

Supporting Information

Radical Copolymerization Kinetics of *N*-*tert*-Butyl Acrylamide and Methyl Acrylate in Polar Media

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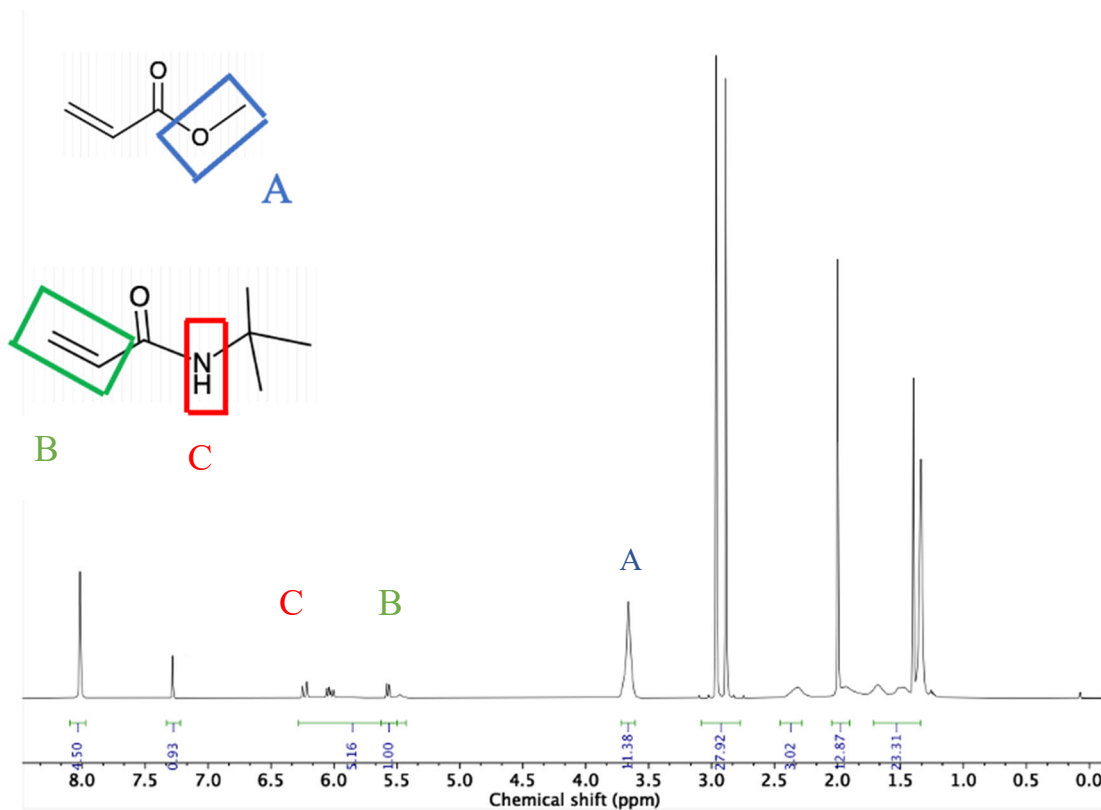


Figure S1 ¹H NMR spectrum of MA-tBuAAM copolymer generated by PLP with $w_{mon} = 0.30$, $\alpha_{EtOH} = 1$, $f_{MA} = 0.595$ at 30 °C and prr of 300 Hz. The copolymer composition using this NMR spectra is 0.637.

Calculation of copolymer composition (from Figure S1):

$$F_{MA} = \frac{\int OCH_{3,MA}(polymer)}{\int NH_{tBuAAm}(polymer)corrected + \int OCH_{3,MA}(polymer)}$$

$$F_{MA} = \frac{11.38ppm/3}{(5.16ppm - 3(1.00ppm)) + 11.38ppm/3}$$

$$F_{MA} = 0.637$$

Table S1 K and a values for poly(tBuAAm) in THF obtained from the triple-detector Viscotek SEC instrument.

