Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Pulsed Laser Polymerisation Studies of Methyl Methacrylate in the presence of $AlCl_3$ and $ZnCl_2$ – Evidence of propagation catalysis

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Materials

Methyl methacrylate (Sigma-Aldrich, 99%) was passed through a column of alumina to remove the inhibitor and stored in a freezer over 4 Å molecular sieves (Sigma-Aldrich). 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP) (Sigma-Aldrich, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Sigma-Aldrich, 99%), zinc chloride (Sigma-Aldrich, 99%), aluminium chloride (Sigma-Aldrich, 99 %) deuterated chloroform (Cambridge Isotope Laboratories, 99.8%, stabilised with silver foil), tetrahydrofuran (THF) (Merck LiChrosolv®) were used as received.

Pulsed Laser Polymerization (PLP)

Solutions of methyl methacrylate (MMA) containing $ZnCl_2$ or $AlCl_3$ ranged from 0 to 10 mol % relative to MMA and photoinitiator (MMMP or DMPA) with concentration ranged from 1-5 mM were prepared via the freeze-thaw degassing of methyl methacrylate with the respective initiator. The degassed solution was transferred via a canular into the the magnetically stirring $ZnCl_2$ or $AlCl_3$ whilst under nitrogen. The mixture was sonicated to fully dissolve Lewis acid into the bulk monomer. This solution was then transferred to a 10 mm pathlength Starna Type 65 jacketed cylindrical cell under a nitrogen blanket in a nitrogen drybox. The samples were allowed to equilibrate at the desired temperature via connection to a Lauda RL6 recirculated bath. Temperature was measured with a Testo 735-2 temperature meter fitted with a 0602 0593 probe and allowed to equilibrate for 2-3 minutes. Polymerisation was initiated in duplicate samples by laser pulsing with frequencies of 5, 10, 12.5, 25 and 50 Hz. During polymerisation, temperature inside the sample and of the jacket bath was logged by Testo Comfort Software X35 at one second intervals. Laser pulsing was carried out by a Quantel Brilliant Nd-YAG laser operating at 355 nm at ~20 mJ per pulse with the beam expanded to ~10mm diameter to uniformly illuminate the cell. After polymerisation, the sample was poured into methanol to precipitate the polymer generated. The polymer was allowed to settle overnight and excess methanol was decanted on the following day. The samples were dried in a miVac Quattro vacuum concentrator at 40 °C for 90 minutes. The product was weighed and further purified via reprecipitation in methanol to remove the Lewis acids. The remaining polymer was dissolved in THF at concentrations approximately 1mg/mL for molecular weight analysis via gel permeation chromatography.

