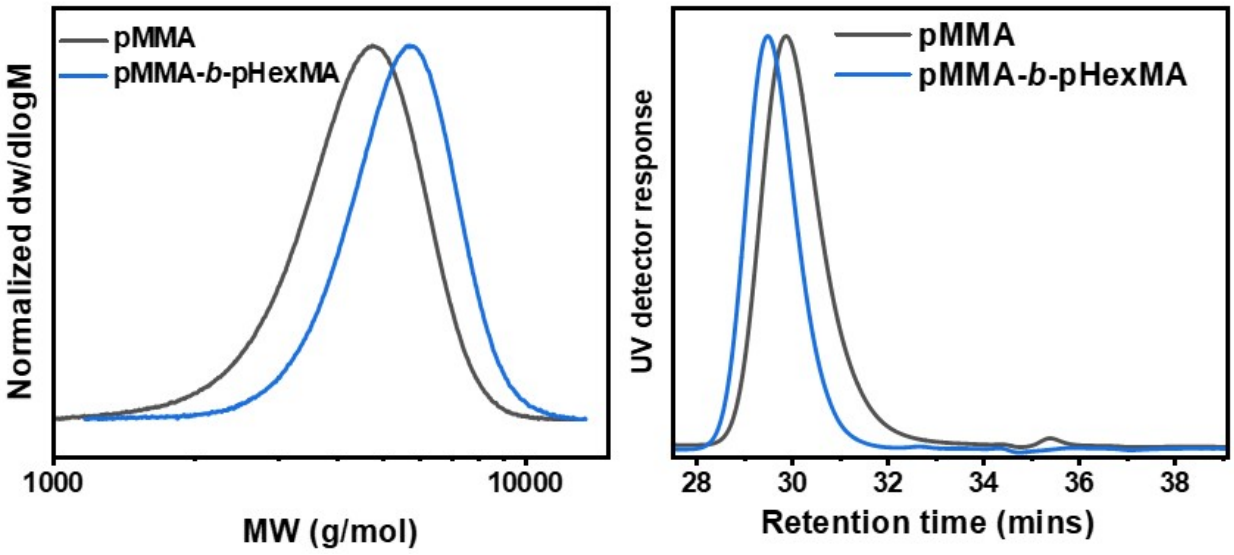


Figure S 18: SEC trace of chain extended PMMA with HexMA and corresponding UV trace.

Table S 7: Characterization data for PMMA-*b*-PHexMA-CTA.

Block	Polymer	[M]:[(macro) CTA]:[AIBN]	Conv. (%)	$M_{n,theo}$	$M_{n,SEC}$	$Đ$	Total DP
1	PMMA-CTA	40:1:0.1	76	3300	3700	1.11	30
2	PMMA-*b*-PHexMA-CTA	12:1:0.1	64	4600	5200	1.08	38

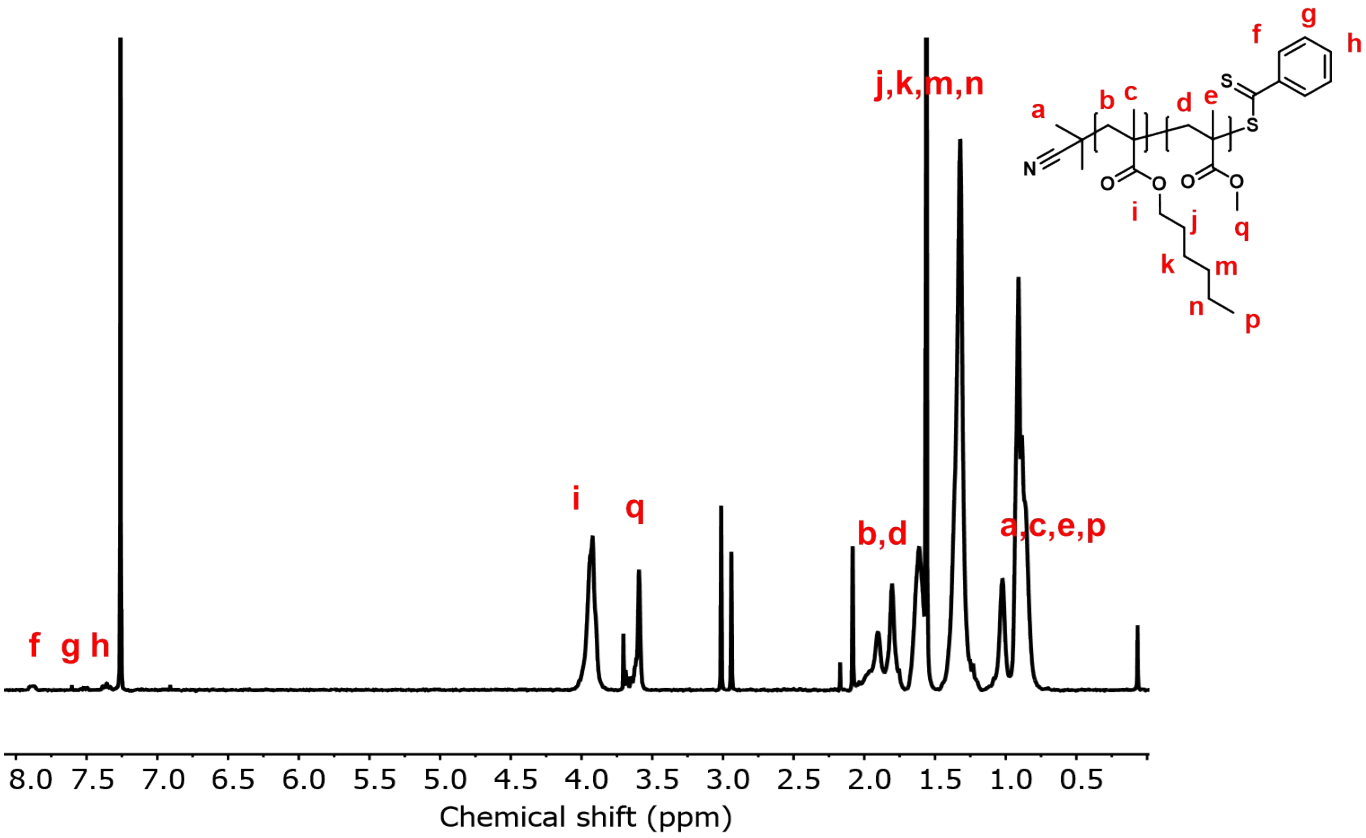


Figure S 19: ^{1}H-NMR spectrum of purified PHexMA-*b*-PMMA prior to depolymerization.

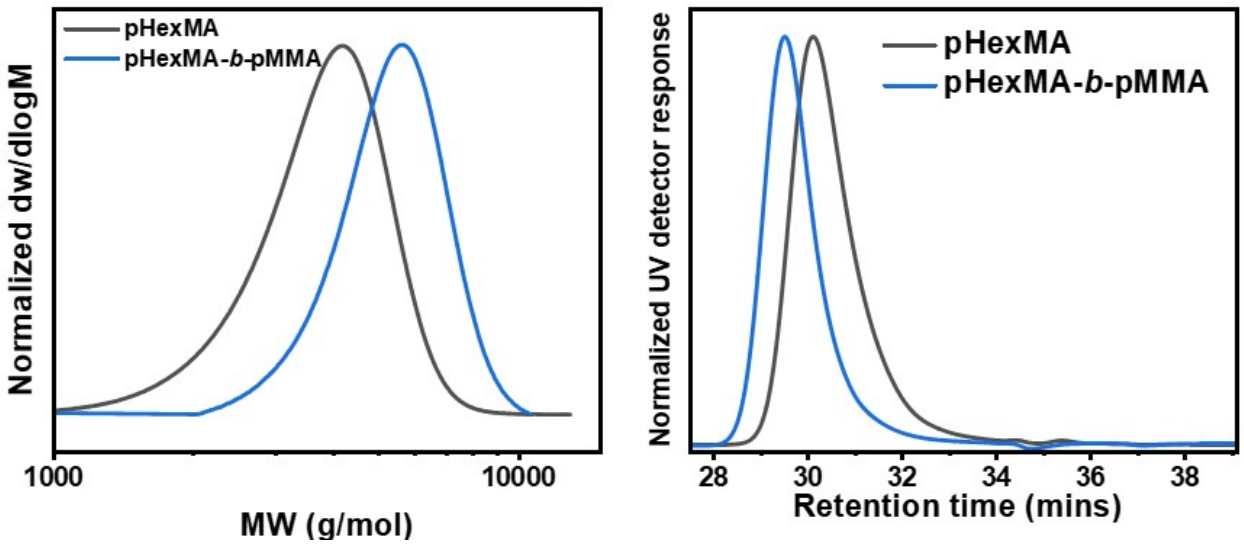


Figure S 20: SEC trace of chain extended PHexMA with MMA and corresponding UV trace.

Table S 8: Characterization data for PMMA-*b*-PHexMA-CTA.

Block	Polymer	[M]:[(macro) CTA]:[AIBN]	Conv (%)	$M_{n,theo}$	$M_{n,SEC}$	$Đ$	Total DP
1	PHexMA-CTA	40:1:0.1	68	4900	3800	1.12	27

2	PHexMA-*b*-PMMA	12:1:0.1	68	5100	5600	1.07	35

Depolymerization kinetics of PMMA-*b*-PHexMA and PHexMA-*b*-PMMA

Table S 9: Kinetic data of depolymerization of PMMA-*b*-PHexMA and PHexMA-*b*-PMMA .

	Depolymerization conversion (%)	
Time (min)	**PMMA-*b*-PHexMA**	**PHexMA-*b*-PMMA**
5	6	4.6
10	16.9	5.7
20	24.2	7
30	34.9	14
45	40.6	22
60	48.9	30
$k_{dp,app}$	0.66	0.34
Pearson's R^2	0.98	0.99

Computational results

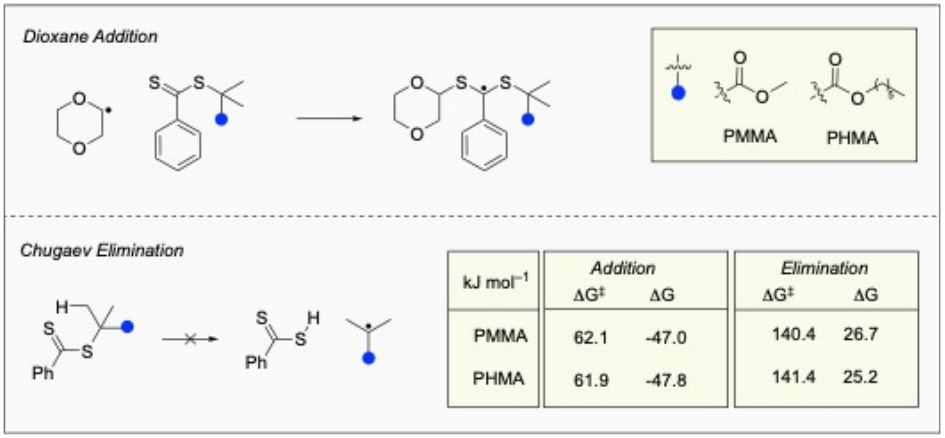


Figure S 21: Gibbs free energy barriers and reaction energies (kJ mol^{-1}, 120 °C) as calculated at the wB97X-D/aug-cc-pVTZ//M062X/6-31G(d) level of theory using SMD to model the 1,4-dioxane solvent environment.