Condition	a	$\log K$	$K \times 10^4$ (dL·g ⁻¹)
$W_{tBuAAm} = 0.10, \alpha_{EtOH} = 1, T = 30\text{ }^{\circ}\text{C}, prr = 100\text{ Hz}$	0.614	-3.591	2.56
$W_{tBuAAm} = 0.10, \alpha_{EtOH} = 1, T = 30\text{ }^{\circ}\text{C}, prr = 300\text{ Hz}$	0.607	-3.541	2.88
$W_{tBuAAm} = 0.15, \alpha_{EtOH} = 1, T = 40\text{ }^{\circ}\text{C}, prr = 300\text{ Hz}$	0.637	-3.710	1.95
$W_{tBuAAm} = 0.15, \alpha_{EtOH} = 1, T = 40\text{ }^{\circ}\text{C}, prr = 100\text{ Hz}$	0.647	-3.702	1.99
$W_{tBuAAm} = 0.15, \alpha_{EtOH} = 1, T = 40\text{ }^{\circ}\text{C}, prr = 200\text{ Hz}^a$	0.657	-3.801	1.58

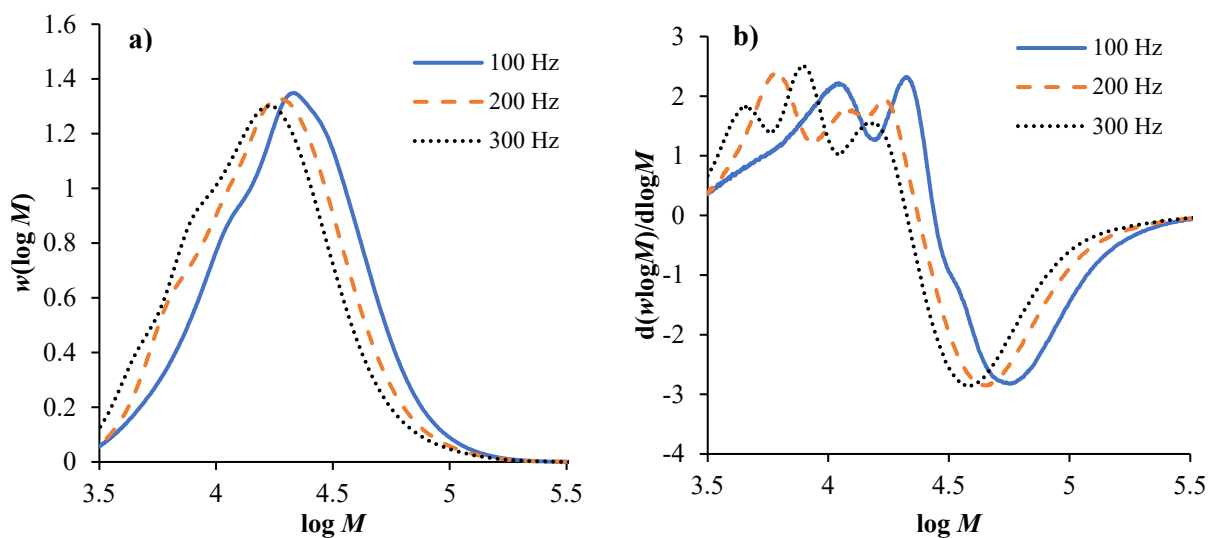


Figure S2 (a) $w(\log M)$ molar mass distribution and (b) differential $w(\log M)$ distribution for 10 wt% tBuAAM in EtOH ($\alpha_{EtOH} = 1$) at 40 °C at 100 Hz, 200 Hz and 300 Hz with 5 mmol·L⁻¹ D1173.

