

Supporting Information

Propagation Rate Coefficients of 2-(Dimethylamino)ethyl Methacrylate Radical Polymerization in Bulk, Alcohols and Alcohol/Water Solutions Determined by PLP-SEC

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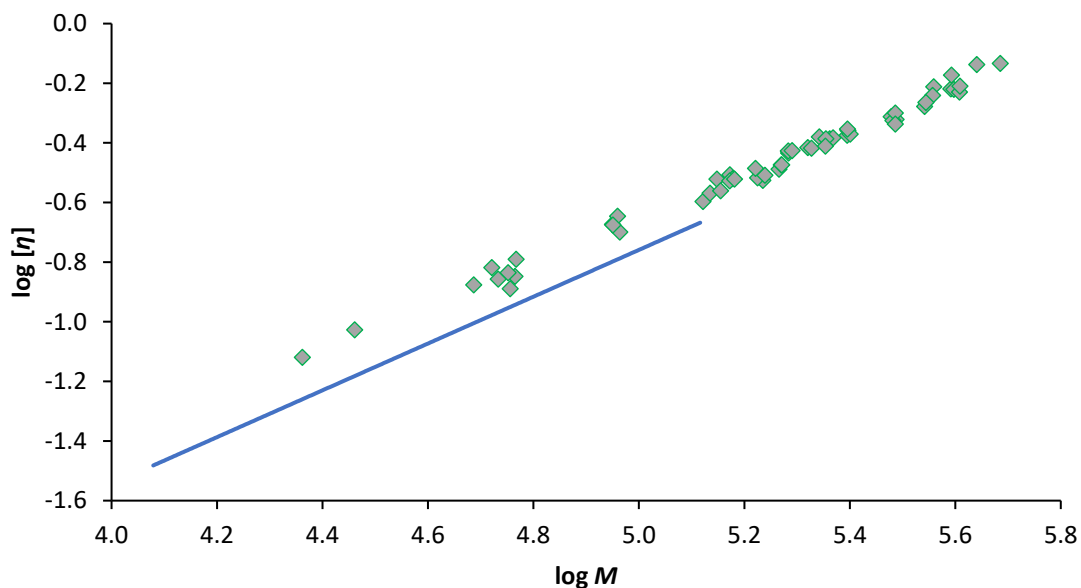


Figure S1: A comparison of the MHKS relationship between PDMAEMA intrinsic viscosity and polymer molar mass in THF estimated in this work (Waters-Wyatt setup (blue line)) to values reported by Kockler et al.¹ (green diamonds). Kockler et al. used their MHKS values for PDMAEMA in combination with PMMA calibration, whereas in this study PS calibration was employed.

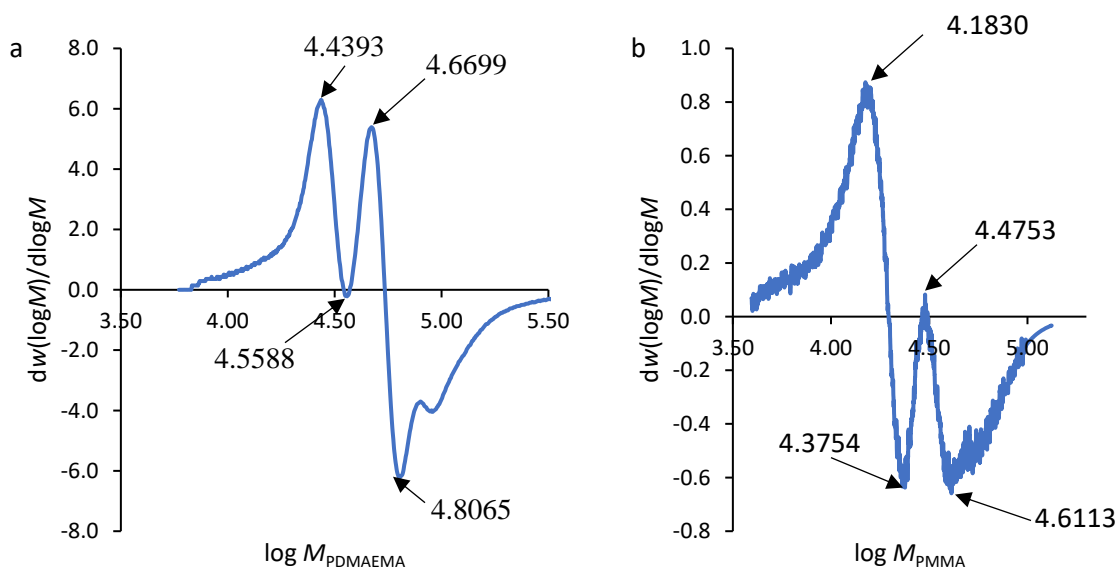


Figure S2: A comparison of PDMAEMA first derivative curves determined by differentiation of the polymer MMDs analyzed by: (a) SEC-RI in THF according to PDMAEMA calibration and (b) SEC-RI in DMF (1 mmol L⁻¹ LiBr) using pMMA calibration. The polymer was generated by PLP by pulsing bulk monomer at 90 °C with a p.r.r. of 100 Hz.