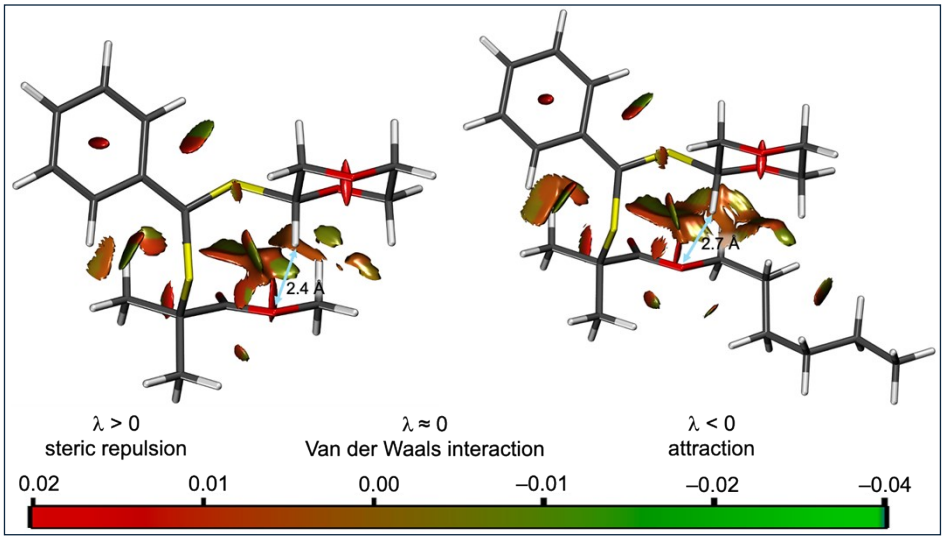


Figure S 22: Non-covalent interaction analyses of the model RAFT adduct radicals.

The blue arrow highlights a stabilizing hydrogen-bonding interaction (green shading) between the ester oxygen of the monomer moiety and the hydrogen of the dioxane moiety in the MMA adduct. This interaction is characterized by a short O···H distance, indicating its strength. However, in the HexMA adduct, steric crowding increases the O···H distance, weakening the interaction and thereby facilitating fragmentation.

Kinetic profile of depolymerization and extrapolation of $k_{dp,app}$

Kinetic profile of depolymerization process of P(n-alkyl)MA (black line) and related first order plot (blue).

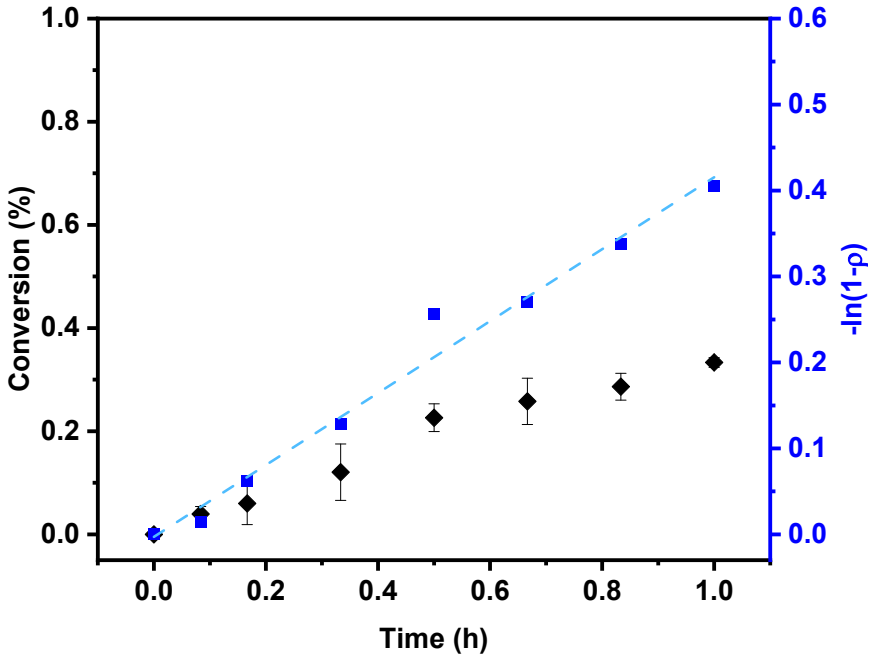


Figure S 23: Kinetic profile of depolymerization process of PMMA.

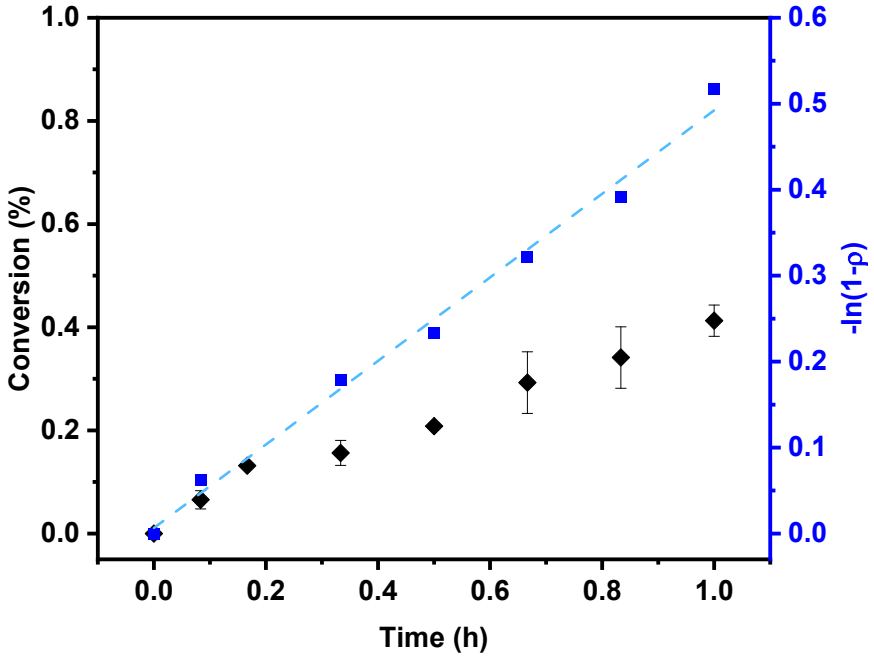


Figure S 24: Kinetic profile of depolymerization process of PEtMA.

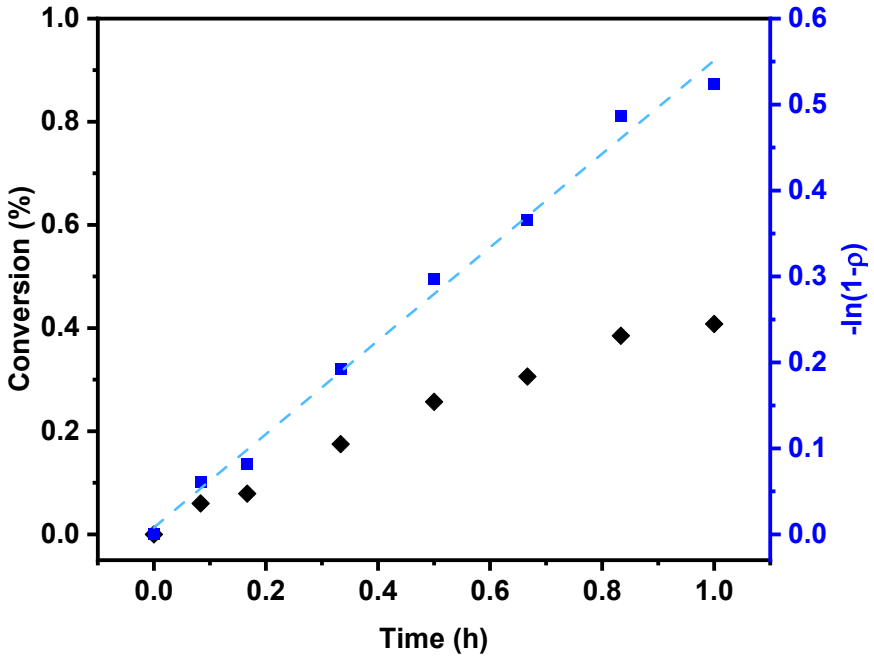


Figure S 25: Kinetic profile of depolymerization process of PBuMA.

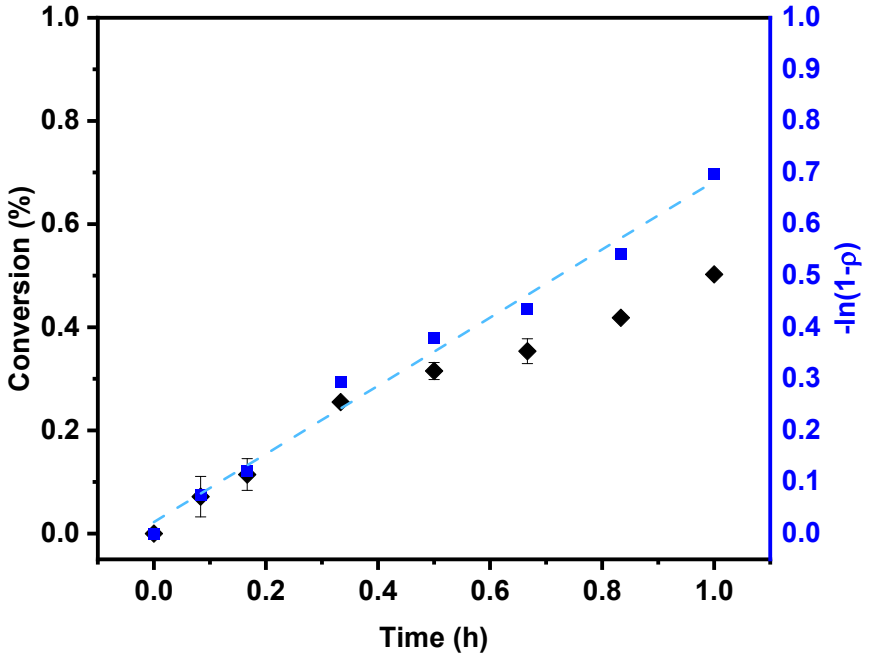


Figure S 26: Kinetic profile of depolymerization process of PHexMA.