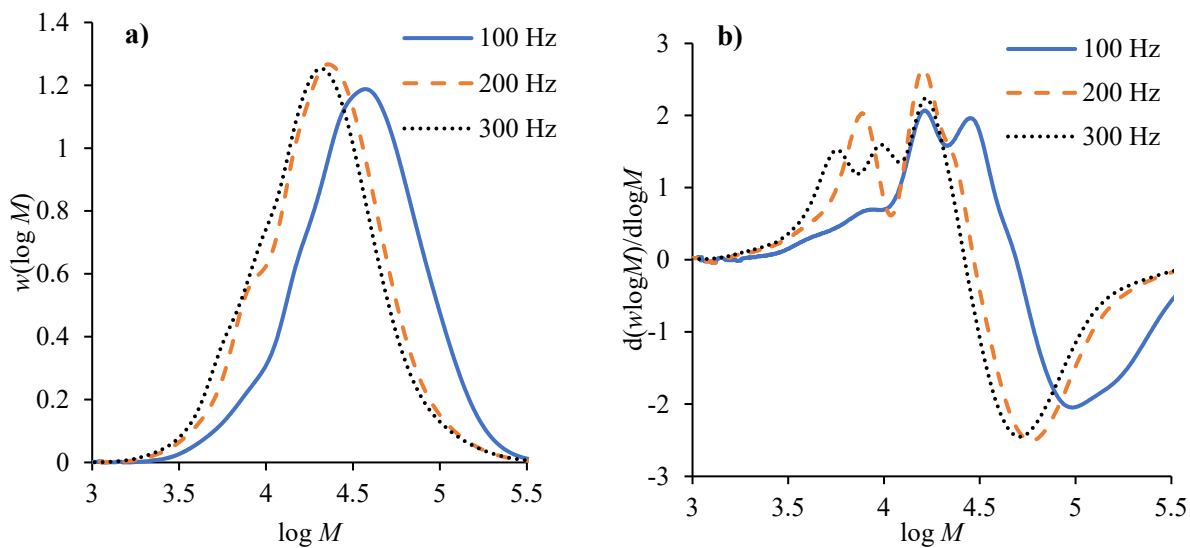


Figure S3 (a) $w(\log M)$ molar mass distribution and (b) differential $w(\log M)$ distribution for 10 wt% tBuAAM in EtOH/H₂O ($\alpha_{EtOH} = 0.75$) at 40 °C at 100,200 and 300 Hz with 5 mmol·L⁻¹ D1173.

Table S2 k_p values for tBuAAm determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{tBuAAm} is weight fraction of monomer in solution, and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{tBuAAm}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} (L·mol ⁻¹ ·s ⁻¹)
30	0.30	5	EtOH	1	100	4.453	0.533	10808
30	0.30	5	EtOH	1	200	4.155	0.504	10884
30	0.30	5	EtOH	1	300	3.974	0.482	10762
40	0.30	5	EtOH	1	100	4.526	0.541	12899
40	0.30	5	EtOH	1	200	4.246	0.513	13539
30	0.15	5	EtOH	1	100	4.180	0.560	12022
30	0.15	5	EtOH	1	200	3.883	0.516	12134
30	0.15	5	EtOH	1	300	3.705	0.543	12081
40	0.15	5	EtOH	1	100	4.272	0.562	15025
40	0.15	5	EtOH	1	200	3.973	0.545	15095
40	0.15	5	EtOH	1	300	3.799	0.509	15169
50	0.15	5	EtOH	1	100	4.351	0.545	18199
50	0.15	5	EtOH	1	200	4.059	0.524	18582
50	0.15	5	EtOH	1	300	3.880	0.480	18458
60	0.15	5	EtOH	1	100	4.427	0.564	21990
60	0.15	5	EtOH	1	200	4.125	0.530	21940
60	0.15	5	EtOH	1	300	3.947	0.451	21844
30	0.10	5	EtOH	1	150	3.850	0.430	12848
30	0.10	5	EtOH	1	200	3.716	0.583	12557
40	0.10	5	EtOH	1	100	4.108	0.547	15656
40	0.10	5	EtOH	1	200	3.815	0.540	15948
40	0.10	5	EtOH	1	300	3.632	0.565	15696
50	0.10	5	EtOH	1	100	4.185	0.545	18885
50	0.10	5	EtOH	1	200	3.886	0.520	18973
50	0.10	5	EtOH	1	300	3.705	0.557	18760
60	0.10	5	EtOH	1	100	4.262	0.586	22853
60	0.10	5	EtOH	1	200	3.961	0.504	22855
60	0.10	5	EtOH	1	300	3.777	0.462	22442
30	0.05	5	EtOH	1	100	3.784	0.550	13687
30	0.05	5	EtOH	1	150	3.578	0.460	13891
40	0.05	5	EtOH	1	100	3.800	0.483	15662
40	0.05	5	EtOH	1	200	3.474	0.452	15881
50	0.05	5	EtOH	1	200	3.596	0.567	19792
50	0.05	5	EtOH	1	300	3.415	0.473	19570

Table S3 k_p values for tBuAAM determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{tBuAAM} is weight fraction of monomer in solution, and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{tBuAAM}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)
30	0.10	5	EtOH/H ₂ O	0.75	100	4.076	0.537	13693
30	0.10	5	EtOH/H ₂ O	0.75	200	3.781	0.460	13884
40	0.10	5	EtOH/H ₂ O	0.75	100	4.159	0.530	16667
40	0.10	5	EtOH/H ₂ O	0.75	200	3.850	0.463	16363
40	0.10	5	EtOH/H ₂ O	0.75	300	3.689	0.540	16941
50	0.10	5	EtOH/H ₂ O	0.75	100	4.251	0.579	20784
50	0.10	5	EtOH/H ₂ O	0.75	200	3.949	0.545	20737
30	0.05	5	EtOH/H ₂ O	0.75	100	3.834	0.430	15854
30	0.05	5	EtOH/H ₂ O	0.75	200	3.521	0.454	15424
40	0.05	5	EtOH/H ₂ O	0.75	100	3.873	0.577	17536
40	0.05	5	EtOH/H ₂ O	0.75	200	3.578	0.460	17989
50	0.05	5	EtOH/H ₂ O	0.75	100	3.969	0.490	22079
50	0.05	5	EtOH/H ₂ O	0.75	200	3.680	0.498	22699
60	0.20	5	EtOH/H ₂ O	0.75	400	4.030	0.520	24743
60	0.20	5	EtOH/H ₂ O	0.75	500	3.930	0.479	24567
30	0.20	5	EtOH/H ₂ O	0.75	100	4.387	0.533	13695
30	0.20	5	EtOH/H ₂ O	0.75	200	4.089	0.511	13791
30	0.20	5	EtOH/H ₂ O	0.75	300	3.905	0.479	13542