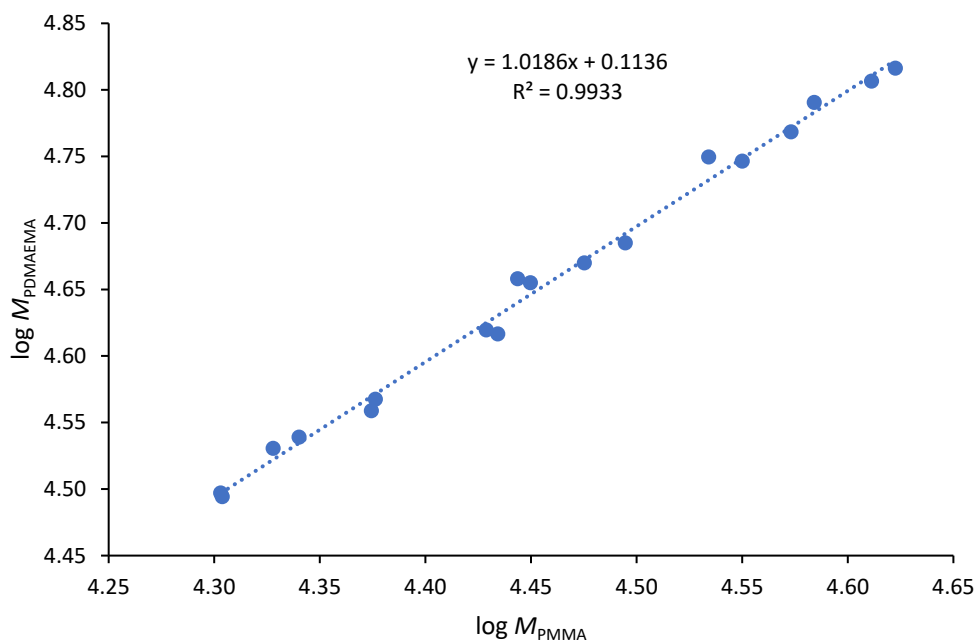


Figure S3: $\log M_{PDMAEMA}$ vs $\log M_{PMMA}$ values obtained from analysis of PDMAEMA MMDs by RI detection in THF (calculated according to universal calibration) and RI detection in DMF (1 mmol L^{-1} LiBr) according to PMMA calibration, respectively. The fit was used to estimate MHKS parameters of PDMAEMA in DMF as $K = 6.99 \times 10^{-5} \text{ dL g}^{-1}$ and $\alpha = 0.663$ from the slope and intercept according to Eq. 2 of the article.

Table S1: Mark-Houwink-Kuhn-Sakurada (MHKS) parameters for PDMAEMA and calibration polymers PS and PMMA analyzed by organic-phase SEC

Polymer-solvent system	K [dL g^{-1}]	a	dn/dc [mL g^{-1}]	Reference
PDMAEMA (THF)	4.98×10^{-5}	0.729	0.086	1
PDMAEMA (THF)	2.07×10^{-5}	0.785	-	This work
PS (THF)	1.14×10^{-4}	0.716	-	2,3
PMMA (DMF ^a)	1.08×10^{-4}	0.694	-	4
PDMAEMA (DMF ^a)	6.99×10^{-5}	0.663	-	This work

^a containing 1 mmol L^{-1} LiBr

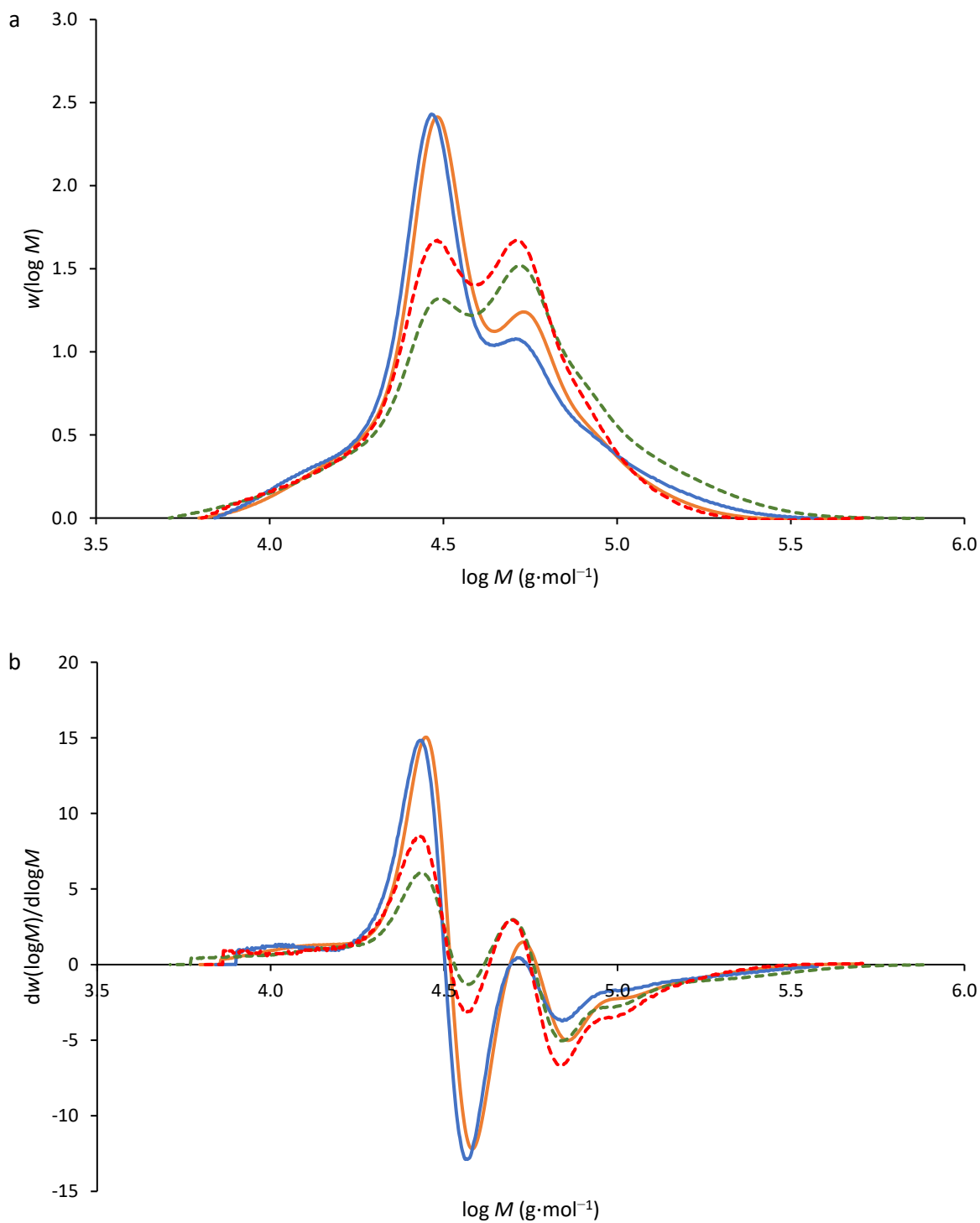


Figure S4: PLP-generated PDMAEMA a) MMDs and b) first derivative plots from SEC analysis in THF of bulk DMAEMA at 30 °C and 20 Hz with 5 mmol L⁻¹ DMPA (solid lines) and 5 mmol L⁻¹ Darocur 1173 (dashed lines), with two repeated polymerization experiments shown for each photoinitiator. The inflection point positions were the same for both initiators, with improved PLP structure obtained using DMPA.