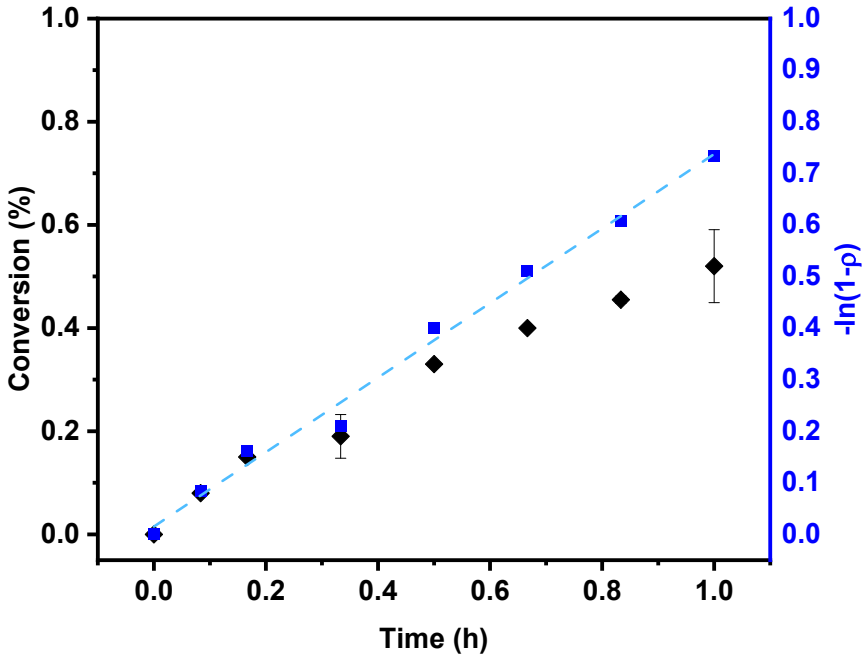


Figure S 27:Kinetic profile of depolymerization process of PLauMA.

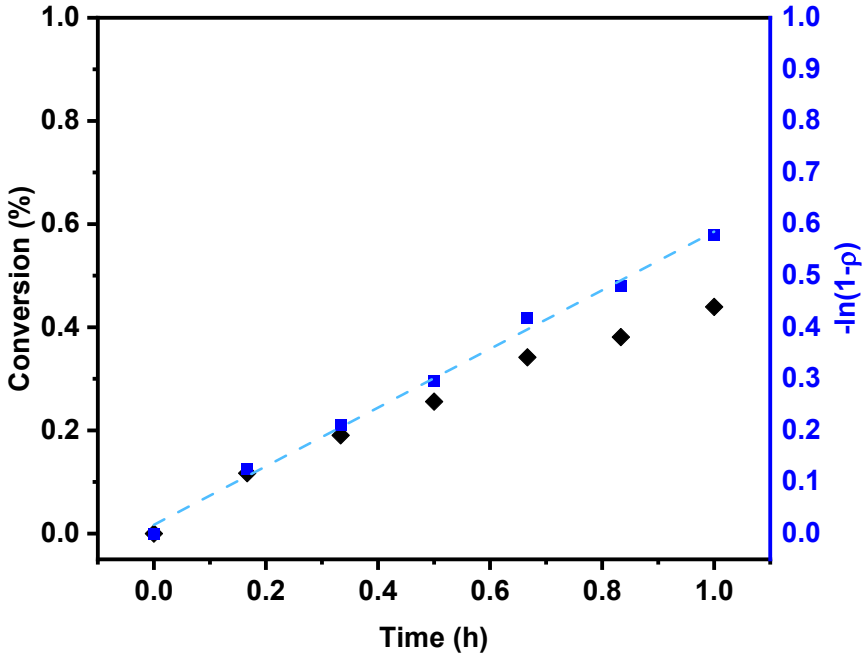


Figure S 28: Kinetic profile of depolymerization process of PEGMA.

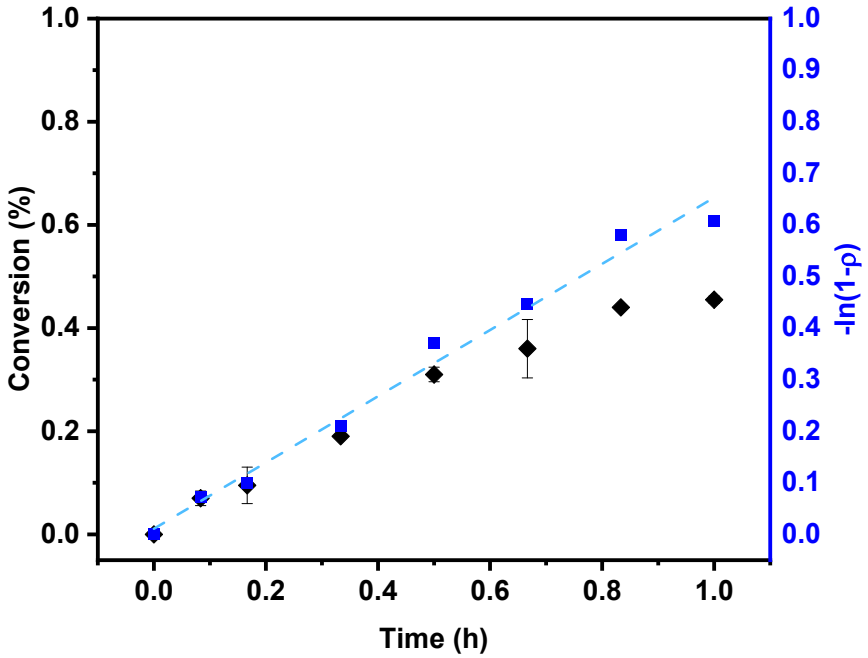


Figure S 29: Kinetic profile of depolymerization process of PTEGMA .

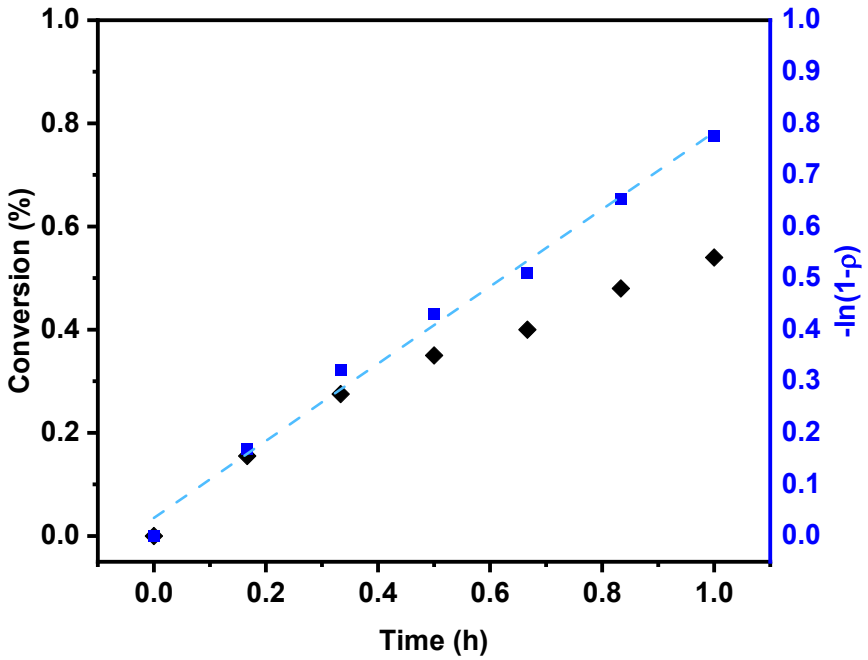


Figure S 30:Kinetic profile of depolymerization process of PPEGMA.

Kinetic profile of depolymerization process of poly block-copolymer (black line) and related first order plot (blue).

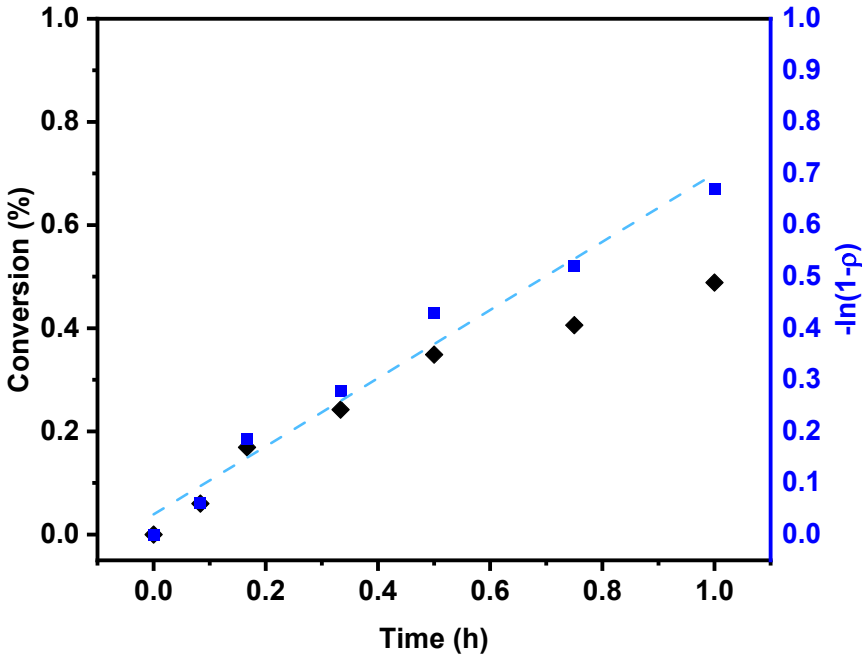


Figure S 31: Kinetic profile of depolymerization process of PMMA-*b*-PHexMA.

