Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

Accelerated cationic ring-opening polymerisation of a methyl ester functionalized 2-oxazoline monomer

Petra JM Bouten,[#,a,b] Dietmar Hertsen,[#,c] Maarten Vergaelen,[b] Bryn D Monnery,[a] Marcel A Boerman,[b] Hannelore Goossens,[c] Saron Catak,[c, d] Jan CM van Hest[b] Veronique Van Speybroeck[*, c] and Richard Hoogenboom[*, a]

SI 1. Experimental

Materials

2-Chloroethylamine hydrochloride, methyl p-toluenesulfonate (MeOTs) and sodium carbonate were purchased from Acros Organics. All other reagents were purchased from Sigma Aldrich and used as received, except 2-methyl-2-oxazoline (MeOx), 2-ethyl-2-oxazoline (EtOx) and MeOTs (98%). These were purified by distillation over barium oxide and stored under argon. Dry solvents were obtained from a solvent purification system from J.C. Meyer, with aluminum oxide drying system and a nitrogen flow.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DMC300 (300 MHz, 75 MHz for ^{13}C) or a Bruker DMX 500 (500 MHz, 125 MHz for ^{13}C).

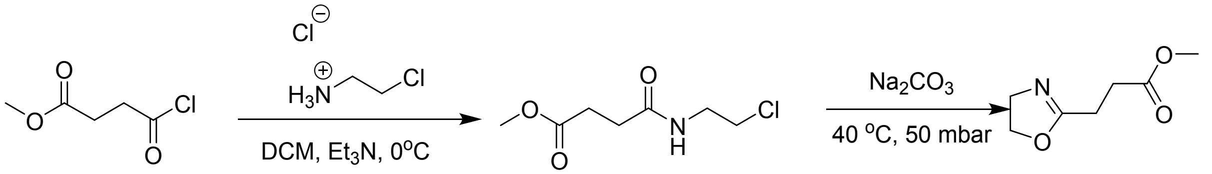
Polymerisation reaction mixtures were prepared in a VIGOR Sci-Lab SG 1200/750 Glovebox system, with the purity levels of 1 ppm for O_2 and H_2O.

Polymerisations were carried out in a Biotage Initiator Microwave System with Robot Sixty utilizing capped reaction vials. These vials were heated to 120 °C overnight, allowed to cool to room temperature and filled with nitrogen prior to use. All microwave polymerizations were performed with temperature control (IR sensor).

Size exclusion chromatography (SEC) was performed on an Agilent 1260 - series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler, a thermostatted column compartment, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). Analyses were performed on a PSS Gram30 column in series with a PSS Gram1000 column at 50 °C. *N,N*-dimethylacetamide (DMA), containing 50 mM of LiCl, was used as an eluent, at a flow rate of 0.593 ml min^{-1}. The SEC traces were analysed using the Agilent Chemstation software with the GPC add on. Number average molecular weights (M_n) and dispersity (Đ) values were calculated against poly(methyl methacrylate) PMMA standards.

Gas chromatography (GC) was performed on 7890A from Agilent Technologies with an Agilent J&W Advanced Capillary GC column (30 m, 0.320 mm, and 0.25 µm). Injections were performed with an Agilent Technologies 7693 auto sampler. Detection was done with a Flame ionization detector (FID) detector. Injector and detector temperatures were kept constant at 250 and 280 °C, respectively. The column was initially set at 50 °C, followed by two heating stages: from 50 °C to 100 °C with a rate of 20 °C /min and from 100 °C to 300 °C with a rate of 40 °C /min, and then held at this temperature for 0.5 minutes. Conversion was determined based on the integration of monomer peaks using acetonitrile (CH_3CN) as an internal standard.

MestOx synthesis



1a **1b** **1**

Scheme S1: Synthesis of 2-methyl ester-functionalised-2-oxazoline (MestOx)

Synthesis of methyl 4-(2-chloroethyl)amino-4-oxobutanoate (1b, MestOx-precursor)

Methyl succinyl chloride (**1a**, 50 g, 332.1 mmol, 40.88 mL) and 2-chloroethylamine hydrochloride (38.52 g, 332.1 mmol) were suspended in dry dichloromethane (375 mL) under an argon atmosphere. The reaction mixture was cooled continuously to 0°C while triethylamine (Et_3N) (72.25 g, 714 mmol, 99.2 mL) was added dropwise within 2 hours. The reaction was allowed to warm to room temperature overnight, after full addition of the TEA. The mixture was washed with water (2x50 mL) and brine (1x 50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting product was purified by filtration column chromatography (neutral Al_2O_3, DCM:MeOH 99:1) yielding product **1b** as a yellow oil (107 g, 664.2 mmol, 83%).