Table S2: Propagation rate coefficients for polymerization of bulk DMAEMA determined from PLP-SEC experiments conducted between 30 and 90 °C with 5 mmol L⁻¹ DMPA at varying laser pulse repetition rates (p.r.r.) and employing different SEC setups for analysis of MMDs of PDMAEMA.

T [°C]	p.r.r. [Hz]	x_p [%]	$\log M_1$	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
30	20	0.5	4.5069	0.52	THF	694
	20	0.6	4.4902	0.48	THF	668
	20	0.5	4.4748	0.48	THF	645
	30	0.8	4.3204	0.52	THF	678
	30	0.9	4.3178	0.52	THF	674
	30	0.5	4.3379	0.52	THF	705
			4.3323	0.47	DMF	696
	30	0.2	4.3640	0.54	Aqueous	749
	30	0.2	4.3581	0.54	Aqueous	739
		30	0.2	4.3563	0.53	Aqueous
50	20	0.6	4.6790	0.48	THF	1053
	20	0.6	4.6820	0.46	THF	1061
	20	0.4	4.6820	0.46	THF	1061
	40	1.1	4.3946	0.53	THF	1094
	40	0.7	4.3732	0.53	THF	1042
	40	0.4	4.3950	0.52	THF	1095
	50	0.7	4.3335	0.53	THF	1188
	50	0.9	4.3361	0.54	THF	1196
			4.3152	0.48	DMF	1139
	70	40	1.0	4.5926	0.51	THF
40		1.3	4.5926	0.51	THF	1764
40		0.6	4.5686	0.52	THF	1669
70		1.1	4.3599	0.54	THF	1806
70		1.2	4.3519	0.54	THF	1773
70		0.6	4.3611	0.53	THF	1811
			4.3678	0.52	DMF	1839
80		1.2	4.3256	0.52	THF	1907
80		1.6	4.3361	0.54	THF	1954
90		50	1.3	4.6190	0.50	THF
	50	1.4	4.6220	0.51	THF	2411
	50	0.7	4.6314	0.52	THF	2464
	100	1.4	4.3732	0.54	THF	2719
	100	1.7	4.3732	0.54	THF	2719
	100	1.3	4.3741	0.53	THF	2724
			4.3740	0.50	DMF	2724

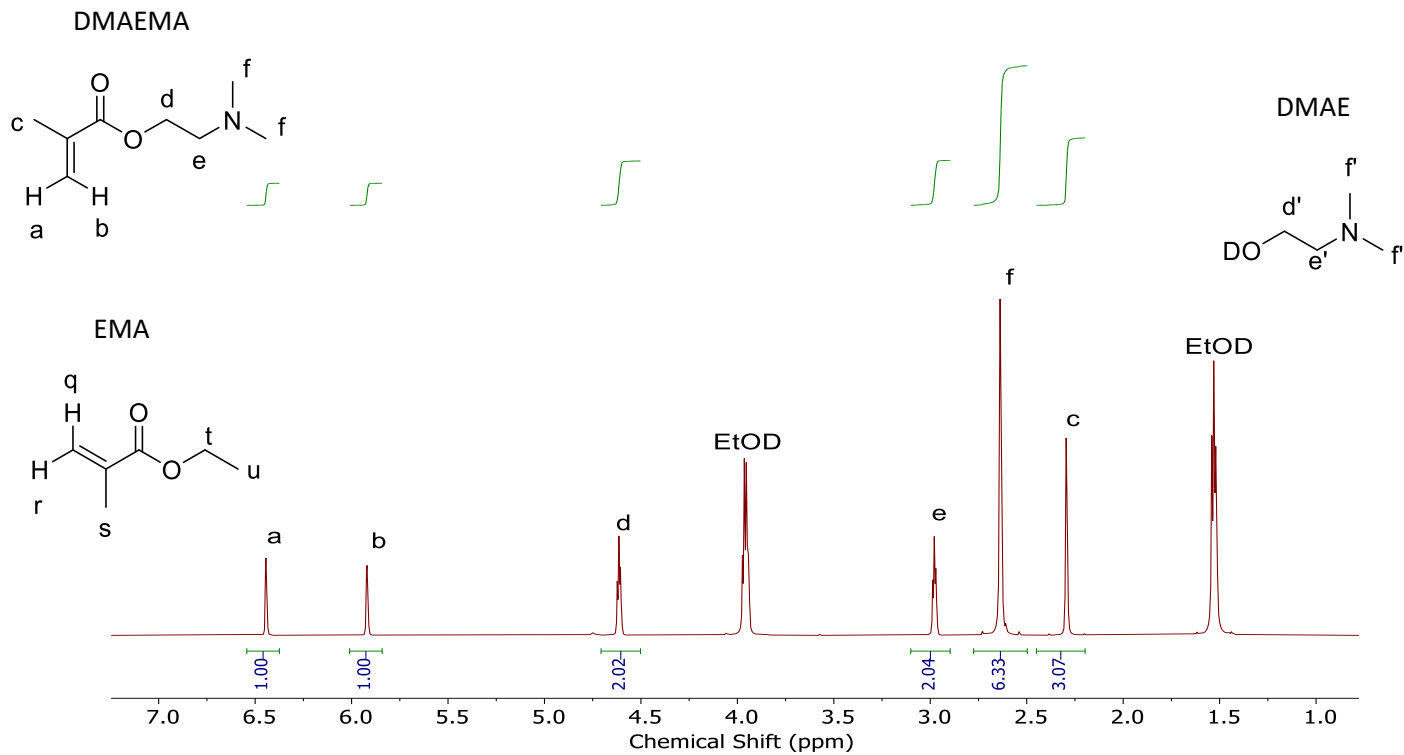


Figure S5: ^1H NMR (700 MHz) spectrum of PLP mixture with $w_{\text{DMAEMA}} = 0.50$ in EtOD held for 4 min at 70 °C. No ethyl methacrylate and 2-dimethylaminoethanol were observed in either spectrum, indicating that DMAEMA ethanolysis does not occur within the timeframe of the PLP experiment.