Solution Density determination

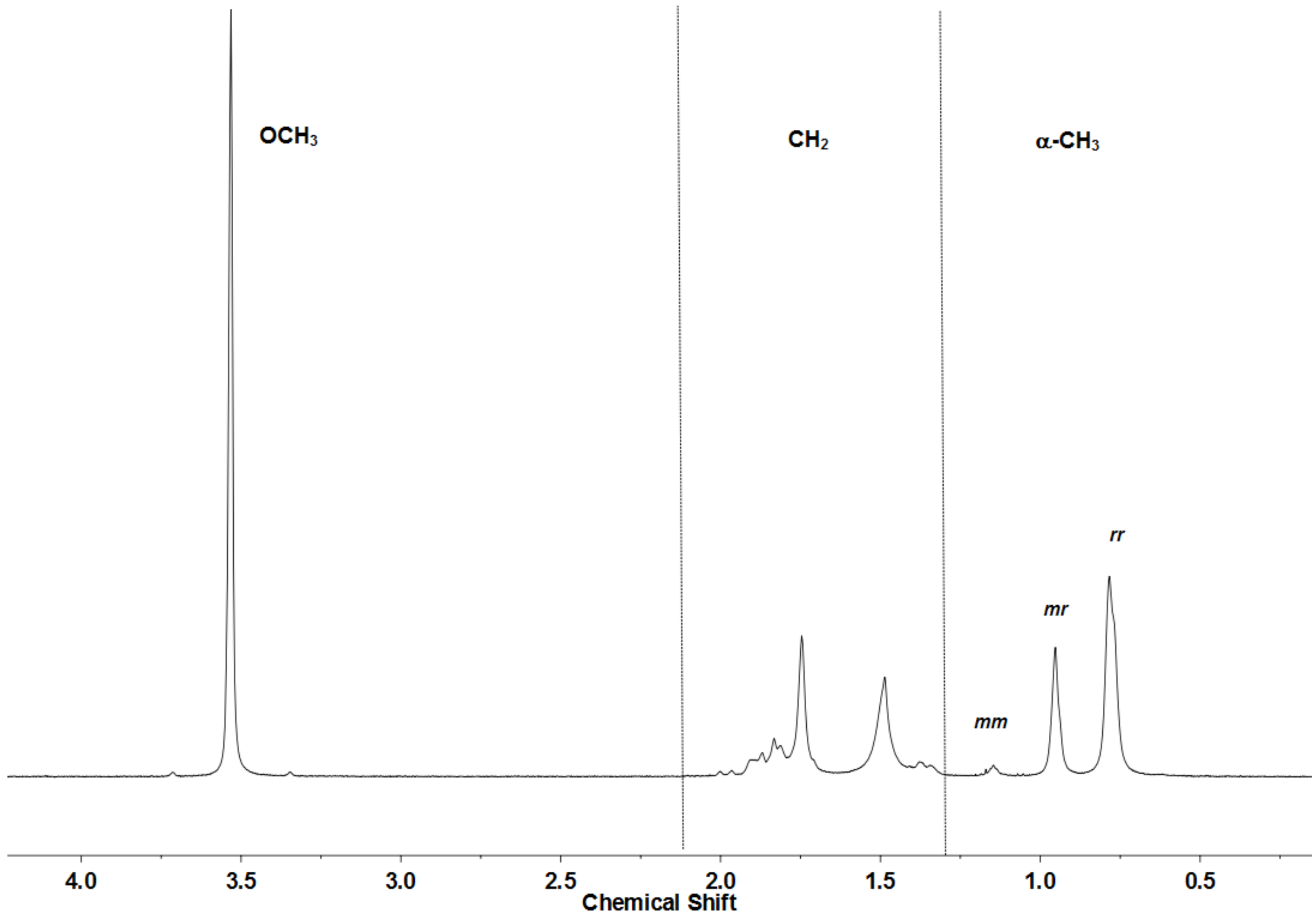
The densities of the Lewis acid and MMA mixture was determined using a Blaubrand® density bottle with a volume 5.3831±0.0100 cm^3 at the corresponding Lewis acid concentrations (including 0.025, 0.05, 0.1 equivalents) across temperatures from 0 °C to 60 °C in order to determine accurate concentrations of MMA. Densities of pure MMA. Densities of pure MMA were calculated from the third-order polynomial taken from the literature[1].

Molecular Weight Determination

Molecular weight distributions of the generated PMMA were determined in THF using an Agilent 1260 Infinity GPC/SEC system equipped with one PL110-1120 PLgel 10μm Guard (50 x 2.5 mm) column and two Viscotek LT5000LMixed Medium Org (300 x 7.8 mm) columns and calibrated to Fluka PMMA ReadyCal™ standards. Subsequently, the data was analysed by *Microsoft Excel*, customized *Python 2.7.13* and *MATLAB_R2014* scripts respectively. PLP conditions and associated k_p values are summarised in the tables below.