^1H NMR (500 MHz, $CDCl_3$): δ 6.1 (broad, 1H, NH), 3.68 (t, 2.1 Hz, 2H, CH_2Cl), 3.61 (m, 5H, OCH_3 & $C\underline{H}_2CH_2Cl$), 2.68 (t, 7.0 Hz, 2 H, $NC{=}OC\underline{H}_2$), 2.52 (t, 7.0 Hz, 2H, $C\underline{H}_2COOCH_3$)
^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9 (C=ONH), 171.1 ($\underline{C}{=}OOCH_3$), 51.4 (OCH_3), 43.5 ($\underline{C}H_2CH_2Cl$), 40.8 (CH_2Cl), 30.5 ($CH_3C{=}O\underline{C}H_2$), 28.8 ($CH_3C{=}OCH_2\underline{C}H_2$)
MS: m/z: calculated 193.05, found 194.1&196.1 [$M+H^+$], 216.1&218.1 [$M+Na^+$]

Synthesis of 2-methoxycarboxyethyl-2-oxazoline (1, MestOx)

The precursor (**1b**, 107 g, 552.6 mmol) and anhydrous sodium carbonate (52.7 g, 497.3 mol) were mixed. The reaction was performed for 24-48 hours, depending on the scale by mounting the flask at a rotary evaporator (40 °C, 50 mbar) to allow good mixing of the salt in the viscous mixture and providing a larger surface area for evaporation of the released CO_2. Subsequently dichloromethane (DCM) was added, the reaction mixture was filtered and the solvent was removed under reduced pressure. The oil was distilled twice over barium oxide under reduced pressure, yielding a colourless liquid that crystallised in time into a white solid (60 g, 381.8 mmol, 69%).

^1H NMR (500 MHz, $CDCl_3$): δ 4.3 (t, 2H, 9.4 Hz, CH_2O), 3. 8 (t, 9.4 Hz, 2H, $CH_2N{=}$), 3.7 (s, 3H, $COOCH_3$), 2.7 (t, 2H, 7.3 Hz, CH_2COO), 2.6 (t, 2H, 7.3 Hz, $CH_2C({=}N)O$)
^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9 ($\underline{C}OOCH_3$), 169.2 ($\underline{C}({=}N)O$), 67.6 (CH_2O), 54.3 (CH_2N), 51.9 (OCH_3), 30.2 ($\underline{C}H_2COO$), 23.2 ($\underline{C}H_2N$)
MS: m/z: calculated 157.07, found 158.1&159.1 [$M+H^+$]

Polymerisation kinetics

Stock solutions (7 mL) for polymerisation kinetics were prepared in the glovebox. Total monomer concentration $[M_{tot}] = 3$ M, monomer to initiator ratio $\frac{[M]}{[I]} = 100$, MeOTs was used as an initiator, CH_3CN was used as solvent. For copolymerisations the ratio of both monomers was 50:50 and $[M_{tot}] = [M_1] + [M_2] = 3$ M. The stock solution was divided in 0.7-0.8 mL portions in separate 0.5-2.0 mL Biotage reaction vials. The polymerisation times used were 1 second (to determine influence of the heating cycle), 2 minutes, 4 minutes, 6 minutes, 8 minutes and 10 minutes. After the polymerizations, a sample was taken for GC in chloroform and for SEC in the SEC eluent. GC was measured to calculate the monomer conversion based on the ratio of the monomer peaks and the acetonitrile solvent peak of the sample as well as of the initial stock solution for time zero. SEC analysis was performed to determine M_n and Đ.

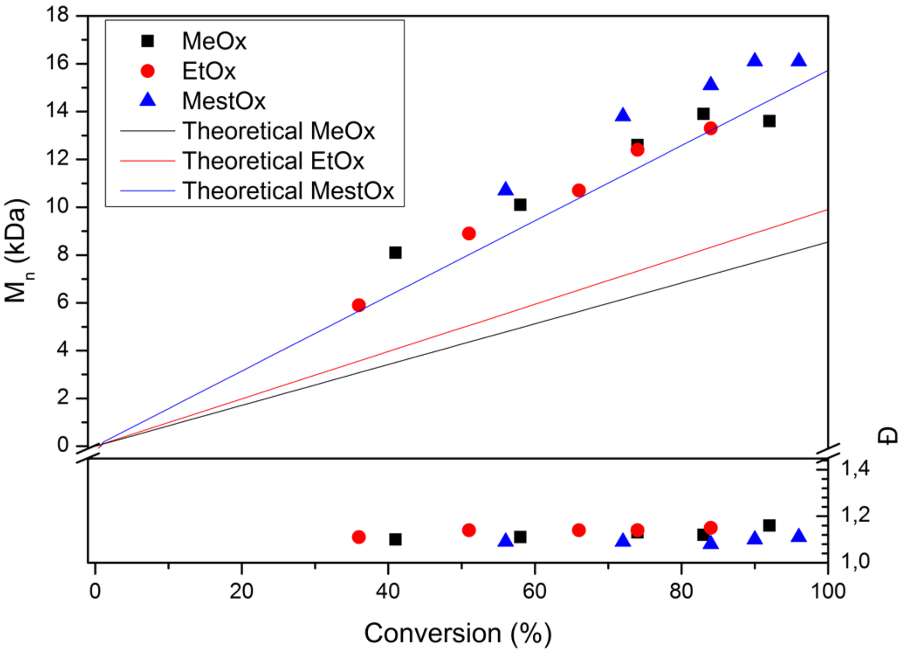


Figure S 1: M_n against conversion plot, including Đ of $PMeOx_{100}$, $PEtOx_{100}$ and $PMestOx_{100}$ homopolymers. The discrepancy between theoretical and experimental M_n values is related to the use of PMMA standards for the calibration.