Table S4 Equation (8) ($k_{p,tBuAAM}$ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) = $e^{-\frac{E_a/R}{T} + A(1-\alpha_{EtOH}) + Bw_{tBuAAM}}$) parameters determined using multiple non-linear regression along with 95% confidence intervals.

	<i>Parameter</i>
$A \cdot 10^{-6}$ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	8.68±2.06
E_a/R (K)	1955±75
A	0.463±0.068
B	-0.753±0.112

Table S5 Mean experimental $k_{p,cop}$ values ($k_{p,cop}^{mean}$) determined for MA-co-tBuAAm in pure EtOH ($\alpha_{EtOH}=1$) by PLP-SEC, along with the range of values obtained at each condition. w_{mon} is the total weight fraction of monomer in solution, with f_{MA} the mol fraction of MA in the mixture. See Tables S8-S9 for complete results from individual PLP experiments.

$T(^{\circ}C)$	w_{mon}	Solvent	α_{EtOH}	f_{MA}	Number of data points	$k_{p,cop}^{mean} \times 10^{-3}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	$k_{p,cop}^{low} \times 10^{-3}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	$k_{p,cop}^{high} \times 10^{-3}$ ($L \cdot mol^{-1} \cdot s^{-1}$)
30	0.50	EtOH	1	0.85	2	21.8	21.6	22.0
30	0.50	EtOH	1	0.73	2	20.8	20.8	20.9
30	0.50	EtOH	1	0.59	2	19.2	19.0	19.4
30	0.30	EtOH	1	0.60	3	21.4	21.4	21.4
30	0.30	EtOH	1	0.27	2	15.6	15.5	15.7
30	0.20	EtOH	1	0.93	2	27.2	27.1	27.4
30	0.20	EtOH	1	0.59	2	22.5	22.2	22.7
30	0.20	EtOH	1	0.27	2	16.4	16.2	16.7
30	0.15	EtOH	1	0.77	3	26.6	26.3	26.8
30	0.15	EtOH	1	0.59	3	23.2	23.0	23.4
30	0.15	EtOH	1	0.39	3	19.7	19.5	20.0
60	0.50	EtOH	1	0.93	2	32.8	32.6	32.9
60	0.50	EtOH	1	0.77	3	30.7	30.5	30.9
60	0.50	EtOH	1	0.59	3	29.3	29.2	29.5
60	0.30	EtOH	1	0.77	3	35.2	35.2	35.3
60	0.30	EtOH	1	0.59	3	33.5	33.3	33.6
60	0.30	EtOH	1	0.27	2	27.3	27.2	27.3
60	0.15	EtOH	1	0.77	2	37.1	37.1	37.1
60	0.15	EtOH	1	0.59	3	34.3	34.2	34.4
60	0.15	EtOH	1	0.27	3	27.9	27.9	28.0

Table S6 Mean experimental $k_{p,cop}$ values ($k_{p,cop}^{mean}$) determined for MA-co-tBuAAm by PLP-SEC in EtOH/H₂O with $\alpha_{EtOH} = 0.75$. w_{mon} is the total weight fraction of monomer in solution, with f_{MA} the mol fraction of MA in the mixture. See Tables S9-S10 for complete results from individual PLP experiments.