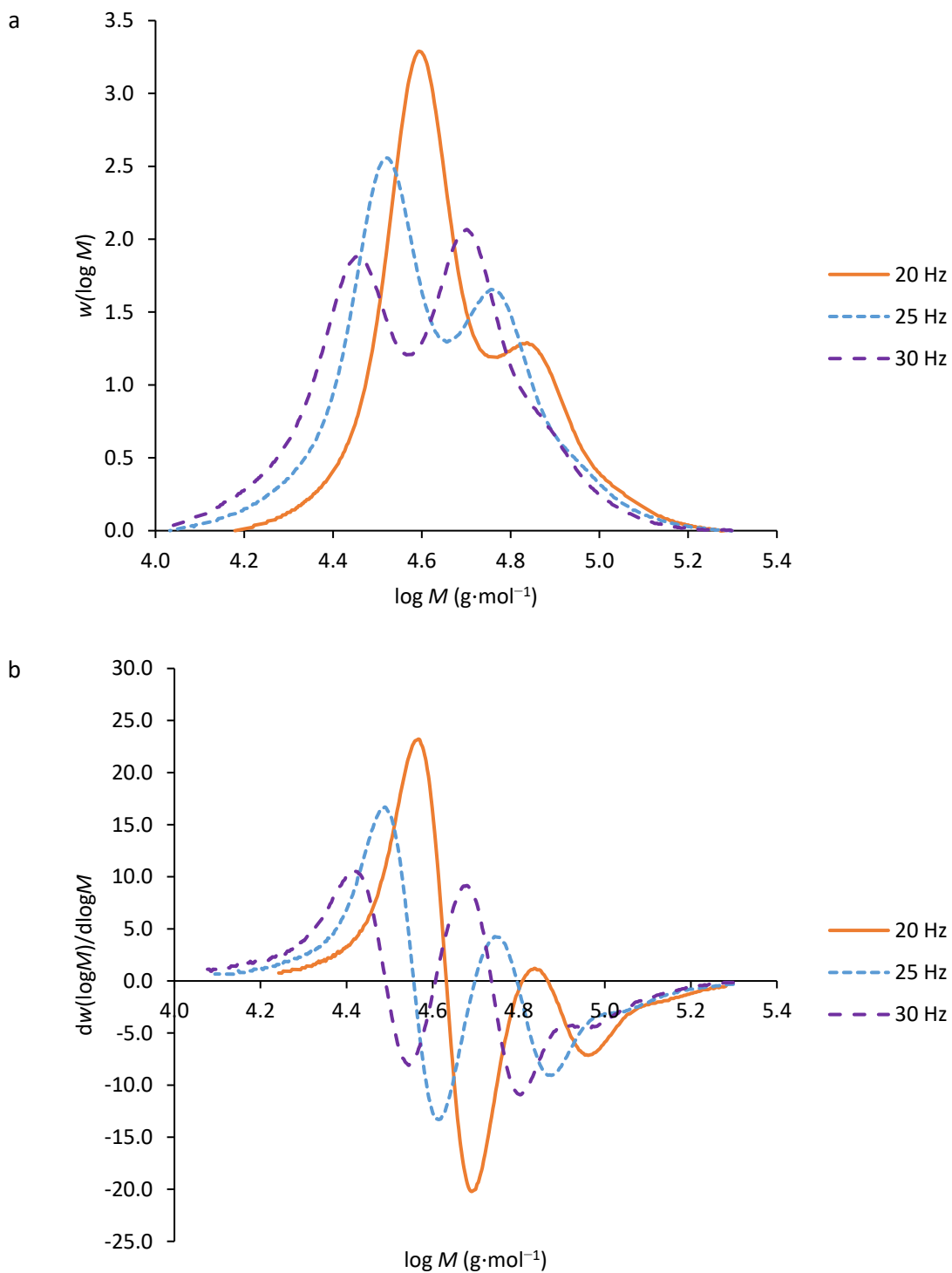


Figure S6: PLP-generated PDMAEMA a) MMDs and b) first derivative plots from SEC analysis in THF of $w_{\text{DMAEMA}} = 0.625$ DMAEMA polymerized in EtOH with 5 mmol L⁻¹ DMPA at 60 °C using p.r.r. 20, 25, and 30 Hz.

Table S3(a): Propagation rate coefficients for polymerization of DMAEMA in EtOH determined from PLP-SEC experiments conducted at 30 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM DMPA unless otherwise noted.

w_{DMAEMA}	p.r.r. [Hz]	x_p [%]	$\log M_1$	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.625	10	0.3	4.5617	0.53	THF	667
	15	0.4	4.4016	0.53	THF	692
	15	0.4	4.4017	0.53	THF	680
0.50	10	0.4	4.4721	0.52	THF	691
	10	0.3	4.4720	0.52	THF	690
	10	0.3	4.4722	0.52	THF	692
0.375	10	0.8	4.3433	0.53	THF	698
	10	0.7	4.3434	0.53	THF	697
	10	0.7	4.3432	0.53	THF	699

Table S3(b): Propagation rate coefficients for polymerization of DMAEMA in EtOH determined from PLP-SEC experiments conducted at 40 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM DMPA unless otherwise noted.

w_{DMAEMA}	p.r.r. [Hz]	x_p [%]	Log M_1	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.625	15	0.7	4.4969	0.54	THF	871
	20	0.7	4.3908	0.54	THF	891
	20	0.7	4.3909	0.54	THF	910
0.50	10	0.3	4.5560	0.52	THF	848
	15	0.4	4.3980	0.51	THF	884
	15	0.4	4.3890	0.50	THF	866
0.375	10	0.3	4.4329	0.52	THF	867
	10	0.4	4.4250	0.52	THF	865
	10	0.4	4.4245	0.51	THF	868
0.30	30	1.3	3.8601	0.47	THF	878
	30	1.3	3.8600	0.47	THF	877
	30	1.3	3.8602	0.47	THF	879
0.25	30	1.2	3.7884	0.48	THF	897
	30	1.2	3.7883	0.48	THF	896
	30	1.2	3.7885	0.48	THF	898
0.20	30	2.0	3.7332	0.52	THF	998 ^a
	35	2.0	3.6753	0.51	THF	1019 ^a
	40	2.1	3.6369	0.51	THF	1066 ^a
0.10	30	4.4	3.4980	0.47	THF	1178 ^a
	30	4.4	3.4979	0.47	THF	1177 ^a
	30	4.4	3.4981	0.47	THF	1179 ^a
0.05	10	7.7	3.7187	0.47	THF	1314 ^a
	10	7.2	3.6994	0.46	THF	1252 ^a
	10	7.3	3.6993	0.46	THF	1284 ^a
	20	8.4	3.4570	0.46	THF	1439 ^a
	20	10.6	3.4719	0.47	THF	1484 ^a
	20	12.0	3.4719	0.46	THF	1484 ^a