Importantly, the experimental M_n values that were obtained relatively to the PMMA calibration are significantly overestimated, especially for MeOx and EtOx, which can be ascribed to the higher rigidity of the poly(2-oxazoline)s compared to PMMA leading to larger hydrodynamic volumes and, in fact, the hydrodynamic volumes are only slightly influenced by the side-chain substituent of the poly(2-oxazoline)s. As the experimental Mn values are deviation from the theoretical values to a different extent, we have evaluated the initiation efficiency of the polymerizations by ^{1}H NMR spectroscopy to ensure the differences are not due to a different initiation efficiency, which would lead to differences in the k_p values as well. In the ^{1}H NMR spectra of the crude polymerization mixtures, the methyl tosylate aromatic signals are fully displaced to lower chemical shifts indicating full initiation. Moreover, the ratio of monomer to initiation was confirmed to be close to 100 as aimed for.

For PEtOx we have recently determined the absolute molar mass for a series of defined polymers leading to a correction factor for SEC measurements in DMA with 50 mM LiCl using PMMA standards. Using this correction factor, the SEC data for PEtOx have been corrected revealing that the obtained Mn values are very close to the theoretical values confirming near quantitative initiation (see Figure S2).

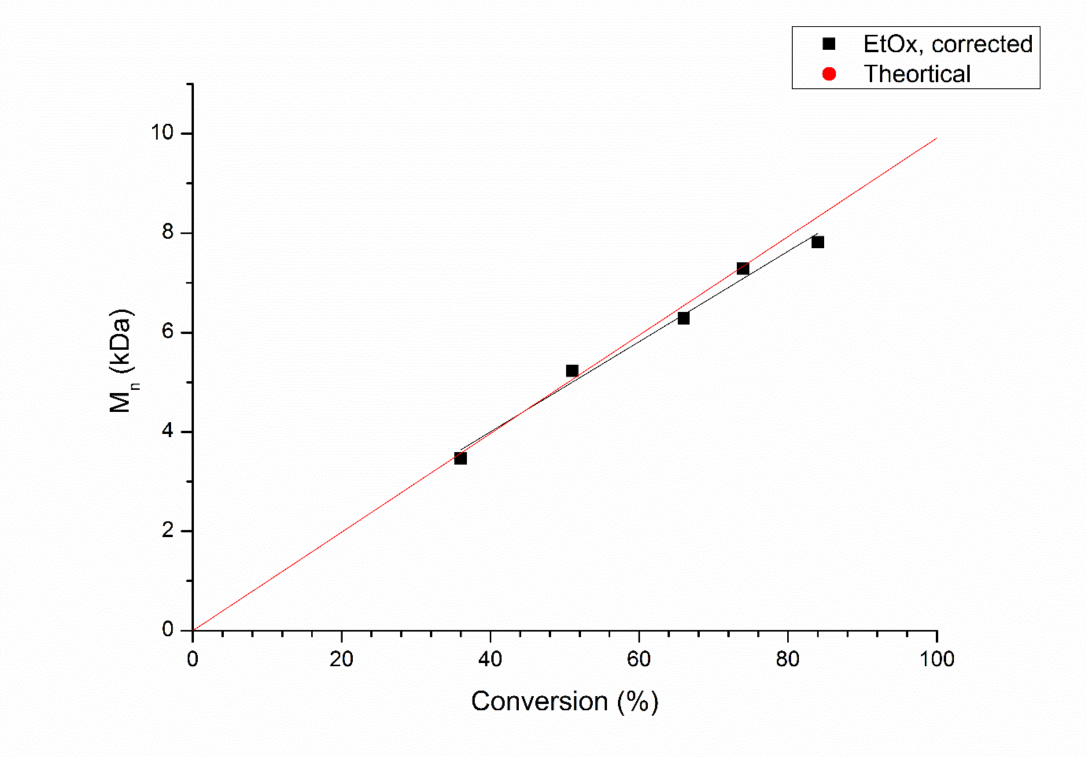


Figure S2: M_n against conversion plot of $PEtOx_{100}$. The Mn values obtained with PMMA are corrected, $M_{n,PEtOx}=0.5876*M_{n,PMMA}$, to obtain the values for PEtOx (**B. D. Monnery, R. Hoogenboom, *manuscript in preparation***)

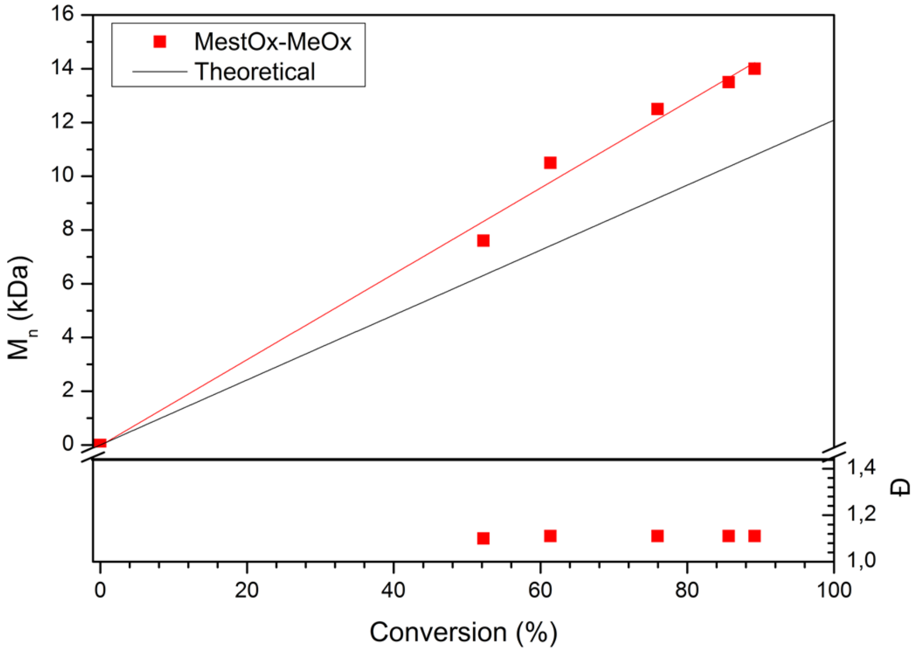


Figure S 3: M_n against conversion plot, including Đ of P($MeOx_{50}$-$MestOx_{50}$) copolymer. The discrepancy with the theoretical M_n values is observed due to the poly(methylmethacrylate) (PMMA) standards used for the SEC calibration.