$T(^{\circ}C)$	w_{mon}	Solvent	α_{EtOH}	f_{MA}	Number of data points	$k_{p,cop}^{mean} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{low} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{high} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)
30	0.50	EtOH/H ₂ O	0.75	0.93	3	27.5	27.4	27.5
30	0.50	EtOH/H ₂ O	0.75	0.81	3	26.7	26.7	26.7
30	0.30	EtOH/H ₂ O	0.75	0.85	2	28.5	28.2	28.9
30	0.30	EtOH/H ₂ O	0.75	0.59	2	23.6	23.5	23.7
30	0.15	EtOH/H ₂ O	0.75	0.82	3	33.0	32.8	33.2
30	0.15	EtOH/H ₂ O	0.75	0.59	3	27.2	27.1	27.3
30	0.15	EtOH/H ₂ O	0.75	0.26	3	18.6	18.3	18.9
60	0.50	EtOH/H ₂ O	0.75	0.93	3	37.8	37.6	37.9
60	0.50	EtOH/H ₂ O	0.75	0.81	2	36.8	37.6	37.9
60	0.15	EtOH/H ₂ O	0.75	0.85	2	49.6	49.5	49.6
60	0.15	EtOH/H ₂ O	0.75	0.61	2	41.6	40.5	42.8
60	0.15	EtOH/H ₂ O	0.75	0.28	2	30.8	30.6	31.0

Table S7 Mean experimental $k_{p,cop}$ values ($k_{p,cop}^{mean}$) determined for MA-co-tBuAAm by PLP-SEC in EtOH/H₂O with $\alpha_{EtOH} = 0.50$. w_{mon} is the total weight fraction of monomer in solution, with f_{MA} the mol fraction of MA in the mixture. See Table S10-S11 for complete results from individual PLP experiments.

$T(^{\circ}C)$	w_{mon}	Solvent	α_{EtOH}	f_{MA}	Number of data points	$k_{p,cop}^{mean} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{low} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{high} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)
30	0.30	EtOH/H ₂ O	0.50	0.85	3	48.5	48.4	48.6
30	0.30	EtOH/H ₂ O	0.50	0.77	3	46.4	46.1	46.7
30	0.30	EtOH/H ₂ O	0.50	0.69	3	44.4	44.1	44.4
30	0.15	EtOH/H ₂ O	0.50	0.85	3	60.8	60.4	61.0
30	0.15	EtOH/H ₂ O	0.50	0.81	3	58.1	58.1	58.2
30	0.15	EtOH/H ₂ O	0.50	0.60	2	57.2	57.1	57.3
30	0.15	EtOH/H ₂ O	0.50	0.55	3	48.7	48.4	48.9
30	0.15	EtOH/H ₂ O	0.50	0.27	2	35.1	35.0	35.2
60	0.30	EtOH/H ₂ O	0.50	0.85	2	73.5	73.5	73.5
60	0.30	EtOH/H ₂ O	0.50	0.77	2	68.6	68.2	69.0
60	0.30	EtOH/H ₂ O	0.50	0.69	2	65.5	65.1	66.0
60	0.15	EtOH/H ₂ O	0.50	0.77	2	81.5	81.4	81.7
60	0.15	EtOH/H ₂ O	0.50	0.60	3	75.4	75.2	75.6
60	0.15	EtOH/H ₂ O	0.50	0.39	3	67.5	67.3	67.6

Table S8 Mean experimental $k_{p,cop}$ values ($k_{p,cop}^{mean}$) determined for MA-co-tBuAAm by PLP-SEC in EtOH/H₂O with $\alpha_{EtOH} = 0.25$. w_{mon} is the total weight fraction of monomer in solution, with f_{MA} the mol fraction of MA in the mixture. See Table S11 for complete results from individual PLP experiments.

$T(^{\circ}C)$	w_{mon}	Solvent	α_{EtOH}	f_{MA}	Number of data points	$k_{p,cop}^{mean} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{low} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{p,cop}^{high} \times 10^{-3}$ (L·mol ⁻¹ ·s ⁻¹)
30	0.15	EtOH/H ₂ O	0.25	0.85	3	92.6	92.2	92.8
30	0.15	EtOH/H ₂ O	0.25	0.77	3	90.5	90.4	90.6
30	0.10	EtOH/H ₂ O	0.25	0.85	3	110.3	110.3	112.8
30	0.10	EtOH/H ₂ O	0.25	0.77	3	105.2	105.2	107.6
30	0.10	EtOH/H ₂ O	0.25	0.69	3	99.7	99.7	99.7