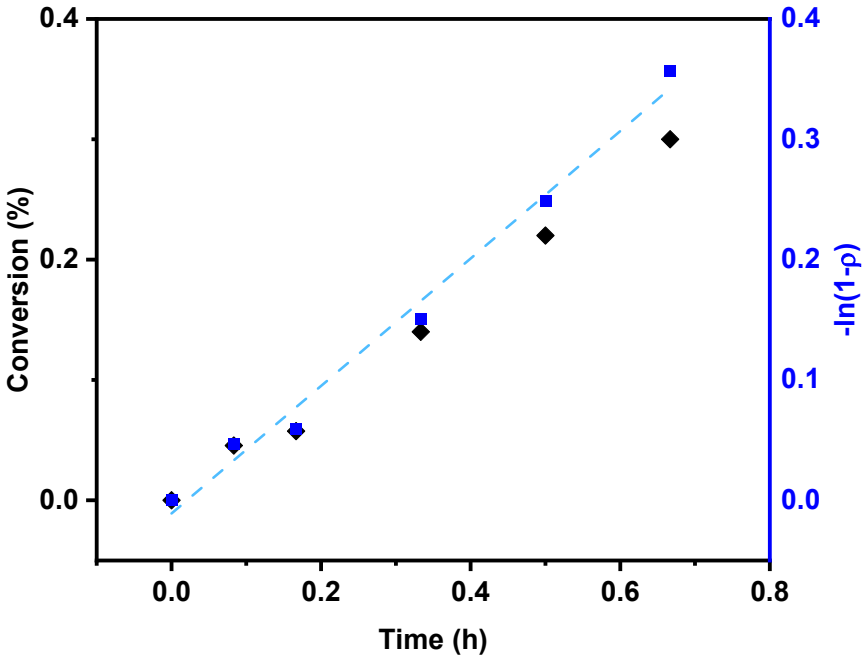


Figure S 32: Kinetic profile of depolymerization process of PHexMA-b-PMMA.

Computational data

Total energies

Table S 10: Addition-fragmentation processes.

Electronic energies (E_e), zero point energies (E_0), enthalpy (H), Gibbs free energies (G), thermal corrections (TC) for T = 393.15 K, and entropy (S) in Hartree obtained at the SMD-(1,4-dioxane)-wB97X-D/aug-cc-pVTZ//SMD-(1,4-dioxane)-M062X/6-31G(d) level of theory

T=393.15K (120 °C)	E_e	E_0	$H_{393.15}$	$G_{393.15}$	$G_{393.15}$ (1M)	TC	S	TS
MMA								
adduct	-1719.6592	-1719.305	-1719.2668	-1719.3856	-1719.3812	0.391083	792.779	0.118713
fragment A[a]	-1412.5967	-1412.3566	-1412.3285	-1412.4226	-1412.4182	0.267006	628.244	0.094075
fragment B[a]	-1373.2419	-1373.0267	-1373.0033	-1373.0881	-1373.0837	0.237393	566.293	0.084798
MMA radical	-346.39176	-346.25662	-346.24148	-346.30617	-346.30184	0.149027	431.953	0.064682
$TS_{acrylate}$ (forming monomer radical)	-1719.6344	-1719.2822	-1719.244	-1719.3632	-1719.3589	0.389127	795.696	0.11915
$TS_{dioxane}$ (forming dioxane radical)	-1719.6139	-1719.2621	-1719.2237	-1719.344	-1719.3397	0.388982	803.313	0.12029
dioxane radical	-307.01938	-306.90859	-306.89865	-306.94942	-306.9451	0.119484	339.068	0.050773
HexMA								
adduct	-1916.2475	-1915.7493	-1915.7004	-1915.8467	-1915.8424	0.545896	977.097	0.146313
fragment A[a]	-1609.1905	-1608.8059	-1608.7675	-1608.8834	-1608.8791	0.421718	773.558	0.115835
HexMA radical	-542.97925	-542.70005	-542.67399	-542.76952	-542.76519	0.304009	637.938	0.095527
$TS_{acrylate}$	-1916.2229	-1915.7268	-1915.6775	-1915.8271	-1915.8227	0.544142	998.485	0.149516
$TS_{dioxane}$	-1916.2026	-1915.7067	-1915.6576	-1915.8049	-1915.8006	0.543776	983.783	0.147315

a) Fragment A denotes the dithioester product of dioxane fragmentation, while fragment B denotes the dithioester product of polymer fragmentation.

Table S 11: Depropagation processes.

Electronic energies (E_e), zero point energies (E_0), enthalpy (H), Gibbs free energies (G), thermal corrections (TC) for T = 393.15 K, and entropy (S) in Hartree obtained at the SMD-(1,4-dioxane)-wB97X-D/aug-cc-pVTZ//SMD-(1,4-dioxane)-M062X/6-31G(d) level of theory

T=393.15K (120 °C)	E_e	E_0	$H_{393.15}$	$G_{393.15}$	$G_{393.15}$ (1M)	TC	S	TS
Monomers								
MMA	-345.80649	-345.68072	-345.667	-345.7267	-345.72238	0.138247	398.713	0.059704
HexMA	-542.39413	-542.12429	-542.09971	-542.18759	-542.18326	0.293175	586.848	0.087876
Monomer radicals								
MMA	-346.39176	-346.25662	-346.24148	-346.30617	-346.30184	0.149027	431.953	0.064682
HEXMA	-542.97925	-542.70005	-542.67399	-542.76952	-542.76519	0.304009	637.938	0.095527
Depropagation transition structures								
MMA	-692.1948	-691.93241	-691.90394	-692.00129	-691.99697	0.289613	650.109	0.097349
HEXMA	-1085.3722	-1084.8216	-1084.7716	-1084.9237	-1084.9194	0.599422	1015.984	0.152136
Dimer radicals								
MMA	-692.23502	-691.96881	-691.94097	-692.03809	-692.03377	0.292798	648.579	0.09712
HEXMA	-1085.4135	-1084.8596	-1084.8098	-1084.9611	-1084.9568	0.60248	1010.333	0.15129

Table S 12: Chugaev elimination process.

Electronic energies (E_e), zero point energies (E_0), enthalpy (H), Gibbs free energies (G), thermal corrections (TC) for T = 393.15 K, and entropy (S) in Hartree obtained at the SMD-(1,4-dioxane)-wB97X-D/aug-cc-pVTZ//SMD-(1,4-dioxane)-M062X/6-31G(d) level of theory

T=393.15K (120 °C)	E_e	E_0	$H_{393.15}$	$G_{393.15}$	$G_{393.15}$ (1M)	TC	S	TS
Chugaev elimination reactants								
MMA	-1412.5911	-1412.351	-1412.3228	-1412.4182	-1412.4139	0.267098	637.212	0.095418
HexMA	-1609.18	-1608.796	-1608.7567	-1608.8805	-1608.8761	0.422036	826.133	0.123708
Chugaev elimination Transition structures								
MMA	-1412.5305	-1412.2974	-1412.2695	-1412.3647	-1412.3604	0.259828	636.101	0.095252
HexMA	-1609.1195	-1608.7424	-1608.7034	-1608.8266	-1608.8223	0.414801	822.639	0.123184
Chugaev elimination products								
MMA	-1412.5706	-1412.3348	-1412.305	-1412.408	-1412.4037	0.264308	687.526	0.102952
HexMA	-1609.1599	-1608.7802	-1608.7395	-1608.8708	-1608.8665	0.419201	877.216	0.131357

Cartesian Coordinates

Cartesian coordinates (in Å) for all structures optimized at the SMD-(1,4-dioxane)-M062X/6-31G(d) level of theory along with their charges, multiplicities and imaginary frequencies, where applicable. The number of imaginary frequencies is zero for all equilibrium structures.

Addition-fragmentation processes

MMA

adduct
0 2

C	-3.751638	-1.856545	-0.099460
C	-1.530137	-1.179151	-0.010755
C	-1.155144	-2.490693	0.665362
C	-3.379069	-3.159386	0.584655
H	-4.044199	-1.113088	0.657295
H	-4.574285	-1.995059	-0.805398
H	-0.870121	-3.224419	-0.105277
H	-0.318513	-2.346973	1.355042
H	-3.158659	-3.925255	-0.174897
H	-4.195090	-3.512863	1.220458
H	-1.736372	-0.404018	0.739141
O	-2.646974	-1.365559	-0.851718
O	-2.252116	-2.965988	1.421209
S	-0.199740	-0.594203	-1.128315
C	1.026355	-0.104708	0.032702
S	0.602694	1.047370	1.288553
C	0.198446	2.598871	0.352181
C	-1.049843	2.452409	-0.517576
O	-1.120535	2.840317	-1.657619
C	1.379303	3.019241	-0.511698
H	2.261222	3.179286	0.114698
H	1.611839	2.259433	-1.263480
H	1.142253	3.948973	-1.036577
C	-0.102920	3.643008	1.435926
H	-0.376988	4.590259	0.959258
H	-0.927859	3.326541	2.079185
H	0.784317	3.813840	2.052662
O	-2.086471	1.933906	0.153067
C	-3.280890	1.776002	-0.617206
H	-3.109119	1.077939	-1.439292
H	-4.025155	1.376722	0.071990
H	-3.610559	2.739938	-1.011545
C	2.365569	-0.641358	-0.060016
C	2.636549	-1.826421	-0.786099
C	3.458131	-0.000831	0.572857
C	3.923662	-2.332342	-0.873461
H	1.819946	-2.352021	-1.268657
C	4.740717	-0.516481	0.479528
H	3.284490	0.913147	1.129602
C	4.986341	-1.684071	-0.243736
H	4.099349	-3.246470	-1.432566
H	5.559565	0.000705	0.970554
H	5.992858	-2.083967	-0.314738

fragment A
0 1

S	0.035920	-1.427437	-1.200291

C	-0.604050	-0.135827	-0.414991
S	0.275693	1.269720	0.131579
C	2.044076	0.999421	-0.286871
C	2.577230	-0.362286	0.163149
O	3.471589	-0.935816	-0.406441
C	2.796598	2.058039	0.540183
H	2.463517	3.064682	0.269651
H	2.647076	1.911387	1.613123
H	3.865710	1.981373	0.318722
C	2.297204	1.212115	-1.775947
H	3.360858	1.067615	-1.982628
H	1.732764	0.501340	-2.382618
H	2.014512	2.229945	-2.057535
O	2.042295	-0.769836	1.317170
C	2.520178	-2.032372	1.784734
H	1.969613	-2.236660	2.702051
H	2.322016	-2.807820	1.040744
H	3.593135	-1.986678	1.984465
C	-2.053678	-0.033540	-0.094062
C	-2.996603	-0.515031	-1.011836
C	-2.498422	0.525928	1.111749
C	-4.354010	-0.426012	-0.734568
H	-2.652100	-0.946152	-1.945994
C	-3.858945	0.597735	1.390998
H	-1.780147	0.872692	1.847899
C	-4.789164	0.128519	0.468037
H	-5.074926	-0.790819	-1.459393
H	-4.190445	1.016721	2.335794
H	-5.850948	0.190908	0.685834

fragment B

0 1

C	3.533766	0.696525	1.089947
C	1.913438	-0.140578	-0.338326
C	2.930110	-1.092269	-0.963950
C	4.560188	-0.232434	0.468380
H	3.532678	1.664819	0.568116
H	3.734747	0.861868	2.151109
H	2.908655	-2.058634	-0.435360
H	2.716841	-1.253564	-2.023647
H	4.607980	-1.168486	1.045722
H	5.551386	0.227972	0.452826
H	1.887333	0.800609	-0.905261
O	2.241494	0.104216	1.007383
O	4.214877	-0.511803	-0.879196
S	0.264810	-0.882355	-0.407512
C	-0.797773	0.495122	-0.122103
S	-0.317862	2.056189	-0.021995
C	-2.218338	0.075330	-0.004865
C	-2.575660	-1.119073	0.636176
C	-3.224812	0.890685	-0.540185