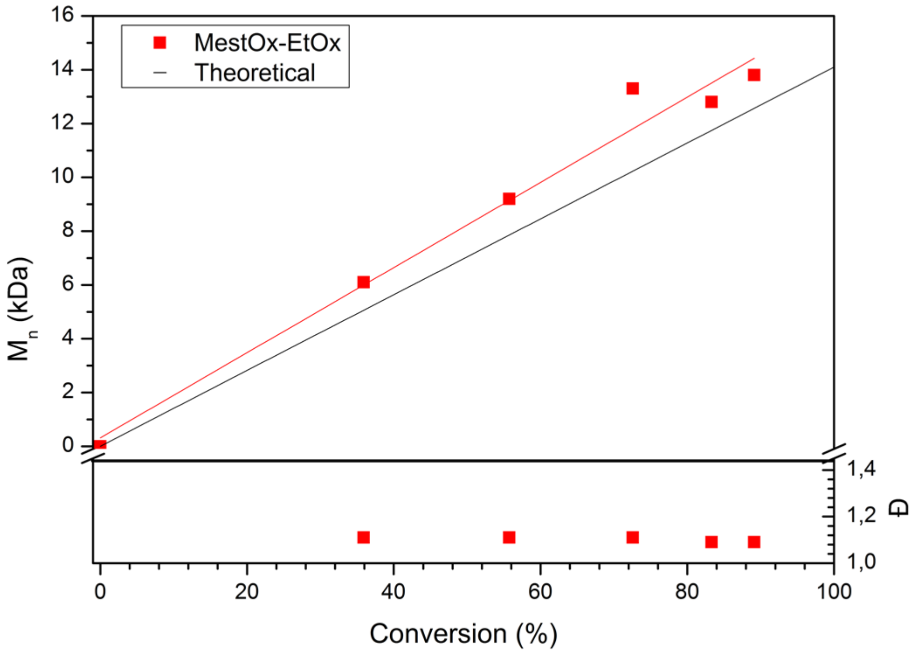


Figure S 4: M_n against conversion plot, including Đ of P($EtOx_{50}$-$MestOx_{50}$) copolymer. The discrepancy with the theoretical M_n values is observed due to the PMMA standards used for the SEC calibration.

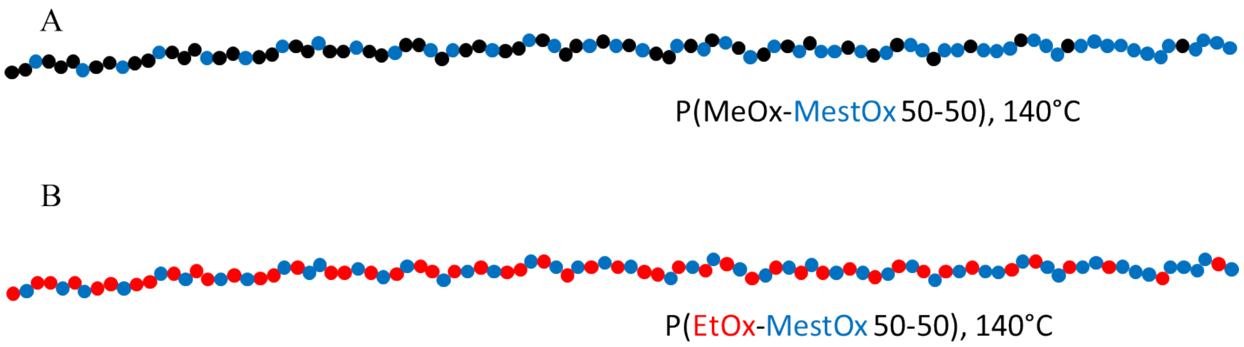


Figure S5: Calculated distribution of residues along the polymer chains of the obtained A) MeOx (black) and MestOx (blue) as well as B) EtOx (red) and MestOx (blue) copolymers.

SI 2. Computational Methodology

All calculations are performed at the M06-2X/6-31+G(d,p) level of theory. Frequency calculations are used to classify stationary points as minima (ground states) or first-order saddle points (transition states). The product and reactant complexes corresponding to each transition state are identified via Intrinsic Reaction Coordinate (IRC) calculations followed by full geometry optimizations. Gibbs free energy corrections are calculated at 140°C (413.5 K) and 1 atm. All Gibbs free energies include an IEF-PCM[2] energy refinement to account for the acetonitrile solvent effect (ε = 35.688). Interaction energies are obtained from Natural Bond Orbital (NBO) analyses at the HF/6-31G(d,p)//M06-2X/6-31+G(d,p) level of theory. The Gaussian09 program package was used for all energy calculations. Hirshfeld-I charges were obtained with the Horton program package[3].