Table S9 k_p values for MA-co-tBuAAM at various temperatures and comonomer compositions determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{mon} is the total weight fraction of monomer in solution and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{mon}	f_{MA}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)
30	0.15	0.39	5	EtOH	1	300	3.901	0.505	19516
30	0.15	0.39	5	EtOH	1	400	3.780	0.551	19693
30	0.15	0.39	5	EtOH	1	500	3.690	0.450	20009
30	0.15	0.59	5	EtOH	1	300	3.970	0.512	23000
30	0.15	0.59	5	EtOH	1	400	3.853	0.501	23425
30	0.15	0.59	5	EtOH	1	500	3.750	0.514	23098
30	0.15	0.77	5	EtOH	1	300	4.029	0.513	26300
30	0.15	0.77	5	EtOH	1	400	3.910	0.483	26663
30	0.15	0.77	5	EtOH	1	500	3.816	0.474	26842
60	0.15	0.27	5	EtOH	1	400	3.918	0.500	27851
60	0.15	0.27	5	EtOH	1	500	3.823	0.460	27974
60	0.15	0.59	5	EtOH	1	300	4.130	0.560	34361
60	0.15	0.59	5	EtOH	1	400	4.040	0.450	34198
60	0.15	0.77	5	EtOH	1	300	4.165	0.473	37126
60	0.15	0.77	5	EtOH	1	500	3.943	0.528	37113
30	0.20	0.27	5	EtOH	1	300	3.950	0.501	16164
30	0.20	0.27	5	EtOH	1	500	3.743	0.528	16727
30	0.20	0.59	5	EtOH	1	300	4.087	0.530	22418
30	0.20	0.59	5	EtOH	1	400	3.958	0.512	22210
30	0.20	0.59	5	EtOH	1	500	3.871	0.485	22722
30	0.20	0.93	5	EtOH	1	300	4.171	0.553	27058
30	0.20	0.93	5	EtOH	1	400	4.034	0.532	27368
30	0.30	0.27	5	EtOH	1	400	3.995	0.495	15484
30	0.30	0.27	5	EtOH	1	500	3.904	0.484	15696
30	0.30	0.60	5	EtOH	1	400	4.130	0.512	21377
30	0.30	0.60	5	EtOH	1	500	4.033	0.509	21372
60	0.30	0.27	5	EtOH	1	300	4.352	0.515	27217
60	0.30	0.27	5	EtOH	1	400	4.230	0.501	27337
60	0.30	0.27	5	EtOH	1	500	4.132	0.481	27333
60	0.30	0.59	5	EtOH	1	300	4.436	0.467	33576
60	0.30	0.59	5	EtOH	1	400	4.308	0.492	33340
60	0.30	0.59	5	EtOH	1	500	4.215	0.507	33641
60	0.30	0.77	5	EtOH	1	400	4.331	0.475	35264
60	0.30	0.77	5	EtOH	1	500	4.246	0.486	35182

Table S10 k_p values for MA-co-tBuAAm at various temperatures and comonomer compositions determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{mon} is the total weight fraction of monomer in solution and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{mon}	f_{MA}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} (L·mol ⁻¹ ·s ⁻¹)
30	0.50	0.59	5	EtOH	1	300	4.443	0.471	19018
30	0.50	0.59	5	EtOH	1	400	4.326	0.512	19369
30	0.50	0.73	5	EtOH	1	300	4.480	0.525	20815
30	0.50	0.73	5	EtOH	1	400	4.354	0.530	20764
30	0.50	0.73	5	EtOH	1	500	4.260	0.525	20903
30	0.50	0.85	5	EtOH	1	300	4.496	0.548	21724
30	0.50	0.85	5	EtOH	1	400	4.369	0.524	21621
30	0.50	0.85	5	EtOH	1	500	4.280	0.525	22018
60	0.50	0.59	5	EtOH	1	300	4.617	0.466	29163
60	0.50	0.59	5	EtOH	1	400	4.495	0.552	29361
60	0.50	0.59	5	EtOH	1	500	4.400	0.497	29490
60	0.50	0.77	5	EtOH	1	300	4.632	0.439	30480
60	0.50	0.77	5	EtOH	1	400	4.513	0.460	30900
60	0.50	0.77	5	EtOH	1	500	4.415	0.521	30822
60	0.50	0.93	5	EtOH	1	400	4.532	0.540	32637
60	0.50	0.93	5	EtOH	1	500	4.438	0.553	32856
30	0.15	0.26	5	EtOH/H ₂ O	0.75	300	3.910	0.452	18886
30	0.15	0.26	5	EtOH/H ₂ O	0.75	400	3.772	0.446	18327
30	0.15	0.26	5	EtOH/H ₂ O	0.75	500	3.679	0.481	18492
30	0.15	0.59	5	EtOH/H ₂ O	0.75	300	4.067	0.516	27293
30	0.15	0.59	5	EtOH/H ₂ O	0.75	400	3.939	0.502	27101
30	0.15	0.59	5	EtOH/H ₂ O	0.75	500	3.844	0.483	27221
30	0.15	0.82	5	EtOH/H ₂ O	0.75	300	4.165	0.546	33071
30	0.15	0.82	5	EtOH/H ₂ O	0.75	400	4.042	0.473	33196
30	0.15	0.82	5	EtOH/H ₂ O	0.75	500	3.940	0.520	32810
60	0.15	0.28	5	EtOH/H ₂ O	0.75	400	3.987	0.456	30946
60	0.15	0.28	5	EtOH/H ₂ O	0.75	500	3.885	0.428	30585
60	0.15	0.61	5	EtOH/H ₂ O	0.75	300	4.225	0.496	40483
60	0.15	0.61	5	EtOH/H ₂ O	0.75	400	4.124	0.547	42777
60	0.15	0.85	5	EtOH/H ₂ O	0.75	400	4.186	0.533	49533
60	0.15	0.85	5	EtOH/H ₂ O	0.75	500	4.090	0.525	49637