Typical ^{1}H-NMR Spectra of PMMA

$ZnCl_2$ 5 mol% with DMPA photoinitiator



Summary of PLP/SEC results for AlCl3

Table 1: Results of PLP of MMA with $AlCl_3$ at different temperatures; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} mol.L^{-1})	[M] (mol.L^{-1})	[$AlCl_3$]/[M]	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	k_p^1 (L.mol^{-1}.s^{-1})	k_p^2 (L.mol^{-1}.s^{-1})
23.2	3.195 [a]	9.080	0.05	22	25	2	2.2	190	398	**524**	**547**
22.5	3.195 [a]	9.087	0.05	22	25	2	1.8	186	398	**512**	**547**
23.2	2.318 [a]	9.110	0.05	22	10	7.5	3.1	467	890	**513**	**489**
21.5	3.195 [a]	9.097	0.05	22	10	5	3.3	467	890	**514**	**489**
22.0	3.195 [a]	9.092	0.05	22	10	5	2.6	467	911	**514**	**501**
22.0	3.195 [a]	9.092	0.05	22	10	5	2.5	467	911	**514**	**501**
21.7	3.195 [a]	9.095	0.05	22	5	10	2.6	851	1658	**467**	**456**
21.7	3.195 [a]	9.095	0.05	22	5	10	2.3	850	1696	**467**	**466**
60.8	3.346 [b]	8.648	0.05	16	50	0.67	3.9	209	436	**1207**	**1260**
60.8	3.346 [b]	8.648	0.05	16	50	0.67	3.9	209	436	**1207**	**1260**
59.9	3.346 [b]	8.664	0.05	16	25	1.33	3.3	416	812	**1201**	**1171**
59.6	3.346 [b]	8.670	0.05	16	25	1.33	1.9	416	812	**1201**	**1171**
58.5	2.891 [a]	8.582	0.05	21	10	2	2.2	999	1776	**1164**	**1035**
58.3	2.891 [a]	8.586	0.05	21	10	2	2.2	999	1776	**1164**	**1035**

Table 1 cont: Results of PLP of MMA with $AlCl_3$ at different temperatures; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} mol.L^{-1})	[M] (mol.L^{-1})	$[AlCl_3]/[M]$	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	k_p^1 (L.mol^{-1}.s^{-1})	k_p^2 (L.mol^{-1}.s^{-1})
48.8	3.443 [b]	8.758	0.05	17	50	0.67	0.9	170	338	**968**	**966**
46.6	2.491 [b]	8.843	0.05	17	50	0.67	1.6	158	282	**895**	**796**
47.2	2.491 [b]	8.836	0.05	17	50	0.67	1.8	158	288	**896**	**815**
47.8	3.443 [b]	8.771	0.05	17	25	1.33	1.0	316	645	**900**	**919**
47.8	3.443 [b]	8.771	0.05	17	25	1.33	1.5	316	645	**900**	**919**
45.7	3.226 [a]	8.910	0.05	19	25	1.25	3.3	309	575	**866**	**806**
45.5	3.226 [a]	8.915	0.05	19	25	1.25	3.3	309	575	**866**	**806**
42.4	3.226 [a]	8.952	0.05	19	50	0.67	2.6	155	302	**864**	**842**
42.3	3.226 [a]	8.953	0.05	19	50	0.67	4.3	155	302	**864**	**842**
10.4	3.161 [a]	9.077	0.05	15	25	3.25	1.9	135	251	**371**	**346**
9.6	3.161 [a]	9.086	0.05	15	25	3.25	1.7	138	240	**379**	**330**
6.1	3.161 [a]	9.125	0.05	15	10	8	1.9	309	602	**338**	**330**
6.4	3.161 [a]	9.122	0.05	15	10	8	1.9	309	602	**338**	**330**
5.7	3.188 [a]	9.130	0.05	15	25	3.5	1.8	126	229	**344**	**313**
2.8	3.188 [a]	9.165	0.05	15	25	3.5	1.9	115	214	**313**	**291**
3.2	3.188 [a]	9.160	0.05	15	25	7	1.8	117	214	**320**	**291**
1.9	3.188 [a]	9.176	0.05	15	12.5	7	2.1	195	407	**265**	**277**
1.9	3.188 [a]	9.176	0.05	15	12.5	7	2.1	195	407	**265**	**277**