C	-3.913476	-1.484333	0.741645
H	-1.811321	-1.744823	1.085913
C	-4.556943	0.512251	-0.447036
H	-2.946907	1.812966	-1.039437
C	-4.905406	-0.674786	0.195942
H	-4.179136	-2.401918	1.256919
H	-5.326350	1.145310	-0.877620
H	-5.948600	-0.965389	0.273572

MMA radical

0 2

C	-0.276807	-0.364326	-0.000168
C	1.091712	0.119396	-0.000412
C	2.200364	-0.871005	0.000226
C	1.378101	1.583128	-0.000072
H	2.454858	1.770526	-0.004505
H	0.943989	2.073937	0.879735
H	0.935971	2.076082	-0.874542
O	-0.608769	-1.538591	-0.000109
O	-1.178866	0.645649	0.000025
C	-2.539938	0.228061	0.000137
H	-3.133176	1.142460	-0.000591
H	-2.763536	-0.366544	0.889642
H	-2.763306	-0.367883	-0.888512
H	1.818000	-1.892548	0.000546
H	2.844038	-0.732360	-0.879008
H	2.843647	-0.731664	0.879639

$TS_{acrylate}$ (forming monomer radical)

0 2

C	3.971092	-0.819865	0.685676
C	1.781157	-1.006987	-0.048007
C	2.229031	-1.897516	-1.198226
C	4.430883	-1.687768	-0.472219
H	4.002133	0.241437	0.395441
H	4.594887	-0.971000	1.570351
H	2.182183	-2.950690	-0.880318
H	1.590970	-1.751870	-2.073361
H	4.468792	-2.739853	-0.150234
H	5.423184	-1.385134	-0.816911
H	1.760060	0.041582	-0.365663
O	2.642392	-1.170946	1.058095
O	3.547870	-1.547494	-1.571327
S	0.135433	-1.458671	0.589914
C	-0.971873	-0.590263	-0.463254
S	-0.496090	0.502379	-1.616236
C	-0.006880	2.691122	-0.501240
C	0.138307	2.141453	0.856497
O	-0.790009	1.923881	1.610026
C	-1.284606	3.417960	-0.775985
H	-1.542228	3.379810	-1.838812

H	-2.104554	3.010231	-0.182750
H	-1.169813	4.478787	-0.505286
C	1.204646	3.085067	-1.285465
H	1.562241	4.070288	-0.951574
H	2.024948	2.374757	-1.166740
H	0.960665	3.170641	-2.349276
O	1.422708	1.880440	1.184345
C	1.612171	1.378486	2.508532
H	1.092298	0.428244	2.642414
H	2.686719	1.237888	2.622593
H	1.243459	2.102308	3.240098
C	-2.392904	-0.896192	-0.188745
C	-2.791565	-2.142521	0.320327
C	-3.377745	0.070987	-0.442752
C	-4.132920	-2.407966	0.570163
H	-2.056010	-2.921419	0.494232
C	-4.714386	-0.196281	-0.184352
H	-3.078849	1.035332	-0.838947
C	-5.098679	-1.436446	0.323677
H	-4.422884	-3.381642	0.952530
H	-5.460301	0.568675	-0.376329
H	-6.145461	-1.644365	0.522817

Number of imaginary frequencies = 1 (-315.4*i* cm^{-1})

$TS_{dioxane}$ (forming dioxane radical)

0 2

C	4.412086	-1.009754	0.194027
C	2.123601	-0.882937	-0.310370
C	2.034116	-2.373171	-0.328608
C	4.260594	-2.515065	0.284675
H	4.785446	-0.734282	-0.801148
H	5.092879	-0.625879	0.956818
H	1.716736	-2.743524	0.661353
H	1.317012	-2.709042	-1.080941
H	3.964660	-2.802025	1.306104
H	5.205986	-3.006702	0.039071
H	1.740759	-0.269877	-1.122665
O	3.152327	-0.353358	0.408490
O	3.294962	-2.961392	-0.646908
S	0.046861	-0.119354	1.224788
C	-1.322384	-0.083391	0.311837
S	-1.848787	1.310600	-0.623673
C	-1.033204	2.778765	0.116096
C	0.495207	2.755468	0.050574
O	1.194010	3.283611	0.879238
C	-1.505756	3.015156	1.546423
H	-2.590587	3.148865	1.558603
H	-1.240750	2.183119	2.202114
H	-1.030114	3.917783	1.938500
C	-1.475844	3.944250	-0.789402
H	-1.028861	4.870966	-0.415806

H	-1.156349	3.793153	-1.823926
H	-2.563998	4.054562	-0.765758
O	0.958976	2.241603	-1.094187
C	2.377055	2.346890	-1.257511
H	2.891655	1.822304	-0.450000
H	2.598543	1.886600	-2.220727
H	2.678696	3.397313	-1.265097
C	-2.193730	-1.269036	0.107894
C	-1.652809	-2.559706	0.210866
C	-3.561551	-1.139574	-0.181073
C	-2.447313	-3.681069	0.017266
H	-0.600178	-2.672383	0.445633
C	-4.356051	-2.265571	-0.366889
H	-4.014011	-0.155153	-0.232440
C	-3.803034	-3.539301	-0.274513
H	-2.006576	-4.670299	0.093476
H	-5.413945	-2.143855	-0.577867
H	-4.424282	-4.417005	-0.423951

Number of imaginary frequencies = 1 (-116.7*i* cm^{-1})

dioxane radical
0 2

C	1.370763	-0.048561	-0.200873
C	-0.544815	1.274829	-0.156609
C	-1.398102	0.076299	0.112446
C	0.516176	-1.213476	0.259272
H	1.476810	-0.079324	-1.292599
H	2.360148	-0.069897	0.261686
H	-1.623421	-0.006976	1.195037
H	-2.349343	0.158684	-0.420211
H	0.446180	-1.214831	1.359211
H	0.953816	-2.160846	-0.066625
H	-0.950125	2.267574	0.013067
O	0.775795	1.195033	0.170824
O	-0.773070	-1.123648	-0.312697

HexMA

adduct
0 2

C	-2.159571	2.846732	0.378268
C	-0.193766	1.614320	0.096009
C	0.418789	2.797110	-0.646496
C	-1.522971	4.021000	-0.339025
H	-2.710705	2.238217	-0.353679
H	-2.847351	3.173948	1.162049
H	0.961700	3.427963	0.075142
H	1.116175	2.449283	-1.413894
H	-1.021412	4.679559	0.386644
H	-2.276914	4.596798	-0.882257
H	-0.627449	0.888624	-0.606114

O	-1.165186	2.052720	1.020666
O	-0.589155	3.546671	-1.292969
S	1.078407	0.780872	1.123490
C	2.094165	0.047681	-0.110862
S	1.347321	-0.980415	-1.329546
C	0.899991	-2.523479	-0.389469
C	-0.021348	-2.202687	0.786626
O	0.212808	-2.522231	1.926683
C	2.156790	-3.214471	0.120012
H	2.797930	-3.491338	-0.721517
H	2.718397	-2.566462	0.798703
H	1.885427	-4.120476	0.670346
C	0.145834	-3.397532	-1.397333
H	-0.164268	-4.328102	-0.909826
H	-0.743632	-2.891935	-1.780157
H	0.798574	-3.654098	-2.237310
O	-1.140215	-1.580285	0.402590
C	-2.022635	-1.177831	1.464651
H	-1.491718	-0.455843	2.093006
H	-2.270720	-2.054061	2.073121
C	3.520280	0.285184	-0.100835
C	4.089116	1.343742	0.648836
C	4.405061	-0.534024	-0.843698
C	5.458022	1.558547	0.657851
H	3.440438	2.003752	1.213767
C	5.771813	-0.308445	-0.828927
H	4.001400	-1.353526	-1.427438
C	6.311536	0.736424	-0.078025
H	5.863445	2.381220	1.239142
H	6.424637	-0.956904	-1.405462
H	7.383019	0.909275	-0.068703
C	-3.248271	-0.567858	0.819966
H	-3.827311	-0.067195	1.604842
H	-2.913314	0.212309	0.126073
C	-4.110240	-1.588174	0.077063
H	-4.569971	-2.269775	0.806062
H	-3.461874	-2.201738	-0.559990
C	-5.199941	-0.948771	-0.784743
H	-4.728874	-0.345731	-1.574136
H	-5.762813	-1.739879	-1.297311
C	-6.178433	-0.070858	-0.004803
H	-6.582610	-0.642343	0.841821
H	-5.645535	0.785974	0.426671
C	-7.322581	0.435787	-0.877611
H	-6.941035	1.018704	-1.723412
H	-7.903064	-0.398430	-1.286538
H	-8.008065	1.075513	-0.313239

fragment A
0 1

S	0.598080	-0.753986	1.885724

C	0.097990	-1.202382	0.387150
S	1.122177	-1.416830	-1.010617
C	2.820896	-0.905703	-0.523547
C	2.850677	0.441485	0.204262
O	3.681072	0.723665	1.031314
C	3.558073	-0.705948	-1.859908
H	3.566363	-1.635433	-2.437484
H	3.095452	0.081313	-2.460864
H	4.595190	-0.426178	-1.649592
C	3.508195	-1.984290	0.306943
H	4.519056	-1.652792	0.558765
H	2.970290	-2.174281	1.237633
H	3.570596	-2.911818	-0.268503
O	1.935878	1.291191	-0.265449
C	1.811033	2.534305	0.443300
H	1.697657	2.307876	1.509704
H	2.728760	3.115859	0.311708
C	-1.330412	-1.483482	0.078670
C	-2.142912	-2.074378	1.056883
C	-1.895313	-1.137825	-1.157310
C	-3.485094	-2.318782	0.801602
H	-1.706484	-2.344408	2.012696
C	-3.244572	-1.373717	-1.403152
H	-1.289926	-0.652270	-1.916571
C	-4.041027	-1.966409	-0.427804
H	-4.100182	-2.785423	1.564504
H	-3.673322	-1.084363	-2.357641
H	-5.093022	-2.151332	-0.622668
C	0.592520	3.247194	-0.107188
H	0.771157	3.514902	-1.156177
H	0.480292	4.188641	0.445916
C	-0.684901	2.416228	0.005678
H	-0.797885	2.066423	1.040366
H	-0.581819	1.513206	-0.612165
C	-1.928205	3.194054	-0.424525
H	-1.725186	3.696262	-1.380161
H	-2.125791	3.990766	0.306490
C	-3.174780	2.319905	-0.577447
H	-3.010007	1.604769	-1.394484
H	-4.017903	2.951314	-0.883469
C	-3.545699	1.554726	0.690170
H	-3.669097	2.239374	1.538164
H	-4.485863	1.009013	0.561102
H	-2.776845	0.822888	0.961443