Table S11 k_p values for MA-co-tBuAAm at various temperatures and comonomer compositions determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{mon} is the total weight fraction of monomer in solution and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{mon}	f_{MA}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} (L·mol ⁻¹ ·s ⁻¹)
30	0.30	0.27	5	EtOH/H ₂ O	0.75	300	4.226	0.550	19096
30	0.30	0.27	5	EtOH/H ₂ O	0.75	400	4.102	0.536	19137
30	0.30	0.27	5	EtOH/H ₂ O	0.75	500	4.015	0.498	19579
30	0.30	0.59	5	EtOH/H ₂ O	0.75	300	4.310	0.525	23500
30	0.30	0.59	5	EtOH/H ₂ O	0.75	400	4.188	0.533	23660
30	0.30	0.85	5	EtOH/H ₂ O	0.75	400	4.263	0.530	28234
30	0.30	0.85	5	EtOH/H ₂ O	0.75	500	4.175	0.551	28819
30	0.50	0.73	5	EtOH/H ₂ O	0.75	300	4.583	0.538	25595
30	0.50	0.73	5	EtOH/H ₂ O	0.75	500	4.366	0.526	25882
30	0.50	0.81	5	EtOH/H ₂ O	0.75	300	4.599	0.501	26742
30	0.50	0.81	5	EtOH/H ₂ O	0.75	400	4.473	0.535	26677
30	0.50	0.81	5	EtOH/H ₂ O	0.75	500	4.377	0.449	26733
30	0.50	0.93	5	EtOH/H ₂ O	0.75	300	4.609	0.500	27541
30	0.50	0.93	5	EtOH/H ₂ O	0.75	400	4.482	0.492	27411
30	0.50	0.93	5	EtOH/H ₂ O	0.75	500	4.385	0.468	27405
60	0.50	0.81	5	EtOH/H ₂ O	0.75	300	4.724	0.483	36720
60	0.50	0.81	5	EtOH/H ₂ O	0.75	400	4.601	0.491	36885
60	0.50	0.93	5	EtOH/H ₂ O	0.75	300	4.730	0.513	37559
60	0.50	0.93	5	EtOH/H ₂ O	0.75	400	4.609	0.456	37901
60	0.50	0.93	5	EtOH/H ₂ O	0.75	500	4.512	0.492	37893
30	0.15	0.27	5	EtOH/H ₂ O	0.50	400	4.073	0.466	35033
30	0.15	0.27	5	EtOH/H ₂ O	0.50	500	3.978	0.495	35188
30	0.15	0.55	5	EtOH/H ₂ O	0.50	300	4.340	0.488	48357
30	0.15	0.55	5	EtOH/H ₂ O	0.50	400	4.220	0.530	48910
30	0.15	0.55	5	EtOH/H ₂ O	0.50	500	4.122	0.523	48788
30	0.15	0.60	5	EtOH/H ₂ O	0.50	400	4.284	0.536	57247
30	0.15	0.60	5	EtOH/H ₂ O	0.50	500	4.186	0.555	57104
30	0.15	0.81	5	EtOH/H ₂ O	0.50	300	4.415	0.553	58080
30	0.15	0.81	5	EtOH/H ₂ O	0.50	400	4.291	0.526	58206
30	0.15	0.81	5	EtOH/H ₂ O	0.50	500	4.193	0.498	58060
30	0.15	0.85	5	EtOH/H ₂ O	0.50	300	4.435	0.522	60992
30	0.15	0.85	5	EtOH/H ₂ O	0.50	400	4.309	0.533	60843
30	0.15	0.85	5	EtOH/H ₂ O	0.50	500	4.209	0.540	60412

Table S12 k_p values for MA-co-tBuAAm at various temperatures and comonomer compositions determined from PLP experiments conducted in EtOH and EtOH/H₂O mixtures using D1173 as initiator. w_{mon} is the total weight fraction of monomer in solution and α_{EtOH} is the weight fraction of EtOH (balance H₂O) in the solvent.