Table 2: Results of PLP of MMA with $AlCl_3$ at different concentrations; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} mol.L-1)	[M] (mol.L-1)	[AlCl3]/[M]	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	kp1 ($L.mol^{-1}.s^{-1}$)	kp2 ($L.mol^{-1}.s^{-1}$)
24.5	2.535 [a]	9.262	0.025	18	25	2	2.1	170	323	**458**	**436**
24.2	2.535 [a]	9.265	0.025	18	25	2	3.0	166	331	**447**	**446**
25.4	2.580 [b]	9.232	0.025	22	12.5	4	1.6	338	724	**458**	**490**
25.4	2.580 [b]	9.232	0.025	22	12.5	4	1.7	338	675	**458**	**457**
24.6	2.580 [b]	9.240	0.025	22	5	10	1.9	812	1696	**439**	**459**
24.0	2.580 [b]	9.263	0.025	22	5	10	1.9	812	1696	**439**	**459**
24.9	2.971 [b]	8.763	0.10	22	12.5	4	3.8	407	831	**584**	**596**
24.5	2.971 [b]	8.763	0.10	22	12.5	4	5.5	407	831	**584**	**596**
24.5	2.971 [b]	8.767	0.10	22	10	5	3.6	536	1022	**615**	**586**
24.6	2.971 [b]	8.785	0.10	22	5	10	4.7	999	1948	**572**	**558**

Summary of PLP/SEC results for ZnCl2

Table 3: Results of PLP of MMA with $ZnCl_2$ at different temperatures; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} $mol.L^{-1}$)	[M] ($mol.L^{-1}$)	$[ZnCl_2]/[M]$	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	k_p^1 ($L.mol^{-1}.s^{-1}$)	k_p^2 ($L.mol^{-1}.s^{-1}$)
24.9	2.119 [a]	9.184	0.05	20	25	2	1.2	162	282	**441**	**383**
24.5	2.119 [a]	9.188	0.05	20	25	2	2.8	162	282	**441**	**383**
24	3.602 [b]	9.168	0.05	22	25	2	4.2	144	263	**394**	**359**
26.3	3.602 [b]	9.154	0.05	22	10	5	6.6	354	724	**388**	**396**
26.3	3.602 [b]	9.154	0.05	22	10	5	6.9	354	724	**388**	**396**
26.2	3.602 [b]	9.156	0.05	22	50	1	7.4	83	158	**455**	**433**
24.9	3.602 [b]	9.169	0.05	22	50	1	4.4	83	155	**454**	**423**
23.5	3.602 [b]	9.183	0.05	22	25	2	4.2	141	263	**385**	**358**
23.8	3.602 [b]	9.195	0.05	22	25	2	4.2	141	263	**385**	**358**
23.8	2.119 [a]	9.195	0.05	20	10	5	2.1	354	707	**385**	**384**
23.7	2.119 [a]	9.196	0.05	20	10	5	4.0	354	707	**385**	**384**
23.6	2.119 [a]	9.197	0.05	20	12.5	4	5.0	309	645	**419**	**438**
23.6	2.119 [a]	9.197	0.05	20	12.5	4	5.1	309	645	**419**	**438**
61	3.758 [a]	8.834	0.05	21	25	2	0.8	389	740	**1100**	**1048**
61.1	3.758 [a]	8.834	0.05	21	25	2	0.9	389	740	**1100**	**1048**