^a Experiment with 10 mM DMPA

Table S3(c): Propagation rate coefficients for polymerization of DMAEMA in EtOH determined from PLP-SEC experiments conducted at 50 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM DMPA unless otherwise noted.

w_{DMAEMA}	p.r.r. [Hz]	x_p [%]	Log M_1	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.625	10	0.7	4.7495	0.46	THF	1050
		0.2	4.7258	0.50	DMF	994
	15	0.7	4.5846	0.52	THF	1078
		0.2	4.5942	0.54	DMF	1102
	20	0.8	4.4803	0.54	THF	1130
		0.2	4.4838	0.53	DMF	1139
	25	0.6	4.3882	0.54	THF	1143
		0.2	4.4017	0.53	DMF	1179
0.50	10	0.7	4.6460	0.50	THF	1054
		0.4	4.6290	0.52	DMF	1014
	15	0.3	4.4942	0.53	THF	1115
		0.4	4.4865	0.52	DMF	1095
	20	0.4	4.3802	0.54	THF	1143
		0.4	4.3908	0.53	DMF	1172
0.375	10	0.2	4.5333	0.50	THF	1105
	15	0.1	4.3909	0.54	THF	1194
	15	0.1	4.3900	0.54	THF	1150
0.30	10	1.2	4.4680	0.53	THF	1199
	10	1.2	4.4679	0.53	THF	1198
	10	1.2	4.4681	0.53	THF	1200
0.25	10	1.2	4.4009	0.52	THF	1238
	10	1.2	4.4008	0.52	THF	1237
	10	1.2	4.4010	0.52	THF	1239
0.20	35	2.2	3.7742	0.54	THF	1294 ^a
	40	2.3	3.7573	0.54	THF	1422 ^a
	40	2.3	3.7572	0.54	THF	1358 ^a
0.10	25	4.9	3.6585	0.47	THF	1436 ^a
	30	4.5	3.6176	0.47	THF	1569 ^a
	30	4.5	3.6175	0.47	THF	1503 ^a
0.05	20	4.0	3.5242	0.48	THF	1696 ^a
	20	4.0	3.5243	0.48	THF	1695 ^a
	20	4.0	3.5241	0.48	THF	1697 ^a

^a Experiment with 10 mM DMPA

Table S3(d): Propagation rate coefficients for polymerization of DMAEMA in EtOH determined from PLP-SEC experiments conducted at 60 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM DMPA unless otherwise noted.

w_{DMAEMA}	p.r.r. [Hz]	x_p [%]	Log M_1	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.625	20	0.9	4.5645	0.54	THF	1387
		0.2	4.5660	0.51	DMF	1392
	25	0.9	4.4803	0.54	THF	1428
		0.2	4.4830	0.50	DMF	1437
	30	1.0	4.4204	0.54	THF	1493
		0.2	4.4208	0.51	DMF	1494
0.5	10	0.8	4.7339	0.46	THF	1305
		0.4	4.7212	0.49	DMF	1267
	15	0.8	4.5904	0.50	THF	1407
		0.2	4.5924	0.53	DMF	1413
	20	0.5	4.4942	0.54	THF	1503
		0.2	4.4929	0.54	DMF	1498
0.375	10	0.6	4.6195	0.47	THF	1362
	20	0.6	4.3093	0.50	THF	1334
	20	0.6	4.3089	0.50	THF	1348
0.30	10	0.4	4.5418	0.51	THF	1440
	10	0.4	4.5417	0.51	THF	1439
	10	0.4	4.5419	0.51	THF	1441
0.25	10	0.7	4.4693	0.51	THF	1473
	10	0.7	4.4692	0.51	THF	1472
	10	0.9	4.4694	0.51	THF	1474
0.20	30	2.2	3.9100	0.49	THF	1533 ^a
	35	2.5	3.8444	0.51	THF	1538 ^a
	40	2.3	3.8226	0.52	THF	1671 ^a
0.10	25	1.2	3.7163	0.48	THF	1659 ^a
	30	1.1	3.6753	0.50	THF	1812 ^a
	30	1.1	3.6752	0.50	THF	1736 ^a
0.05	20	4.0	3.7782	0.50	THF	1920 ^a
	20	4.0	3.7780	0.50	THF	1919 ^a
	20	4.0	3.7783	0.50	THF	1921 ^a

^a Experiment with 10 mM DMPA

Table S3(e): Propagation rate coefficients for polymerization of DMAEMA in EtOH determined from PLP-SEC experiments conducted at 70 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM DMPA unless otherwise noted.

w_{DMAEMA}	p.r.r. [Hz]	x_p [%]	Log M_1	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.625	10	0.9	4.9340	0.47	THF	1641
	15	0.8	4.7589	0.49	THF	1645
	20	0.9	4.6371	0.51	THF	1657
	25	1.0	4.5503	0.53	THF	1696
	30	1.1	4.4803	0.53	THF	1732
0.5	15	0.6	4.6430	0.50	THF	1605
	20	0.3	4.5305	0.51	THF	1652
	25	0.6	4.4556	0.54	THF	1738
0.375	10	0.6	4.6971	0.52	THF	1647
	15	0.6	4.5446	0.52	THF	1739
	20	0.9	4.4366	0.53	THF	1808
	25	0.8	4.3433	0.54	THF	1823
0.30	10	0.8	4.6107	0.50	THF	1706
	10	0.8	4.6106	0.50	THF	1705
	10	0.8	4.6108	0.50	THF	1707
0.25	10	0.9	4.5446	0.52	THF	1771
	15	0.8	4.3723	0.52	THF	1787
	15	0.8	4.3720	0.52	THF	1779
0.20	10	1.6	4.4529	0.53	THF	1804 ^a
	10	2.6	4.4502	0.50	THF	1792 ^a
	10	2.4	4.4528	0.53	THF	1799 ^a
0.10	25	1.9	3.7936	0.48	THF	2005 ^a
	25	1.9	3.7950	0.45	DMF	2011 ^a
	30	1.6	3.7428	0.51	THF	2140 ^a
	30	1.6	3.7427	0.51	THF	2073 ^a
	30	1.6	3.7490	0.45	DMF	2171 ^a
0.05	30	4.8	3.7284	0.53	THF	2065 ^b
	15	6.5	3.7380	0.46	THF	2132 ^a
	20	7.2	3.6369	0.46	THF	2252 ^a
	20	7.2	3.6370	0.46	THF	2192 ^a

^a Experiment with 10 mM DMPA

^b Experiment with 20 mM DMPA

Table S4: Propagation rate coefficients for polymerization of DMAEMA in BuOH determined from PLP-SEC experiments conducted with $w_{\text{DMAEMA}} = 0.5$ and 5 mM DMPA at various temperatures and laser pulse repetition rates (p.r.r.).