References

2. Cossi, M., Barone, V., Mennucci, B. and Tomasi, J., *Chemical Physics Letters,* 1998, **286**, 253-260.
3. T. Verstraelen, Horton Program, http://molmod.ugent.be/software/

SI 3. Cartesian Coordinates and Energies of Transition States

All structures optimized at the M06-2X/6-31+G(d,p) level of theory, Gibbs free energies at 140°C (413.5 K) and 1 atm.

TS1

G = -1165.981087 Ha

C	2.746604	-4.110994	-0.920254
C	3.616363	-2.865875	-0.648894
N	2.666928	-1.927833	-0.035507
C	1.554980	-2.539582	0.157417
O	1.496388	-3.808049	-0.255206
C	0.319624	-1.985778	0.771231
C	3.193275	-0.022446	0.483426
C	2.257618	0.593404	-0.542994
N	2.016801	1.988279	-0.161018
C	0.800195	2.643500	-0.623174
C	2.934951	2.468883	0.671477
C	2.925547	3.891681	1.139328
O	3.820323	1.658187	1.046644
H	2.848406	-0.236605	1.486686
H	4.202534	-0.307711	0.229528
H	1.294473	0.087347	-0.589902
H	2.710433	0.559858	-1.540836
H	0.624396	2.324836	-1.653283
H	0.957268	3.724300	-0.623606
H	4.035956	-2.441701	-1.564785
H	4.437139	-3.065989	0.046887
H	2.528382	-4.260038	-1.979201
H	3.140388	-5.030705	-0.489291
C	-0.407135	2.235774	0.250805
H	-0.185380	1.277416	0.735376
H	-0.580757	2.975748	1.036740
N	-1.635386	2.083103	-0.509962
C	-2.719767	3.018506	-0.250891
H	-3.476093	2.951571	-1.032133
H	-3.187439	2.836629	0.724400
H	-2.325887	4.037731	-0.265299
C	-1.751082	0.919354	-1.213132
O	-0.765563	0.202616	-1.387026
C	-4.170561	0.187248	-0.719270
H	-4.556337	1.094422	-0.241054
H	-5.024079	-0.300933	-1.193235
H	3.748048	4.031238	1.838310
H	1.981823	4.128772	1.637588
H	3.048803	4.570765	0.291482
C	-3.103239	0.515188	-1.775182
H	-2.901583	-0.367355	-2.384760

H	-3.489216	1.290681	-2.444743
C	-3.658118	-0.690323	0.402580
O	-2.552715	-0.600467	0.895611
O	-4.584052	-1.551076	0.818343
C	-4.218012	-2.387080	1.924476
H	-5.098590	-2.987285	2.140902
H	-3.375585	-3.023489	1.646702
H	-3.944157	-1.773719	2.784607
H	-0.362100	-1.633139	-0.011226
H	0.551765	-1.142509	1.423762
H	-0.183535	-2.763427	1.347163

TS2

G = -1165.983989 Ha

C	-2.845448	-2.345166	-1.498978
C	-1.318735	-2.458697	-1.676895
N	-0.802836	-1.961091	-0.396095
C	-1.792721	-1.795599	0.399481
O	-3.001506	-2.098637	-0.082434
C	-1.733091	-1.309616	1.805403
C	1.130753	-2.121957	0.216322
C	1.634577	-1.145915	-0.835209
N	2.951849	-0.670767	-0.402338
C	3.500751	0.592046	-0.874802
C	3.509999	-1.451459	0.520125
C	4.874742	-1.190690	1.079896
O	2.829896	-2.436822	0.898639
H	0.811859	-1.731280	1.172805
H	1.018362	-3.176022	0.014408
H	0.951175	-0.301650	-0.903397
H	1.725041	-1.635257	-1.812339
H	3.228186	0.710957	-1.928770
H	4.590581	0.527963	-0.828642
H	-0.956279	-1.837705	-2.500078
H	-0.982038	-3.488937	-1.839910
H	-3.260367	-1.480143	-2.021101
H	-3.397726	-3.250391	-1.747564
C	3.018433	1.794271	-0.052239
H	2.969803	1.513386	1.003824
H	3.746435	2.605340	-0.159540
N	1.718413	2.319849	-0.452397
C	1.752810	3.438076	-1.390989
H	0.800296	3.549611	-1.904958
H	2.004804	4.379925	-0.888600
H	2.512417	3.236666	-2.149902
C	0.609538	1.973174	0.269127
O	0.630787	1.021421	1.048269
C	-1.801170	2.427765	0.944198
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H	-2.408861	3.293263	1.217208
H	5.630707	-1.262415	0.292987
H	5.078080	-1.938897	1.843740
H	4.930865	-0.193510	1.524288
C	-0.623810	2.839354	0.070980
H	-0.921243	2.803954	-0.982003
H	-0.341628	3.875971	0.286423
C	-2.702324	1.430414	0.254592
O	-2.387522	0.756198	-0.705749
O	-3.902752	1.388981	0.830200
C	-4.897062	0.561309	0.206682
H	-5.816592	0.752809	0.755332
H	-5.009416	0.846565	-0.841603
H	-4.612782	-0.489475	0.275047
H	-0.962565	-0.538419	1.889708
H	-1.501182	-2.137236	2.482528
H	-2.703497	-0.898227	2.089854