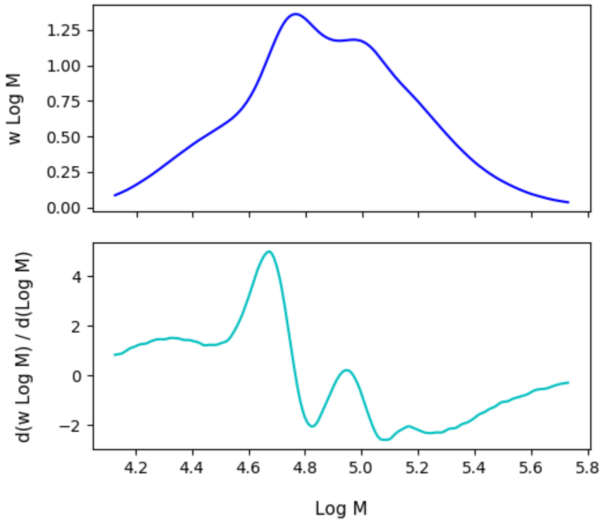
Table 3 cont: Results of PLP of MMA with $ZnCl_2$ at different temperatures; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} mol.L^{-1})	[M] (mol.L^{-1})	[$ZnCl_2$]/[M]	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	k_p^1 (L.mol^{-1}.s^{-1})	k_p^2 (L.mol^{-1}.s^{-1})
54.6	4.180 [b]	8.880	0.052	20	12.5	4	1.4	675	1411	**951**	**993**
55.4	4.180 [b]	8.874	0.052	20	12.5	4	1.4	675	1411	**951**	**994**
52.7	4.180 [b]	8.897	0.052	20	10	5	1.5	793	1658	**892**	**932**
52.8	4.180 [b]	8.896	0.052	20	10	5	1.4	793	1696	**892**	**953**
45.3	2.471 [a]	8.974	0.051	20	12.5	4	0.6	489	976	**681**	**680**
45.5	2.471 [a]	8.972	0.051	20	12.5	4	1.0	489	976	**682**	**680**
2.7	4.180 [b]	9.394	0.052	20	25	3	0.7	72	141	**193**	**188**
3.7	4.180 [b]	9.384	0.052	20	25	3	0.7	76	144	**202**	**192**
3.3	4.180 [b]	9.388	0.052	20	12.5	6	0.9	170	346	**226**	**231**
0.1	4.180 [b]	9.418	0.052	20	12.5	6	0.9	148	282	**196**	**187**
4.2	2.160 [a]	9.379	0.052	20	12.5	6	1.0	172	350	**227**	**235**
4.3	2.160 [a]	9.378	0.052	20	12.5	6	1.5	172	350	**227**	**335**
-0.8	2.160 [a]	9.427	0.052	20	10	7.5	1.0	158	316	**168**	**168**
-0.4	2.160 [a]	9.423	0.052	20	10	7.5	0.9	158	309	**168**	**164**

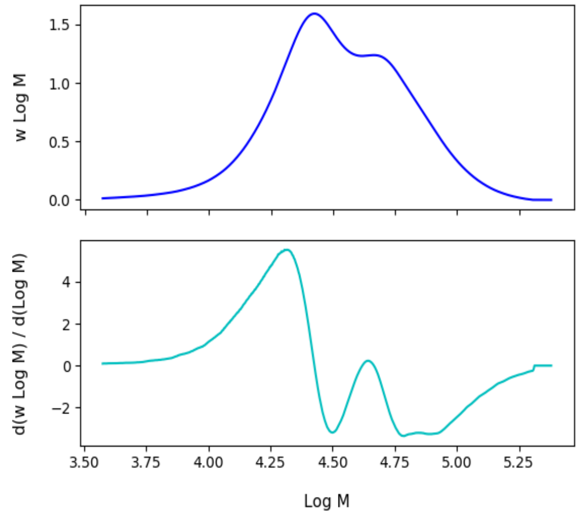
Table 3 cont: Results of PLP of MMA with $ZnCl_2$ at different temperatures; a: MMMP, b: DMPA