T [°C]	p.r.r. [Hz]	x_p [%]	Log M_1	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
30	10	0.8	4.4886	0.54	THF	709
	15	0.8	4.3171	0.52	THF	716
	15	0.8	4.3168	0.52	THF	713
50	15	0.8	4.5164	0.54	THF	1163
	20	0.7	4.3856	0.54	THF	1147
	25	0.7	4.2886	0.52	THF	1147
70	25	1.1	4.4914	0.54	THF	1879
	30	0.8	4.4177	0.54	THF	1903
	35	0.9	4.3538	0.54	THF	1916
	40	0.8	4.2398	0.46	THF	1899
90	35	1.2	4.5164	0.53	THF	2863
	40	1.0	4.4666	0.54	THF	2917
	45	0.8	4.4096	0.53	THF	2878
	50	1.1	4.3723	0.54	THF	2935

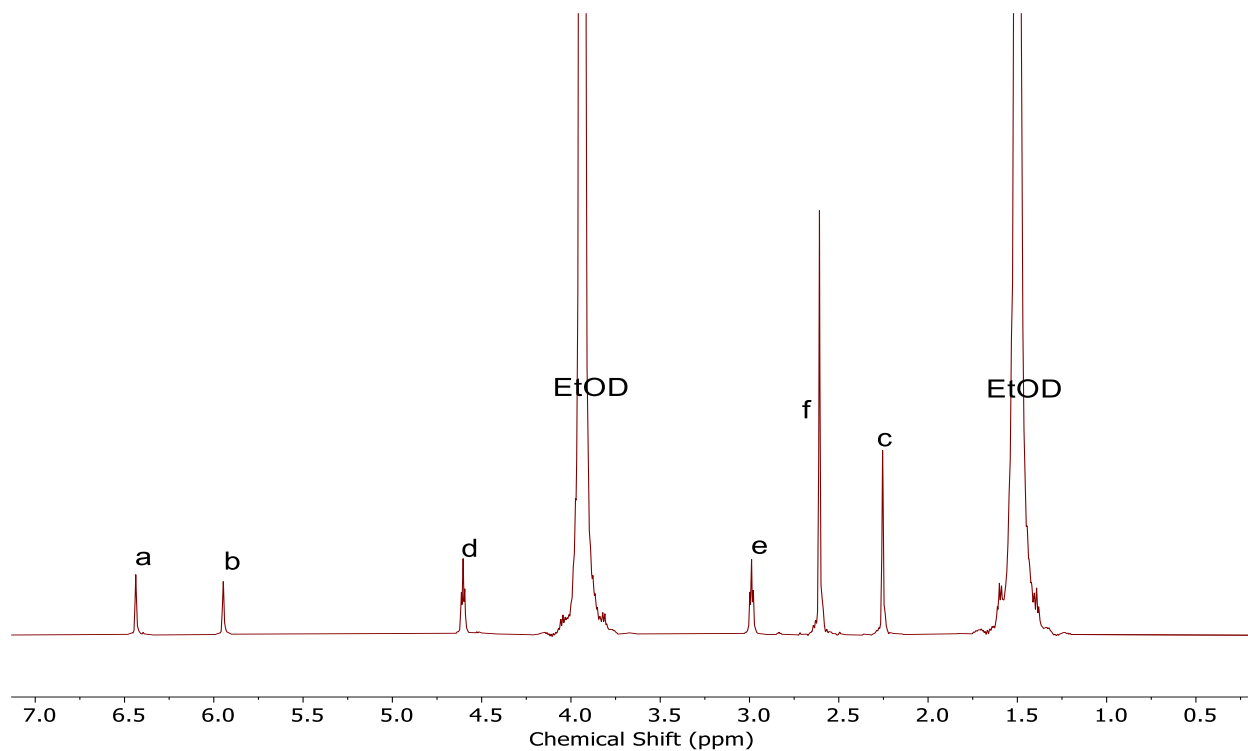


Figure S7: ¹H NMR (600 MHz) spectrum of PLP mixture with $w_{\text{DMAEMA}} = 0.5$ in EtOD/D₂O mixture at $\alpha_{\text{EtOD}} = 0.75$ held for ~4 min at 60 °C. No ethyl methacrylate or 2-dimethylaminoethanol were observed in either spectrum, indicating that DMAEMA solvolysis does not occur within the timeframe of the PLP experiment.