TS3

G = -1165.990826 Ha

C	-4.138339	-1.217505	0.559010
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H	-4.354138	-1.090682	1.624691
H	-3.833696	-2.254573	0.391944
H	-6.223419	-0.536371	0.209541
H	-5.552005	-1.523188	-1.117712
O	-4.837383	0.404085	-0.993199
C	-3.554560	0.563436	-0.662362
C	-2.855282	1.717785	-1.281088
N	-3.067672	-0.293403	0.160551
H	-3.331794	2.641902	-0.942097
H	-2.975222	1.666115	-2.365943
H	-1.797672	1.728697	-1.016820
C	-1.334069	-0.273536	1.165128
C	-0.629949	-1.184929	0.169292
N	0.533284	-1.794343	0.818943
C	1.240848	-2.893760	0.165419
C	0.928798	-1.138129	1.914816
C	2.154219	-1.512605	2.682052
O	0.203200	-0.182819	2.280426
H	-1.280591	0.797737	1.050053
H	-1.880139	-0.692323	2.000787
H	-0.316684	-0.591314	-0.698698
H	-1.299067	-1.983555	-0.157431
H	0.542929	-3.322796	-0.559948
H	1.459103	-3.678102	0.897241
C	2.534523	-2.466736	-0.536095
H	3.274509	-2.140075	0.196342
H	2.942089	-3.330426	-1.071400
N	2.334861	-1.377108	-1.478761
C	1.828238	-1.688943	-2.808385
H	2.132054	-2.704144	-3.070886
H	0.733176	-1.629662	-2.861618
H	2.249785	-1.015181	-3.554742
C	2.519032	-0.102865	-1.024571
O	2.850784	0.123409	0.136184
C	2.372095	2.368404	-1.260364
H	3.353576	2.523823	-0.810728
H	2.177344	3.200166	-1.945898
H	2.398478	-2.571780	2.588778
H	1.998776	-1.257375	3.729820
H	2.980121	-0.915639	2.283464
C	2.297288	1.041734	-2.003761
H	1.320134	0.930686	-2.485719
H	3.056818	1.001328	-2.792361
C	1.329713	2.409274	-0.169951
O	0.269248	1.808326	-0.227358
O	1.673231	3.187051	0.842247
C	0.749537	3.249430	1.938512
H	1.207455	3.915796	2.665912
H	-0.206767	3.653812	1.599023
H	0.609110	2.249867	2.356314

SI 4. Cartesian Coordinates and Energies of Pre-reactive Complexes

All structures optimized at the M06-2X/6-31+G(d,p) level of theory, Gibbs free energies at 140°C (413.5 K) and 1 atm.

PRC1

G = -1166.014219 Ha

C	-2.746605	4.110994	-0.920254
C	-3.616363	2.865875	-0.648894
N	-2.666928	1.927833	-0.035507
C	-1.554980	2.539582	0.157417
O	-1.496389	3.808049	-0.255206
C	-0.319624	1.985778	0.771231
C	-3.193275	0.022446	0.483426
C	-2.257618	-0.593404	-0.542994
N	-2.016801	-1.988279	-0.161018
C	-0.800195	-2.643500	-0.623174
C	-2.934951	-2.468883	0.671477
C	-2.925547	-3.891681	1.139328
O	-3.820323	-1.658187	1.046644
H	-2.848406	0.236605	1.486686
H	-4.202534	0.307711	0.229528
H	-1.294473	-0.087347	-0.589902
H	-2.710433	-0.559858	-1.540836
H	-0.624396	-2.324836	-1.653283
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H	-4.035956	2.441701	-1.564785
H	-4.437139	3.065988	0.046887
H	-2.528383	4.260038	-1.979201
H	-3.140389	5.030705	-0.489291
C	0.407135	-2.235774	0.250805
H	0.185380	-1.277416	0.735376
H	0.580757	-2.975748	1.036740
N	1.635386	-2.083103	-0.509962
C	2.719767	-3.018506	-0.250891
H	3.476093	-2.951571	-1.032133
H	3.187439	-2.836629	0.724400
H	2.325887	-4.037731	-0.265299
C	1.751082	-0.919354	-1.213132
O	0.765563	-0.202616	-1.387026
C	4.170561	-0.187248	-0.719270
H	4.556337	-1.094421	-0.241054
H	5.024079	0.300934	-1.193235
H	-3.748048	-4.031238	1.838310
H	-1.981823	-4.128772	1.637588
H	-3.048803	-4.570765	0.291482
C	3.103239	-0.515188	-1.775182
H	2.901583	0.367355	-2.384760
H	3.489216	-1.290681	-2.444743
C	3.658118	0.690323	0.402580
O	2.552715	0.600467	0.895611
O	4.584052	1.551077	0.818343
C	4.218012	2.387080	1.924476
H	5.098590	2.987286	2.140902
H	3.375585	3.023489	1.646702
H	3.944157	1.773719	2.784607
H	0.362100	1.633139	-0.011226
H	-0.551765	1.142509	1.423762
H	0.183535	2.763427	1.347163