Average T (°C) from log	[I] (10^{-3} mol.L^{-1})	[M] (mol.L^{-1})	[$ZnCl_2$]/[M]	Laser Power (mJ/pulse)	Flashing frequency (Hz)	Time (min)	Conversion (%)	L1	L2	k_p^1 (L.mol^{-1}.s^{-1})	k_p^2 (L.mol^{-1}.s^{-1})
23.0	2.203 [a]	9.322	0.025	18	25	2	0.5	135	263	**361**	**352**
24.4	2.203 [a]	9.307	0.025	18	25	2	0.8	138	263	**370**	**353**
22.8	2.203 [a]	9.324	0.025	18	10	5	1.2	338	691	**363**	**371**
22.7	2.203 [a]	9.325	0.025	18	10	5	1.6	338	675	**363**	**362**

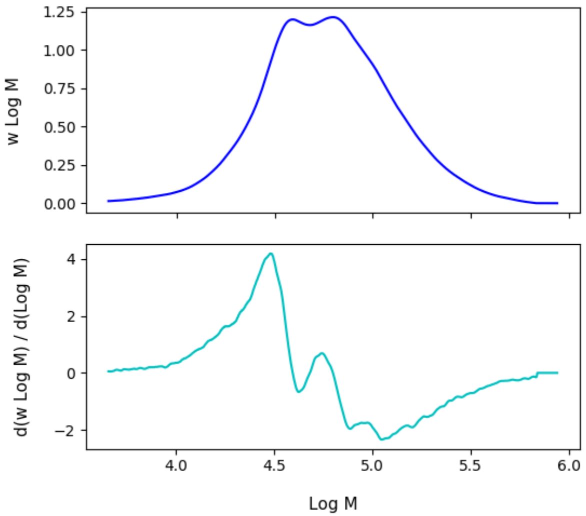
Selected PLP traces



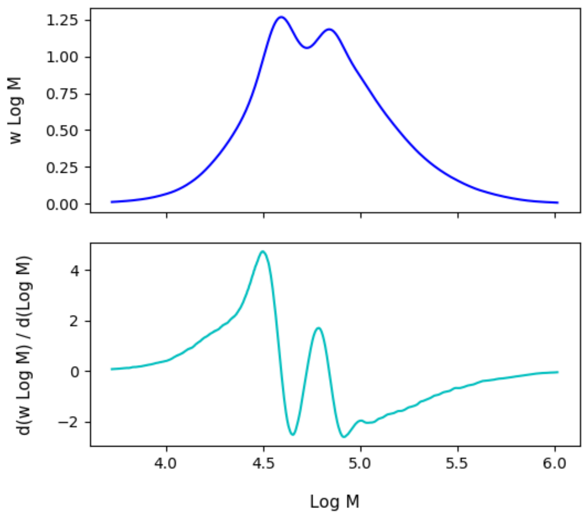
25 °C, $[AlCl_3]/[MMA]$=0.05, 10 Hz



60 °C, $[AlCl_3]/[MMA]$=0.05, 50 Hz