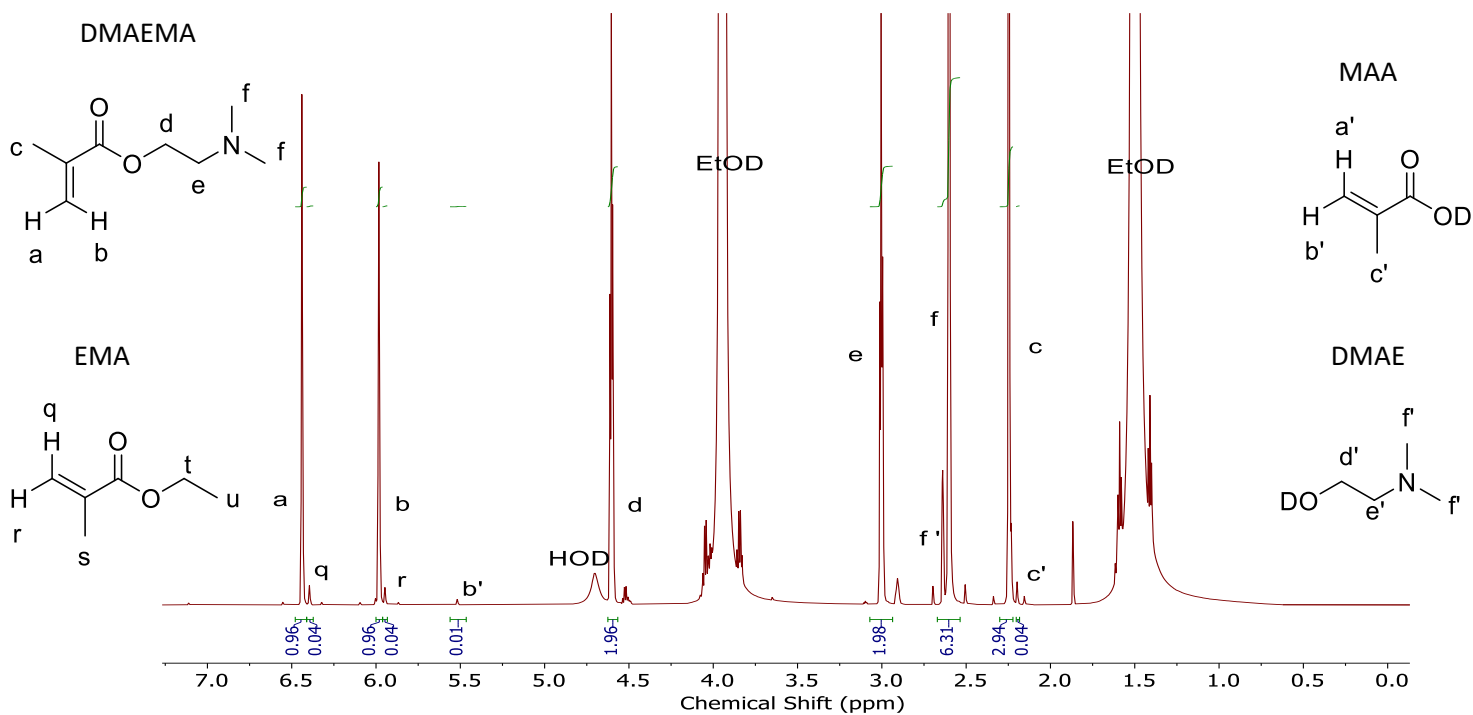


Figure S8: ^1H NMR (700 MHz) spectrum of PLP mixture with $w_{\text{DMAEMA}} = 0.5$ in EtOD/D₂O mixture at $\alpha_{\text{EtOD}} = 0.50$ held for ~4 min at 60 °C. Methacrylic acid, ethyl methacrylate and 2-dimethylaminoethanol were observed in both spectra, indicating that a small amount (< 5%) of DMAEMA solvolysis occurred within the timeframe of the PLP experiment.

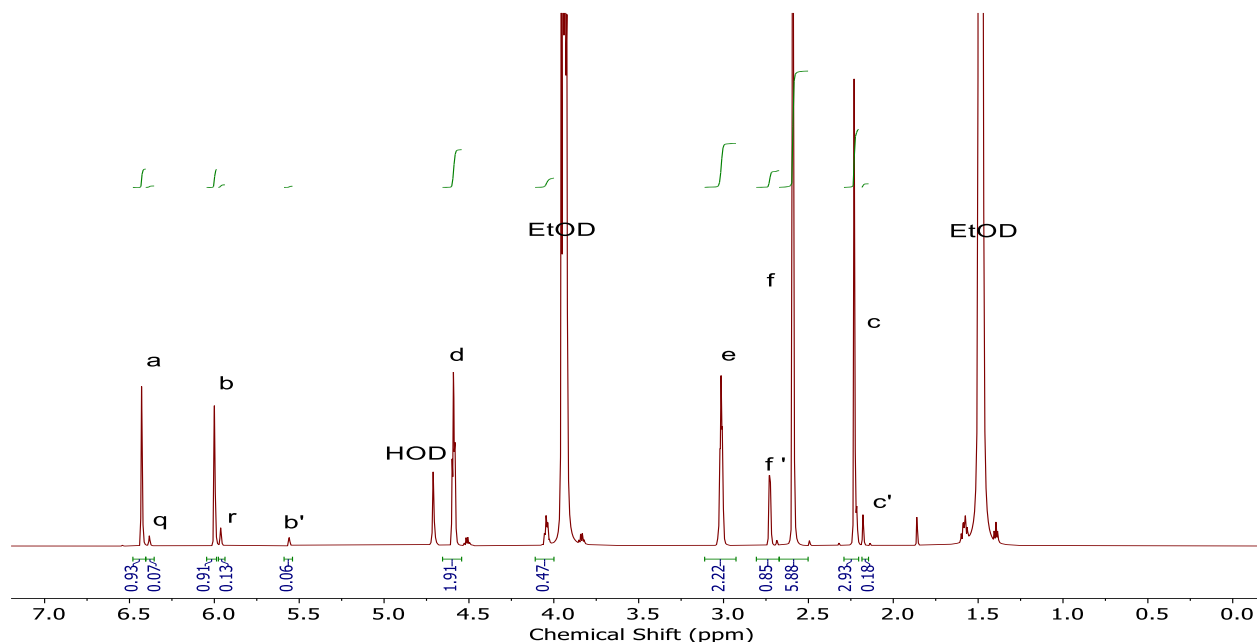


Figure S9: ^1H NMR (700 MHz) spectrum of PLP mixture with $w_{\text{DMAEMA}} = 0.5$ in EtOD/D₂O mixture with $\alpha_{\text{EtOD}} = 0.25$ held for ~4 min at 60 °C. Methacrylic acid, ethyl methacrylate and 2-dimethylaminoethanol were observed in both spectra, indicating that some DMAEMA solvolysis (<10%) occurred.