PRC2

G = -1166.026968 Ha

C	3.415925	-0.677693	2.174210
C	1.887882	-0.473711	2.258365
N	1.354352	-1.103452	1.036719
C	2.361993	-1.557965	0.395411

O	3.589262	-1.374670	0.921682
C	2.362311	-2.281011	-0.908708
C	-1.349653	-2.172353	0.041387
C	-1.948566	-1.315456	1.161899
N	-3.175902	-0.812786	0.510672
C	-3.922239	0.351606	0.995754
C	-3.334502	-1.383607	-0.652079
C	-4.387906	-1.110723	-1.653004
O	-2.431438	-2.273365	-0.937143
H	-0.524631	-1.661377	-0.448907
H	-1.074723	-3.182319	0.337455
H	-1.283619	-0.490205	1.425630
H	-2.219196	-1.877871	2.059534
H	-3.709877	0.436585	2.064583
H	-4.994118	0.164632	0.884534
H	1.630216	0.590041	2.272059
H	1.447825	-0.948250	3.140690
H	3.970516	0.259175	2.115994
H	3.817661	-1.312569	2.966030
C	-3.511935	1.624745	0.249308
H	-3.724178	1.518650	-0.818058
H	-4.104645	2.461369	0.631298
N	-2.099515	1.934049	0.417484
C	-1.761190	2.922644	1.437943
H	-0.717653	2.836411	1.734755
H	-1.948866	3.942150	1.083139
H	-2.373970	2.743202	2.325362
C	-1.208909	1.414982	-0.483762
O	-1.575454	0.603814	-1.335354
C	1.146378	1.209844	-1.379334
H	0.865140	0.166182	-1.556520
H	1.081555	1.711570	-2.348735
H	-5.259785	-0.628542	-1.213209
H	-4.673864	-2.046841	-2.134796
H	-3.941481	-0.453357	-2.407484
C	0.236657	1.835809	-0.336377
H	0.585284	1.522336	0.654011
H	0.313743	2.928531	-0.352712
C	2.581414	1.226266	-0.902134
O	2.939586	1.576709	0.201628
O	3.416638	0.775216	-1.838532
C	4.804638	0.721018	-1.465140
H	5.330138	0.377805	-2.353797
H	5.149701	1.713219	-1.170235
H	4.934300	0.021233	-0.636420
H	1.345937	-2.460154	-1.256847
H	2.883248	-3.234889	-0.796439
H	2.900266	-1.689396	-1.655708

PRC3

G = -1166.026692 Ha

C	-4.527487	-1.385697	0.433661
C	-5.675937	-0.725292	-0.361148
H	-4.704525	-1.369601	1.513827
H	-4.361059	-2.425439	0.138412
H	-6.523894	-0.421103	0.253116
H	-6.029248	-1.334155	-1.196322
O	-5.065365	0.461866	-0.905245
C	-3.752875	0.406428	-0.595353
C	-2.934922	1.527110	-1.135375
N	-3.343141	-0.569059	0.118055
H	-3.328037	2.476172	-0.760888
H	-3.015824	1.547569	-2.225373
H	-1.891143	1.419637	-0.838707
C	-0.847583	-0.446636	1.609320
C	-0.491556	-1.305422	0.393785
N	0.807662	-1.874189	0.815752

C	1.504525	-2.911316	0.049325
C	1.245678	-1.259569	1.881533
C	2.540283	-1.466681	2.567868
O	0.413779	-0.382962	2.364145
H	-1.124681	0.571416	1.358636
H	-1.583337	-0.910320	2.265930
H	-0.350380	-0.705416	-0.510460
H	-1.215058	-2.098493	0.212464
H	0.757963	-3.335631	-0.627060
H	1.822132	-3.709196	0.728186
C	2.703699	-2.374589	-0.737483
H	3.490247	-2.044949	-0.056277
H	3.102292	-3.188918	-1.350511
N	2.359404	-1.252980	-1.592956
C	1.749281	-1.519764	-2.891316
H	2.002988	-2.537188	-3.194263
H	0.656682	-1.427325	-2.862330
H	2.138718	-0.842207	-3.652085
C	2.559106	0.006134	-1.102229
O	2.996951	0.188463	0.031573
C	2.267421	2.477525	-1.231171
H	3.248885	2.652733	-0.785891
H	2.045105	3.329045	-1.882709
H	2.936373	-2.464572	2.376054
H	2.405247	-1.313723	3.638694
H	3.239416	-0.722395	2.173196
C	2.228407	1.175867	-2.014611
H	1.239321	1.029613	-2.459984
H	2.954407	1.204056	-2.835348
C	1.241986	2.459216	-0.125491
O	0.332827	1.652504	-0.049155
O	1.422089	3.440189	0.747995
C	0.480214	3.510003	1.826225
H	0.783686	4.365363	2.425093
H	-0.528757	3.653246	1.433504
H	0.521311	2.591011	2.415388

SI 5. Cartesian Coordinates and Energies of Isolated Monomers and Cations

All structures optimized at the M06-2X/6-31+G(d,p) level of theory, Gibbs free energies at 140°C (413.5 K) and 1 atm.

MeOx monomer

G = -286.432512 Ha

C	-1.428371	0.765450	-0.034075
C	-1.388588	-0.776291	0.047196
H	-1.863979	1.125346	-0.969306
H	-1.986586	1.214761	0.788276
H	-1.907699	-1.276792	-0.769203
H	-1.754826	-1.162022	1.000307
O	0.012160	-1.082053	-0.051313
C	0.667250	0.111359	0.000364
C	2.150844	0.005370	0.007702
H	2.474857	-0.579744	0.870019
H	2.486258	-0.512278	-0.892794
N	-0.019576	1.172966	0.029778
H	2.584920	1.001063	0.047629