HexMA radical
0 2

C	-2.428322	-0.538127	-0.047401
C	-3.646384	0.241684	0.082136
C	-4.953949	-0.465492	0.068209
C	-3.584180	1.724941	0.225731

H	-4.586565	2.151038	0.316465
H	-3.086298	2.188183	-0.635052
H	-3.001392	2.015826	1.108297
O	-2.381416	-1.751714	-0.170499
O	-1.318378	0.235276	-0.016921
C	-0.078141	-0.467388	-0.137056
H	-0.066378	-1.019267	-1.083885
H	0.000145	-1.201688	0.672688
H	-4.819433	-1.542313	-0.041954
H	-5.510419	-0.269374	0.994763
H	-5.583872	-0.099865	-0.754111
C	1.041362	0.551770	-0.073755
H	0.902962	1.285985	-0.876831
H	0.973618	1.098741	0.874848
C	2.413557	-0.107663	-0.198627
H	2.521758	-0.863958	0.589438
H	2.477334	-0.644668	-1.155844
C	3.555837	0.903801	-0.109490
H	3.542294	1.373774	0.883909
H	3.374835	1.708142	-0.834510
C	4.939139	0.301933	-0.364936
H	5.685260	1.104650	-0.331108
H	4.971892	-0.107666	-1.383030
C	5.326683	-0.786103	0.633728
H	6.359068	-1.114375	0.478410
H	5.244396	-0.419367	1.663606
H	4.685542	-1.668421	0.542038

$TS_{acrylate}$ (forming monomer radical)

0 2

C	-0.105466	3.927995	1.018934
C	1.060518	2.222858	-0.010256
C	0.485121	2.614811	-1.363061
C	-0.722558	4.311727	-0.313826
H	-0.740213	3.194459	1.536017
H	0.035656	4.803140	1.658064
H	1.157660	3.340438	-1.846378
H	0.361055	1.742728	-2.008607
H	-0.116528	5.097728	-0.790080
H	-1.743194	4.680385	-0.181126
H	0.418564	1.480741	0.473541
O	1.187278	3.364293	0.806982
O	-0.798826	3.180577	-1.167540
S	2.746901	1.539280	-0.112676
C	2.474627	-0.152024	-0.510820
S	0.975451	-0.842406	-0.690964
C	0.138426	-1.513488	1.576252
C	-0.875559	-0.447035	1.591720
O	-0.743274	0.611872	2.182669
C	1.342136	-1.285480	2.428328
H	2.185926	-1.892288	2.085267

H	1.632466	-0.232034	2.435828
H	1.127131	-1.574523	3.467655
C	-0.271289	-2.916484	1.258004
H	-0.756199	-3.370545	2.135390
H	-0.981226	-2.958449	0.429658
H	0.601402	-3.528579	1.012182
O	-1.951006	-0.734274	0.840147
C	-2.860697	0.356413	0.626449
H	-2.311370	1.176405	0.148118
H	-3.228830	0.709688	1.595861
C	3.727651	-0.932342	-0.642549
C	4.944533	-0.320112	-0.984052
C	3.717172	-2.320309	-0.427915
C	6.108869	-1.070656	-1.097915
H	4.982309	0.744500	-1.191502
C	4.883559	-3.064526	-0.534944
H	2.781069	-2.806987	-0.173383
C	6.085888	-2.443573	-0.869645
H	7.036305	-0.578142	-1.372852
H	4.854300	-4.134804	-0.355593
H	6.997146	-3.027174	-0.956047
C	-3.989640	-0.148530	-0.248782
H	-4.622540	0.712501	-0.493311
H	-3.569831	-0.514939	-1.194540
C	-4.814570	-1.248087	0.419965
H	-5.295290	-0.837939	1.319443
H	-4.136494	-2.038724	0.761392
C	-5.879982	-1.857463	-0.492627
H	-5.392409	-2.319065	-1.362871
H	-6.384822	-2.671579	0.044070
C	-6.933094	-0.862106	-0.979012
H	-7.361263	-0.337763	-0.113819
H	-6.460792	-0.094716	-1.604208
C	-8.046199	-1.540493	-1.771867
H	-7.641782	-2.059099	-2.648268
H	-8.567734	-2.283959	-1.159028
H	-8.788187	-0.817706	-2.124990

Number of imaginary frequencies = 1 (-312.5*i* cm^{-1})

$TS_{dioxane}$ (forming dioxane radical)

0 2

C	2.154488	2.846070	-1.645320
C	0.363284	1.636011	-0.726058
C	-0.352685	2.910818	-0.419538
C	1.350179	4.111737	-1.425845
H	2.857679	2.705830	-0.813160
H	2.707565	2.876997	-2.586665
H	-1.042956	3.163672	-1.242359
H	-0.923134	2.821188	0.507687
H	0.703873	4.303333	-2.297077
H	2.018915	4.965802	-1.287083

H	0.517914	0.862955	0.022825
O	1.294985	1.697269	-1.717843
O	0.567421	3.989563	-0.254934
S	-1.666102	0.055242	-1.563249
C	-2.274161	-0.396245	-0.099957
S	-1.595367	-1.714829	0.855053
C	-0.880284	-2.908969	-0.344954
C	0.285622	-2.366670	-1.174691
O	0.477580	-2.696471	-2.319364
C	-1.961581	-3.475311	-1.258603
H	-2.742894	-3.947989	-0.657815
H	-2.410593	-2.697888	-1.880778
H	-1.519401	-4.222498	-1.922454
C	-0.294255	-4.021758	0.543742
H	0.165019	-4.780779	-0.097739
H	0.467371	-3.633888	1.225436
H	-1.085336	-4.499928	1.128731
O	1.140075	-1.629481	-0.458871
C	2.317021	-1.207079	-1.175318
H	2.001558	-0.587100	-2.017157
H	2.822930	-2.097339	-1.565293
C	-3.354912	0.343797	0.598280
C	-3.641579	1.671903	0.239996
C	-4.122100	-0.248625	1.615326
C	-4.642574	2.384134	0.885032
H	-3.071310	2.138072	-0.555884
C	-5.126727	0.467306	2.256746
H	-3.951626	-1.283373	1.890614
C	-5.388497	1.786628	1.899976
H	-4.841257	3.411178	0.594698
H	-5.711624	-0.014212	3.034227
H	-6.171978	2.344384	2.403663
C	3.206914	-0.443076	-0.217062
H	4.032006	-0.027284	-0.808481
H	2.652087	0.411228	0.192062
C	3.746648	-1.306070	0.923186
H	4.402247	-2.083127	0.505720
H	2.907214	-1.826071	1.399591
C	4.509417	-0.509737	1.983109
H	3.825511	0.206175	2.460475
H	4.839064	-1.194399	2.775614
C	5.725248	0.244627	1.445364
H	6.365605	-0.451351	0.886411
H	5.401160	1.010273	0.729369
C	6.532466	0.907113	2.557659
H	5.914326	1.615093	3.120914
H	6.909716	0.161400	3.266020
H	7.391780	1.456365	2.160705

Number of imaginary frequencies = 1 (-141.8*i* cm^{-1})

Monomers

MMA
0 1
C 2.104480 -0.934014 -0.000026
H 1.808260 -1.978070 -0.000029
H 3.166192 -0.705173 -0.000047
C 1.187141 0.032883 -0.000004
C 1.502589 1.501065 0.000021
H 1.077583 1.995372 0.879219
H 2.583766 1.658242 0.000046
H 1.077612 1.995416 -0.879163
C -0.248056 -0.393820 0.000004
O -0.639060 -1.538397 0.000034
O -1.078087 0.661713 -0.000024
C -2.467607 0.335274 -0.000010
H -2.997505 1.287110 -0.000031
H -2.725007 -0.243903 -0.889853
H -2.725006 -0.243851 0.889870

HexMA
0 1
C -2.486105 -0.577199 -0.044827
C -3.737500 0.236046 0.085973
C -4.893550 -0.427109 0.076290
C -3.616084 1.726937 0.218844
H -4.604777 2.183806 0.305539
H -3.105726 2.159251 -0.647557
H -3.027388 1.997000 1.101139
O -2.444193 -1.780863 -0.161015
O -1.389998 0.195863 -0.017552
C -0.138681 -0.496373 -0.134204
H -0.126882 -1.051891 -1.078259
H -0.058441 -1.224053 0.680585
C 0.969305 0.534811 -0.076567
H 0.823681 1.262678 -0.883978
H 0.896472 1.086017 0.869066
C 2.347624 -0.112712 -0.198040
H 2.463671 -0.862569 0.594982
H 2.416074 -0.655040 -1.151870
C 3.479480 0.911039 -0.116198
H 3.461473 1.387482 0.873994
H 3.289969 1.708422 -0.846645
C 4.868563 0.321254 -0.368213
H 5.606300 1.131865 -0.340851
H 4.904837 -0.095397 -1.383311
C 5.267918 -0.755221 0.638265
H 6.303517 -1.073889 0.484527

H	5.182675	-0.381667	1.665439
H	4.636026	-1.644916	0.553726
H	-4.910410	-1.507717	-0.022985
H	-5.843364	0.091785	0.167073