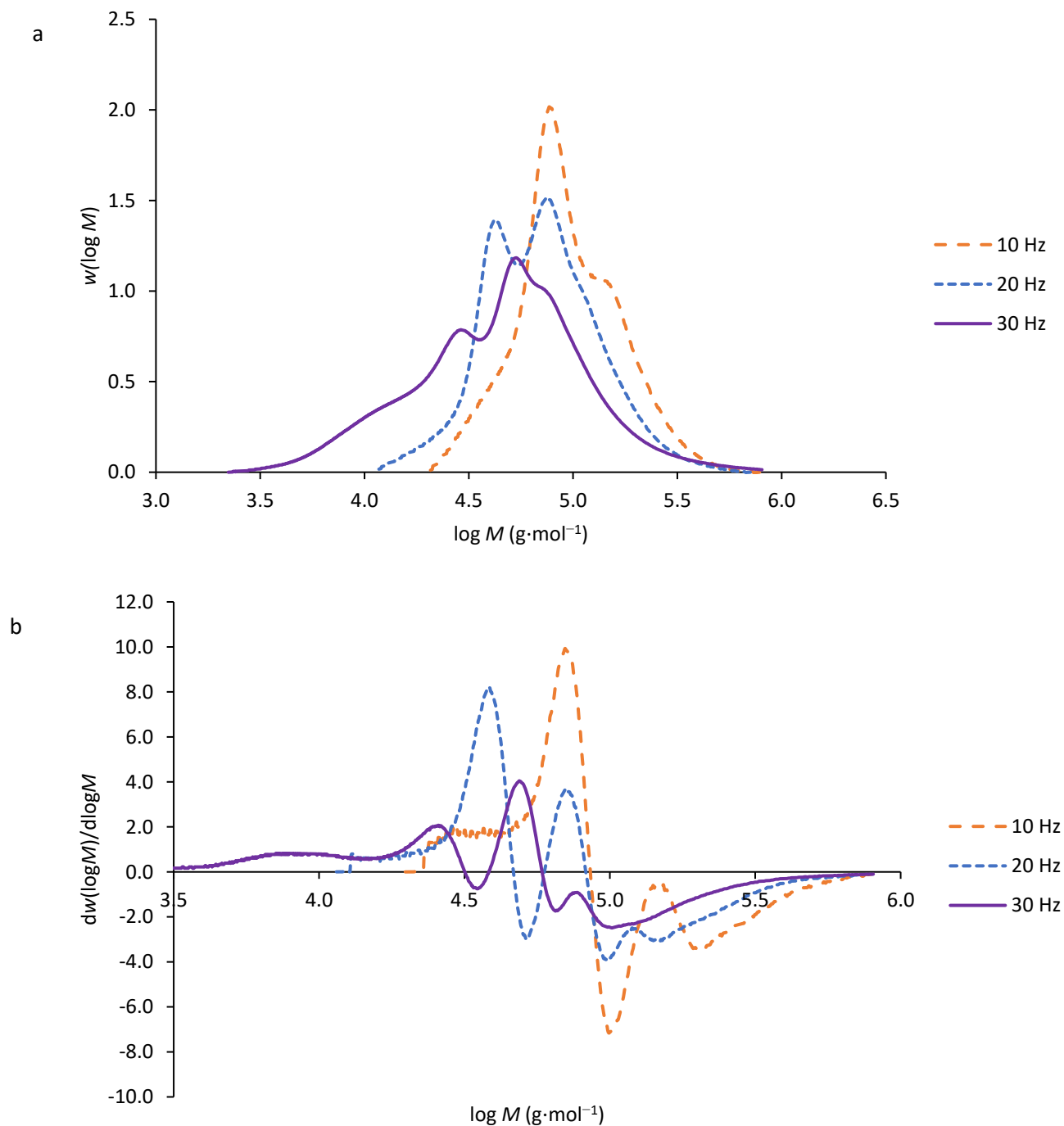


Figure S10: a) MMDs and b) first derivative curves from SEC analysis in THF for PDMAEMA generated by PLP with $w_{\text{DMAEMA}} = 0.50$ in EtOH/H₂O solution at $\alpha_{\text{EtOH}} = 0.75$ at 60 °C and p.r.r. = 10, 20, and 30 Hz.

Table S5(a): Propagation rate coefficients for polymerization of DMAEMA in EtOH/H₂O solutions determined from PLP-SEC experiments conducted at 25 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM Darocur 1173.

w_{DMAEMA}	α_{EtOH}	p.r.r. [Hz]	x_p [%]	$\log M_1$	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.50	0.50	10	0.3	4.6112	0.53	Aqueous	903
		10	0.3	4.6087	0.52	Aqueous	898
		10	0.3	4.6256	0.54	Aqueous	934
0.50	0.25	10	0.7	4.6955	0.50	Aqueous	1033
		10	0.7	4.7008	0.50	Aqueous	1045
		10	0.7	4.6963	0.50	Aqueous	1034

Table S5(b): Propagation rate coefficients for polymerization of DMAEMA in EtOH/H₂O solutions determined from PLP-SEC experiments conducted at 40 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM Darocur 1173.

w_{DMAEMA}	α_{EtOH}	p.r.r. [Hz]	x_p [%]	$\log M_1$	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.50	0.75	10	0.4	4.6460	0.51	THF	1013
		20	0.5	4.3829	0.52	THF	1105
		20	0.5	4.3828	0.52	THF	1059
	0.50	10	0.3	4.7778	0.50	THF	1330
		20	0.4	4.5109	0.54	THF	1438
		20	0.4	4.5108	0.54	THF	1384
	0.25	10	0.7	4.8588	0.49	THF	1551
		20	1.1	4.5933	0.53	THF	1683
		20	1.1	4.5932	0.53	THF	1617

Table S5(c): Propagation rate coefficients for polymerization of DMAEMA in EtOH/H₂O solutions determined from PLP-SEC experiments conducted at 60 °C at varying laser pulse repetition rates (p.r.r.) tabulated as a function of weight fraction DMAEMA (w_{DMAEMA}) in solution. Experiments were conducted with 5 mM Darocur 1173.

w_{DMAEMA}	α_{EtOH}	p.r.r. [Hz]	x_p [%]	$\log M_1$	M_1/M_2	SEC setup	k_p [L mol ⁻¹ s ⁻¹]
0.20	0.75	10	5.7	4.4831	0.53	THF	1826
		10	5.6	4.4832	0.53	THF	1825
		10	5.5	4.4830	0.53	THF	1827
0.50	0.75	10	0.4	4.8456	0.48	THF	1638
		20	0.6	4.5817	0.54	THF	1784
		30	0.6	4.4096	0.53	THF	1800
	0.50	10	0.2	4.9193	0.50	THF	1877
		20	0.3	4.6549	0.54	THF	2042
		20	0.3	4.6548	0.54	THF	1960
	0.25	20	0.7	4.7589	0.52	THF	2508
		30	1.1	4.6136	0.54	THF	2692
		30	1.1	4.6137	0.54	THF	2599

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