MestOx monomer

G = -553.473583 Ha

C	-3.420328	-1.108866	-0.041532
C	-3.846040	0.370561	0.080676
H	-3.802649	-1.724171	0.773731
H	-3.742295	-1.562025	-0.982173
H	-4.288449	0.607006	1.050043
H	-4.510068	0.708142	-0.713857
O	-2.604851	1.088344	-0.030835
C	-1.621283	0.149810	-0.013104
C	-0.235193	0.698693	-0.017601
H	-0.117870	1.337372	-0.897325
H	-0.120082	1.361955	0.843754
C	0.810804	-0.402549	-0.000991
H	0.695570	-1.044740	0.875451
H	0.701551	-1.065994	-0.862205
N	-1.953145	-1.071192	-0.001186
C	2.207294	0.160935	-0.002983
O	2.490208	1.329350	-0.020746
O	3.126151	-0.816352	0.018005
C	4.486503	-0.381272	0.018022
H	4.690141	0.228145	0.899024
H	5.086116	-1.287519	0.031953
H	4.697444	0.205579	-0.876413

MeOx cation

G = -326.132113 Ha

C	-1.147190	1.092374	-0.033729
C	-1.877066	-0.260400	0.031878
H	-1.330040	1.639498	-0.959839
H	-1.361934	1.738143	0.817999
H	-2.527964	-0.453785	-0.816415
H	-2.411466	-0.421754	0.965243
O	-0.801089	-1.245684	-0.016212
C	0.347457	-0.638490	-0.002584
C	1.588811	-1.447113	-0.003861
H	2.172994	-1.231617	0.893239
H	1.325108	-2.501784	-0.022713
N	0.261032	0.659652	0.009204
C	1.360091	1.620391	0.012631
H	2.310425	1.092537	0.043594
H	1.270972	2.261267	0.890196
H	1.308294	2.227463	-0.891911
H	2.192479	-1.202628	-0.880136

MestOx cation (interacting)

G = -593.168311 Ha

C	-2.457682	0.780300	-0.890156
C	-2.247701	-0.563332	-1.596548
H	-1.914109	1.603381	-1.360722
H	-3.507531	1.045132	-0.773254
H	-1.829504	-0.481712	-2.595487

H	-3.138339	-1.189358	-1.603735
O	-1.261210	-1.236682	-0.759917
C	-1.122414	-0.570321	0.351588
C	-0.188499	-1.118019	1.371035
H	-0.113960	-0.426441	2.208137
H	-0.611415	-2.058825	1.734110
C	1.193045	-1.372886	0.756184
H	1.888794	-1.719396	1.520473
H	1.145119	-2.151304	-0.009789
N	-1.844034	0.508202	0.420580
C	-1.725400	1.566071	1.422178
H	-1.615991	1.134202	2.413870
H	-2.638488	2.157587	1.399825
H	-0.861917	2.187899	1.176706
C	1.724762	-0.112280	0.109553
O	1.022532	0.841973	-0.144747
O	3.009702	-0.188869	-0.154648
C	3.603008	0.950973	-0.806594
H	3.482534	1.835817	-0.183145
H	4.652037	0.700245	-0.926383
H	3.128093	1.110945	-1.773614

MestOx cation (extended)

G = -593.165744 Ha

C	-3.582765	0.040438	0.046862
C	-3.106174	-1.422553	0.061837
H	-4.196476	0.284502	-0.820744
H	-4.108677	0.333446	0.956636
H	-3.387476	-1.983556	-0.826047
H	-3.385679	-1.968630	0.958880
O	-1.649685	-1.320512	0.056904
C	-1.297110	-0.071193	-0.012140
C	0.146794	0.285100	-0.058258
H	0.322473	0.846827	-0.981814
H	0.353474	0.981124	0.760108
C	1.062802	-0.934291	0.021115
H	0.903987	-1.480057	0.954374
H	0.867408	-1.638419	-0.788485
N	-2.299758	0.759279	-0.034038
C	-2.242236	2.216592	-0.098081
H	-1.207548	2.542788	-0.171792
H	-2.693620	2.632603	0.803423
H	-2.794836	2.555450	-0.974870
C	2.539117	-0.585615	-0.037592
O	3.395782	-1.404484	-0.187073
O	2.758151	0.725440	0.115745
C	4.142696	1.121684	0.104974
H	4.598617	0.846132	-0.845042
H	4.140735	2.199257	0.238109
H	4.673198	0.629045	0.918626

SI 6. NBO Interaction Energies

Selected NBO interactions (Figure 5) were calculated at the HF/6-31G(d,p)//M06-2X/6-31+G(d,p) level of theory (Table S1). It should be noted that the sum of these interaction energies cannot fully explain the Gibbs free energy order of TS1-3.

It has been reported that the augmented Rydberg orbital's extension associated with diffuse functions can lead to errors in the interaction energies. [1] Moreover, these energies can only be calculated if the wave function is fully defined.[2] Hence, NBO calculations were performed at the HF/6-31G(d,p) level of theory.

Table S1: NBO interaction energies (ΔE_{int}) and interaction distances in transition states TS1-3 (energies in kJ/mol, distances in Å, HF/6-31G(d,p)//M06-2X/6-31+G(d,p)).

TS1		**a**	**b**		
	ΔE_{int}	22.1	16.2		
	distance	2.21	2.33		
TS2		**c**	**d**	**e**	**f**
	ΔE_{int}	4.9	16.3	15.8	15.9
	distance	2.38	2.38	2.84	2.31
TS3		**g**	**h**	**i**	
	ΔE_{int}	20.9	11.2	5.8	
	distance	2.20	2.24	2.47	

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SI 8. G09 Full Reference

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