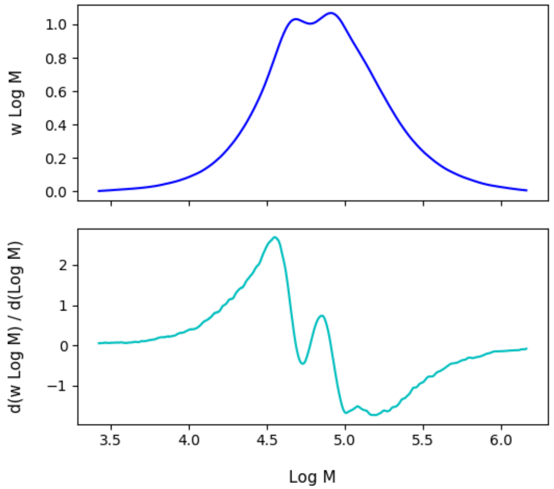


40 °C, $[AlCl_3]/[MMA]$=0.05, 50 Hz

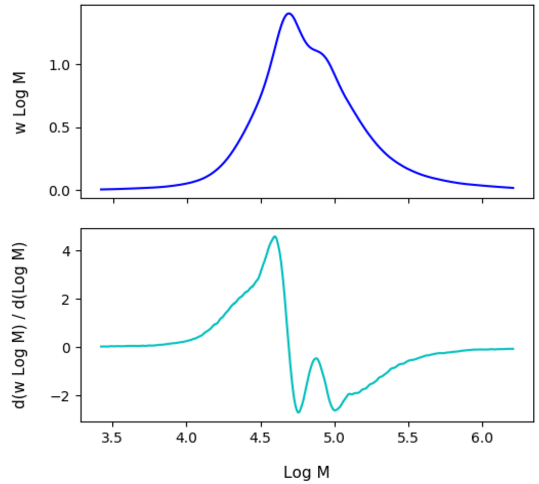


5 °C, $[AlCl_3]/[MMA]$=0.05, 10 Hz

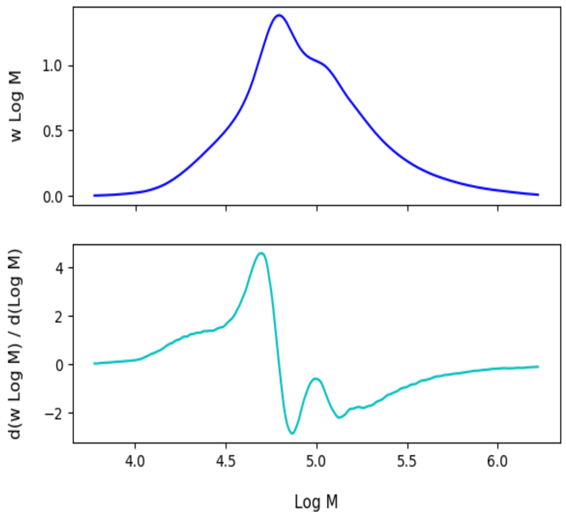
Selected PLP Traces continued



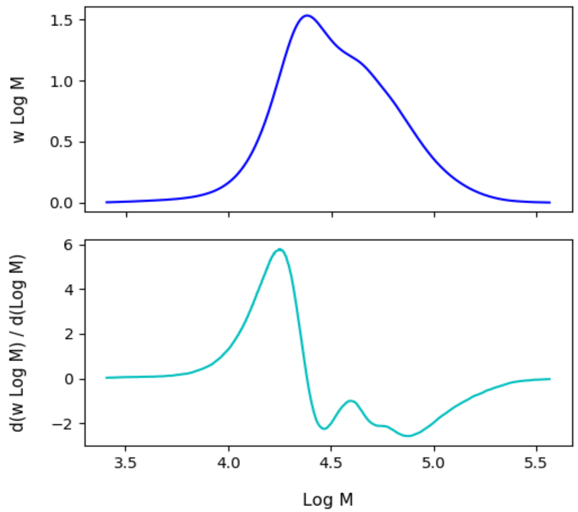
25°C, $[ZnCl_2]/[MMA]=0.05$, 10 Hz



60°C, $[ZnCl_2]/[MMA]=0.05$, 25 Hz



45°C, $[ZnCl_2]/[MMA]=0.05$, 12.5 Hz



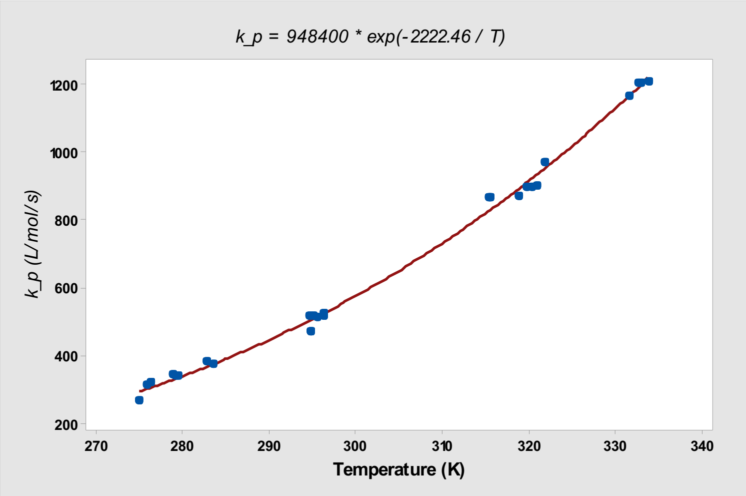
0°C, $[ZnCl_2]/[MMA]=0.05$, 10 Hz

Arrhenius parameter determination & Joint confidence interval

Arrhenius parameters was obtained via fitting of data from tables 1-3. The model used was:

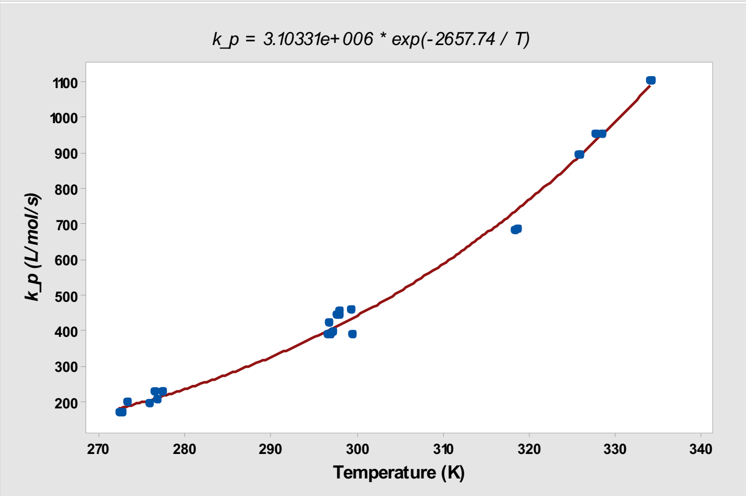
$$k = A \cdot \exp\left(-\frac{B}{T}\right)$$

The parameters calculated via the nonlinear least square regression are summarised below. The 95 % confidence interval was generated using customized *Matlab_2014b* scripts.



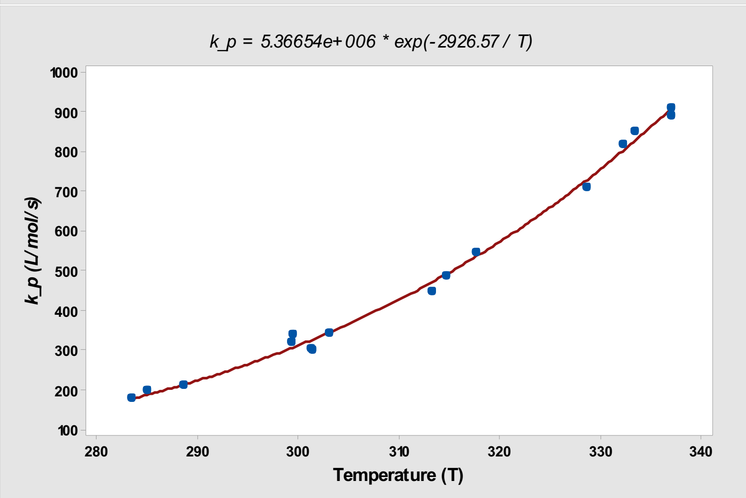
$AlCl_3$

E_A=18.5 kJ.mol^{-1}
A=0.948e6 L.mol^{-1}.s^{-1}
SSE=10409



$ZnCl_2$

E_A=22.1 kJ.mol^{-1}
A=3.10e6 L.mol^{-1}.s^{-1}
SSE=14924



Bulk MMA k_p data from ref[2]

E_A=24.3 kJ.mol^{-1}
A=5.37e6 L.mol^{-1}.s^{-1}
SSE=5085

References

1. M. Stickler and G. Meyerhoff, *Makromol Chem*, 1978, **179**, 2729-2745.
2. N. Garcia, P. Tiemblo and J. Guzman, *Macromolecules*, 2007, **40**, 4802-4808.