Monomer radicals

MMA
0 2

C	-0.276807	-0.364326	-0.000168
C	1.091712	0.119396	-0.000412
C	2.200364	-0.871005	0.000226
C	1.378101	1.583128	-0.000072
H	2.454858	1.770526	-0.004505
H	0.943989	2.073937	0.879735
H	0.935971	2.076082	-0.874542
O	-0.608769	-1.538591	-0.000109
O	-1.178866	0.645649	0.000025
C	-2.539938	0.228061	0.000137
H	-3.133176	1.142460	-0.000591
H	-2.763536	-0.366544	0.889642
H	-2.763306	-0.367883	-0.888512
H	1.818000	-1.892548	0.000546
H	2.844038	-0.732360	-0.879008
H	2.843647	-0.731664	0.879639

HexMA
0 2

C	-2.428322	-0.538127	-0.047401
C	-3.646384	0.241684	0.082136
C	-4.953949	-0.465492	0.068209
C	-3.584180	1.724941	0.225731
H	-4.586565	2.151038	0.316465
H	-3.086298	2.188183	-0.635052
H	-3.001392	2.015826	1.108297
O	-2.381416	-1.751714	-0.170499
O	-1.318378	0.235276	-0.016921
C	-0.078141	-0.467388	-0.137056
H	-0.066378	-1.019267	-1.083885
H	0.000145	-1.201688	0.672688
H	-4.819433	-1.542313	-0.041954
H	-5.510419	-0.269374	0.994763
H	-5.583872	-0.099865	-0.754111
C	1.041362	0.551770	-0.073755
H	0.902962	1.285985	-0.876831
H	0.973618	1.098741	0.874848
C	2.413557	-0.107663	-0.198627
H	2.521758	-0.863958	0.589438
H	2.477334	-0.644668	-1.155844
C	3.555837	0.903801	-0.109490
H	3.542294	1.373774	0.883909

H	3.374835	1.708142	-0.834510
C	4.939139	0.301933	-0.364936
H	5.685260	1.104650	-0.331108
H	4.971892	-0.107666	-1.383030
C	5.326683	-0.786103	0.633728
H	6.359068	-1.114375	0.478410
H	5.244396	-0.419367	1.663606
H	4.685542	-1.668421	0.542038

Depropagation transition structures

MMA
0 2

C	-2.333689	2.042589	-0.647690
H	-1.801538	2.846474	-1.167147
H	-3.088602	2.519469	-0.005610
H	-2.862475	1.432126	-1.381844
C	-1.386149	1.237169	0.187061
C	-0.462606	1.969850	1.105948
H	0.287111	1.300705	1.531818
H	0.043445	2.788037	0.585464
H	-1.031675	2.405476	1.940416
C	-1.753947	-0.120956	0.609150
C	0.008526	0.541802	-1.446771
H	0.333190	1.570628	-1.573504
H	-0.847289	0.208892	-2.027935
C	0.877690	-0.374180	-0.934316
O	-2.696629	-0.682850	-0.179841
C	-3.067850	-2.009711	0.186093
H	-3.806009	-2.326742	-0.550408
H	-2.202205	-2.676559	0.168173
H	-3.503875	-2.024316	1.188177
C	0.579751	-1.841260	-0.873162
H	0.498419	-2.180308	0.165492
H	-0.363061	-2.056880	-1.384624
H	1.374022	-2.429435	-1.345188
C	2.131564	0.143570	-0.342249
O	2.458070	1.312617	-0.298291
O	2.900746	-0.844984	0.148668
C	4.125162	-0.416901	0.740564
H	4.622491	-1.322927	1.085571
H	4.747007	0.102259	0.007242
H	3.931247	0.253315	1.581491
O	-1.242301	-0.715038	1.538796

Number of imaginary frequencies = 1 (-522.8*i* cm^{-1})

HexMA
0 2

C	0.154487	-1.634322	-0.561866
C	1.291278	-2.229787	-1.301317
C	2.262917	-1.372144	-1.720137

C	1.366061	-3.718138	-1.451643
H	1.372490	-4.212023	-0.473513
H	2.267753	-4.007342	-1.997836
H	0.494371	-4.104964	-1.991382
O	-0.008592	-0.441564	-0.385967
O	-0.693141	-2.571466	-0.107025
C	-1.804268	-2.099194	0.665720
H	-1.457123	-1.313881	1.343762
H	-2.119367	-2.963727	1.255762
C	-2.934892	-1.601271	-0.218514
H	-2.572023	-0.759481	-0.818483
H	-3.220311	-2.401632	-0.912572
C	-4.144806	-1.170561	0.608203
H	-4.488533	-2.013341	1.224308
H	-3.845435	-0.377582	1.307273
C	-5.302217	-0.671417	-0.253832
H	-4.958464	0.171038	-0.869931
H	-5.601687	-1.463193	-0.954756
H	2.075946	-0.302418	-1.689792
H	3.059438	-1.723554	-2.371131
C	2.784703	-0.788280	0.967084
C	3.774305	-1.188186	-0.046907
C	4.280089	-2.591814	0.056166
C	4.683948	-0.159259	-0.643724
H	5.152671	-0.541304	-1.556622
H	5.494042	0.083903	0.059338
H	4.160689	0.771035	-0.873162
O	2.142203	-1.575075	1.638839
O	2.635069	0.544596	1.048114
C	1.618223	1.002721	1.950652
H	1.920231	0.754042	2.973930
H	0.688551	0.474209	1.723735
H	3.495536	-3.269739	0.396978
H	4.677264	-2.941282	-0.902823
H	5.102548	-2.642910	0.784882
C	1.470153	2.498120	1.754939
H	0.754894	2.862033	2.503994
H	2.428652	2.988714	1.968131
C	0.988299	2.873720	0.355156
H	1.713309	2.511942	-0.384848
H	0.049102	2.346210	0.143644
C	0.789793	4.377636	0.183691
H	1.731205	4.899611	0.407908
H	0.057803	4.736823	0.921382
C	0.321870	4.764806	-1.217519
H	-0.616531	4.241384	-1.441617
H	1.055101	4.409428	-1.953148
C	0.122592	6.268785	-1.376411
H	-0.211778	6.527137	-2.386029
H	-0.627682	6.641818	-0.670371
H	1.055402	6.810673	-1.184443

C	-6.515964	-0.236747	0.564612
H	-6.858188	-1.079643	1.179113
H	-6.215092	0.553335	1.264808
C	-7.663556	0.261043	-0.308333
H	-7.999576	-0.521089	-0.998082
H	-8.524374	0.567316	0.294017
H	-7.353230	1.122255	-0.910243

Number of imaginary frequencies = 1 (-518.4*i* cm^{-1})

Dimer radicals

MMA
0 2

C	-1.440287	2.492772	-0.456717
H	-0.641030	3.240756	-0.467232
H	-2.211119	2.828400	0.245295
H	-1.884640	2.437271	-1.453866
C	-0.872862	1.131681	-0.034602
C	-0.243168	1.225452	1.354144
H	0.142044	0.260425	1.696353
H	0.589611	1.935326	1.327996
H	-0.972547	1.574196	2.091093
C	-2.021489	0.128139	-0.103913
C	0.183228	0.692557	-1.093460
H	0.918735	1.496899	-1.175964
H	-0.336585	0.599262	-2.055040
C	0.860030	-0.597980	-0.768986
O	-2.216488	-0.548051	1.036436
C	-3.258269	-1.525260	0.987603
H	-3.270995	-1.995068	1.970260
H	-4.219143	-1.049848	0.778700
H	-3.050250	-2.266436	0.211878
C	0.146037	-1.896859	-0.928139
H	-0.372102	-2.171401	0.003963
H	-0.607029	-1.839975	-1.719174
H	0.849833	-2.704946	-1.142533
C	2.180971	-0.643483	-0.158945
O	2.746303	-1.669443	0.179022
O	2.739589	0.578638	0.003889
C	4.030213	0.566872	0.606305
H	4.340508	1.609876	0.667125
H	3.986822	0.126043	1.605464
H	4.736631	-0.003136	-0.002294
O	-2.692550	-0.051268	-1.094567

HexMA
0 2

C	-1.651512	0.802561	-0.957141
C	-0.312755	0.310501	-0.663413
C	0.841645	1.177633	-1.039499
C	-0.104157	-0.957130	0.094859

H	-0.127818	-0.774043	1.180397
H	0.871476	-1.393101	-0.141992
H	-0.888325	-1.686703	-0.119491
O	-1.892359	1.842069	-1.550312
O	-2.623431	-0.017149	-0.502536
C	-3.963034	0.415917	-0.761892
H	-4.103410	0.523439	-1.843403
H	-4.114981	1.402419	-0.309846
C	-4.905913	-0.615880	-0.177235
H	-4.696171	-1.591452	-0.632820
H	-4.706694	-0.714189	0.896847
C	-6.367714	-0.236490	-0.405055
H	-6.564983	0.746985	0.043302
H	-6.554612	-0.127988	-1.482339
C	-7.341107	-1.259883	0.175304
H	-7.143782	-2.244211	-0.271939
H	-7.154820	-1.368733	1.252885
H	0.527738	1.882020	-1.815558
H	1.653584	0.557619	-1.436999
C	1.927036	1.085945	1.230393
C	1.407726	2.018734	0.141792
C	2.583447	2.859222	-0.375840
C	0.327769	2.921912	0.732478
H	-0.098331	3.553105	-0.052881
H	0.746147	3.562058	1.514351
H	-0.481637	2.338895	1.181584
O	1.582390	1.100906	2.388839
O	2.841727	0.223436	0.754865
C	3.363630	-0.719966	1.703200
H	2.530214	-1.291525	2.125354
H	3.842219	-0.170882	2.521306
H	3.351696	2.230792	-0.834955
H	2.223017	3.571035	-1.125671
H	3.043732	3.428649	0.438712
C	4.349183	-1.611211	0.975523
H	4.686699	-2.379976	1.682090
H	3.827799	-2.134298	0.163540
C	5.553367	-0.854486	0.419117
H	5.206210	-0.086534	-0.283272
H	6.056159	-0.322634	1.239038
C	6.553562	-1.771310	-0.280827
H	6.047020	-2.308665	-1.094986
H	6.900983	-2.539503	0.424544
C	7.759453	-1.023502	-0.845396
H	8.264710	-0.486766	-0.031989
H	7.411119	-0.257727	-1.550493
C	8.750499	-1.950358	-1.542165
H	9.607175	-1.397812	-1.940080
H	9.133765	-2.707320	-0.848988
H	8.274952	-2.476500	-2.377262
C	-8.805229	-0.888271	-0.048738

H	-9.000643	0.095117	0.398232
H	-8.989581	-0.779789	-1.125447
C	-9.767040	-1.917964	0.535569
H	-9.620520	-2.022545	1.616277
H	-10.810670	-1.635917	0.365763
H	-9.609191	-2.903247	0.083140

Chugaev elimination processes

Chugaev elimination reactants

MMA
0 1

C	1.949990	0.652807	0.168911
S	-0.994372	2.400613	-0.064445
C	-0.985159	0.758988	-0.028236
S	0.390442	-0.318515	-0.112107
C	2.286508	1.564605	-1.017156
H	2.269698	1.011651	-1.958464
H	3.291715	1.976858	-0.870707
C	3.021289	-0.446052	0.237461
O	3.793519	-0.588149	1.151513
O	3.023359	-1.207122	-0.861858
C	4.008435	-2.244856	-0.884141
H	3.859092	-2.772917	-1.824590
H	3.866724	-2.921247	-0.038632
H	5.011938	-1.816119	-0.841257
C	-2.250976	-0.027285	0.010782
C	-2.371662	-1.182210	0.795928
C	-3.351426	0.404688	-0.742045
C	-3.572452	-1.883337	0.830512
H	-1.537456	-1.512315	1.406232
C	-4.541428	-0.309288	-0.717251
H	-3.256533	1.296223	-1.352981
C	-4.656463	-1.453623	0.070882
H	-3.659547	-2.765227	1.457187
H	-5.382304	0.027758	-1.315175
H	-5.590421	-2.006672	0.093943
C	1.935303	1.396650	1.498478
H	2.920400	1.843888	1.660295
H	1.189994	2.191513	1.489954
H	1.733921	0.716234	2.328822
H	1.578872	2.392444	-1.071784

HexMA
0 1

C	0.710296	-2.109257	0.021314
S	3.832315	-1.345541	-1.182649
C	2.945270	-0.232483	-0.363427

S	1.279722	-0.345190	0.157944
C	0.538150	-2.550187	-1.437187
H	-0.076435	-1.840315	-1.994434
H	0.044696	-3.529046	-1.453460
C	-0.683377	-2.061909	0.667962
O	-1.031421	-2.767609	1.581254
O	-1.478103	-1.170933	0.069071
C	-2.815124	-1.070027	0.592551
H	-2.757363	-0.829755	1.659184
H	-3.304317	-2.044627	0.492405
C	3.499991	1.109048	-0.024047
C	3.239322	1.717721	1.211354
C	4.313182	1.771474	-0.953659
C	3.789002	2.960122	1.509934
H	2.635358	1.204189	1.952131
C	4.844027	3.019222	-0.656987
H	4.511846	1.301781	-1.911288
C	4.585890	3.615945	0.576375
H	3.596068	3.412529	2.477520
H	5.461251	3.528168	-1.390588
H	5.008206	4.588696	0.808989
C	1.585258	-3.061898	0.826230
H	1.130377	-4.056550	0.805866
H	2.584714	-3.127768	0.396936
H	1.656026	-2.745606	1.869231
H	1.509963	-2.646014	-1.922598
C	-3.537570	0.006276	-0.189556
H	-2.988709	0.950354	-0.089658
H	-3.531177	-0.258575	-1.253718
C	-4.974903	0.181174	0.297313
H	-5.512234	-0.772689	0.204980
H	-4.971828	0.432588	1.366803
C	-5.729600	1.262119	-0.473152
H	-5.192738	2.216467	-0.380794
H	-5.731271	1.012133	-1.543251
C	-7.168359	1.443440	0.005324
H	-7.164799	1.692185	1.074493
H	-7.703004	0.489223	-0.087768
C	-7.911260	2.525973	-0.771111
H	-8.939570	2.642216	-0.415393
H	-7.410623	3.495126	-0.669269
H	-7.952015	2.284782	-1.839030

Chugaev elimination Transition structures

MMA
0 1

C	1.879933	-0.302854	1.085872
S	-0.474345	2.196343	0.204757
C	-0.833058	0.637916	-0.413896

S	0.396664	-0.284314	-1.068217
C	1.791621	0.961540	1.669482
H	0.866158	1.587563	0.949810
H	2.606305	1.662361	1.500742
C	2.996153	-0.615699	0.130279
O	3.284646	-1.741798	-0.201359
O	3.642006	0.476331	-0.283033
C	4.671615	0.238156	-1.245283
H	5.081349	1.217485	-1.488023
H	4.251819	-0.231205	-2.138034
H	5.446167	-0.407410	-0.825521
C	-2.215498	0.110632	-0.280023
C	-2.453779	-1.270132	-0.227276
C	-3.305989	0.988212	-0.208165
C	-3.747476	-1.756621	-0.087619
H	-1.615027	-1.955945	-0.286282
C	-4.600208	0.497862	-0.086860
H	-3.138340	2.059373	-0.262572
C	-4.824643	-0.875412	-0.020362
H	-3.915227	-2.827739	-0.032938
H	-5.435317	1.190121	-0.046047
H	-5.835902	-1.257700	0.080068
C	1.173815	-1.480446	1.687170
H	1.743037	-1.817789	2.563609
H	0.173981	-1.194800	2.027217
H	1.104406	-2.313365	0.987907
H	1.301364	1.021398	2.640652

Number of imaginary frequencies = 1 (-889.3*i* cm^{-1})

HexMA

0 1

C	0.559063	1.849432	0.886804
S	1.792995	-1.411382	1.555171
C	2.347357	-0.742947	0.076350
S	1.271157	0.077716	-0.902975
C	0.514514	1.205758	2.123984
H	0.971035	-0.016314	1.871729
H	-0.458112	0.912131	2.513000
C	-0.687973	1.965872	0.055689
O	-0.787595	2.730184	-0.876135
O	-1.662399	1.159117	0.475636
C	-2.855135	1.158022	-0.326408
H	-2.579718	0.923358	-1.360180
H	-3.292286	2.162217	-0.312946
C	3.790934	-0.839987	-0.261786
C	4.395117	0.104670	-1.103603
C	4.571975	-1.883521	0.253657
C	5.748308	0.016086	-1.404958
H	3.796196	0.913245	-1.509591
C	5.921145	-1.979176	-0.063822

H	4.115075	-2.630793	0.894981
C	6.514861	-1.026991	-0.889318
H	6.205388	0.763309	-2.046181
H	6.509488	-2.800477	0.333140
H	7.570566	-1.099264	-1.132601
C	1.673629	2.791523	0.544888
H	1.489757	3.746713	1.054711
H	2.630451	2.399953	0.902104
H	1.728328	2.985742	-0.526023
H	1.255308	1.507886	2.863497
C	-3.798159	0.123698	0.250900
H	-3.297084	-0.851589	0.252972
H	-4.014909	0.377701	1.295762
C	-5.097837	0.043938	-0.547673
H	-5.585918	1.028285	-0.554536
H	-4.869458	-0.195959	-1.595099
C	-6.067313	-0.996659	0.008222
H	-5.578945	-1.980966	0.015206
H	-6.295407	-0.758591	1.056598
C	-7.369593	-1.084707	-0.784339
H	-7.139712	-1.321615	-1.831215
H	-7.856343	-0.100767	-0.790272
C	-8.328570	-2.128373	-0.220532
H	-9.255725	-2.177474	-0.799753
H	-7.874142	-3.125182	-0.231706
H	-8.594245	-1.897116	0.816926

Number of imaginary frequencies = 1 (-889.1i cm^{-1})

Chugaev elimination products

MMA
0 1

C	-2.921617	0.949972	0.976934
S	0.340466	-1.479966	0.919340
C	0.928919	-0.252747	-0.191530
S	-0.062954	0.571727	-1.207205
C	-2.624596	0.378286	2.145023
H	-0.942872	-1.417787	0.513844
H	-2.604532	-0.699151	2.269420
C	-3.230699	0.123817	-0.227505
O	-3.706666	0.568040	-1.244250
O	-2.933518	-1.184423	-0.071112
C	-3.136180	-1.987468	-1.235441
H	-2.839235	-2.998010	-0.954785
H	-2.517394	-1.620993	-2.058351
H	-4.186124	-1.969762	-1.534889
C	2.392450	-0.026295	-0.109240
C	2.918181	1.234089	-0.426163
C	3.269223	-1.050459	0.276868
C	4.284549	1.465140	-0.349135

H	2.241388	2.029430	-0.719378
C	4.638227	-0.818241	0.339112
H	2.888242	-2.042931	0.497461
C	5.148855	0.439807	0.031212
H	4.676651	2.449186	-0.585622
H	5.306295	-1.624513	0.624471
H	6.217878	0.621252	0.085608
C	-3.008623	2.431025	0.754173
H	-4.016267	2.713394	0.433635
H	-2.762405	2.974510	1.669051
H	-2.322957	2.744359	-0.039555
H	-2.409521	0.982343	3.021983

HexMA

0 1

C	0.466341	3.385153	0.691060
S	0.966640	-0.501318	1.411520
C	1.876963	-0.423283	-0.088556
S	1.447868	0.555445	-1.334818
C	0.528420	3.046350	1.979768
H	0.004669	0.358631	1.023879
H	-0.218916	2.410200	2.442396
C	-0.643277	2.893851	-0.180063
O	-0.896454	3.358947	-1.265960
O	-1.348490	1.882967	0.367444
C	-2.390094	1.344710	-0.462845
H	-1.951129	1.033514	-1.416640
H	-3.120972	2.133981	-0.668337
C	3.068919	-1.306066	-0.108680
C	4.181596	-0.952450	-0.884702
C	3.108813	-2.495157	0.633727
C	5.308220	-1.762917	-0.907847
H	4.155193	-0.030493	-1.455627
C	4.233805	-3.310637	0.596288
H	2.247481	-2.805199	1.217440
C	5.337306	-2.944904	-0.169634
H	6.167487	-1.470601	-1.503038
H	4.244747	-4.235396	1.164198
H	6.217757	-3.579737	-0.192920
C	1.438230	4.300250	0.006177
H	0.924607	5.186739	-0.378542
H	2.223408	4.616810	0.696287
H	1.900363	3.802817	-0.852511
H	1.326845	3.417217	2.616372
C	-3.018013	0.179424	0.273494
H	-2.254869	-0.588949	0.452954
H	-3.370945	0.520653	1.254524
C	-4.177018	-0.424821	-0.517464
H	-4.939745	0.345776	-0.694244
H	-3.819364	-0.740389	-1.507002

C	-4.816279	-1.615882	0.192493
H	-4.053605	-2.387852	0.365839
H	-5.168270	-1.301839	1.185162
C	-5.980666	-2.223131	-0.586967
H	-5.628009	-2.534370	-1.578760
H	-6.742269	-1.451368	-0.758219
C	-6.608418	-3.413292	0.131420
H	-7.440848	-3.834811	-0.440308
H	-5.872628	-4.209907	0.287353
H	-6.992647	-3.119952	1.114629

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