$T(^{\circ}\text{C})$	w_{mon}	f_{MA}	C_{D1173} (mM)	Solvent	α_{EtOH}	f (Hz)	$\log M_1$ RI	M_1/M_2	RI k_{p1} ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)
60	0.15	0.39	5	EtOH/H ₂ O	0.50	300	4.472	0.541	67481
60	0.15	0.39	5	EtOH/H ₂ O	0.50	400	4.348	0.532	67627
60	0.15	0.39	5	EtOH/H ₂ O	0.50	500	4.249	0.530	67303
60	0.15	0.60	5	EtOH/H ₂ O	0.50	300	4.517	0.472	75558
60	0.15	0.60	5	EtOH/H ₂ O	0.50	400	4.390	0.545	75200
60	0.15	0.60	5	EtOH/H ₂ O	0.50	500	4.294	0.543	75358
60	0.15	0.77	5	EtOH/H ₂ O	0.50	400	4.423	0.505	81361
60	0.15	0.77	5	EtOH/H ₂ O	0.50	500	4.328	0.522	81720
30	0.30	0.69	5	EtOH/H ₂ O	0.50	300	4.605	0.530	44356
30	0.30	0.69	5	EtOH/H ₂ O	0.50	400	4.482	0.519	44555
30	0.30	0.69	5	EtOH/H ₂ O	0.50	500	4.381	0.480	44137
30	0.30	0.77	5	EtOH/H ₂ O	0.50	300	4.622	0.540	46123
30	0.30	0.77	5	EtOH/H ₂ O	0.50	400	4.502	0.533	46649
30	0.30	0.77	5	EtOH/H ₂ O	0.50	500	4.403	0.537	46425
30	0.30	0.85	5	EtOH/H ₂ O	0.50	300	4.643	0.531	48424
30	0.30	0.85	5	EtOH/H ₂ O	0.50	400	4.520	0.515	48640
30	0.30	0.85	5	EtOH/H ₂ O	0.50	500	4.421	0.507	48407
60	0.30	0.69	5	EtOH/H ₂ O	0.50	300	4.760	0.499	65079
60	0.30	0.69	5	EtOH/H ₂ O	0.50	500	4.544	0.536	65961
60	0.30	0.77	5	EtOH/H ₂ O	0.50	400	4.655	0.533	68220
60	0.30	0.77	5	EtOH/H ₂ O	0.50	500	4.563	0.537	68996
60	0.30	0.85	5	EtOH/H ₂ O	0.50	400	4.686	0.513	73507
60	0.30	0.85	5	EtOH/H ₂ O	0.50	500	4.589	0.531	73491
30	0.15	0.77	5	EtOH/H ₂ O	0.25	300	4.630	0.458	90619
30	0.15	0.77	5	EtOH/H ₂ O	0.25	400	4.505	0.461	90606
30	0.15	0.77	5	EtOH/H ₂ O	0.25	500	4.407	0.498	90379
30	0.15	0.85	5	EtOH/H ₂ O	0.25	300	4.639	0.460	92153
30	0.15	0.85	5	EtOH/H ₂ O	0.25	400	4.517	0.489	92778
30	0.15	0.85	5	EtOH/H ₂ O	0.25	500	4.420	0.497	92759
30	0.10	0.69	5	EtOH/H ₂ O	0.25	300	4.496	0.443	99683
30	0.10	0.69	5	EtOH/H ₂ O	0.25	400	4.371	0.461	99669
30	0.10	0.69	5	EtOH/H ₂ O	0.25	500	4.274	0.455	99648
30	0.10	0.77	5	EtOH/H ₂ O	0.25	300	4.518	0.467	105164
30	0.10	0.77	5	EtOH/H ₂ O	0.25	400	4.400	0.499	106858
30	0.10	0.77	5	EtOH/H ₂ O	0.25	500	4.306	0.507	107577

30	0.10	0.85	5	EtOH/H ₂ O	0.25	300	4.538	0.518	110313
30	0.10	0.85	5	EtOH/H ₂ O	0.25	400	4.421	0.520	112348
30	0.10	0.85	5	EtOH/H ₂ O	0.25	500	4.326	0.524	112843

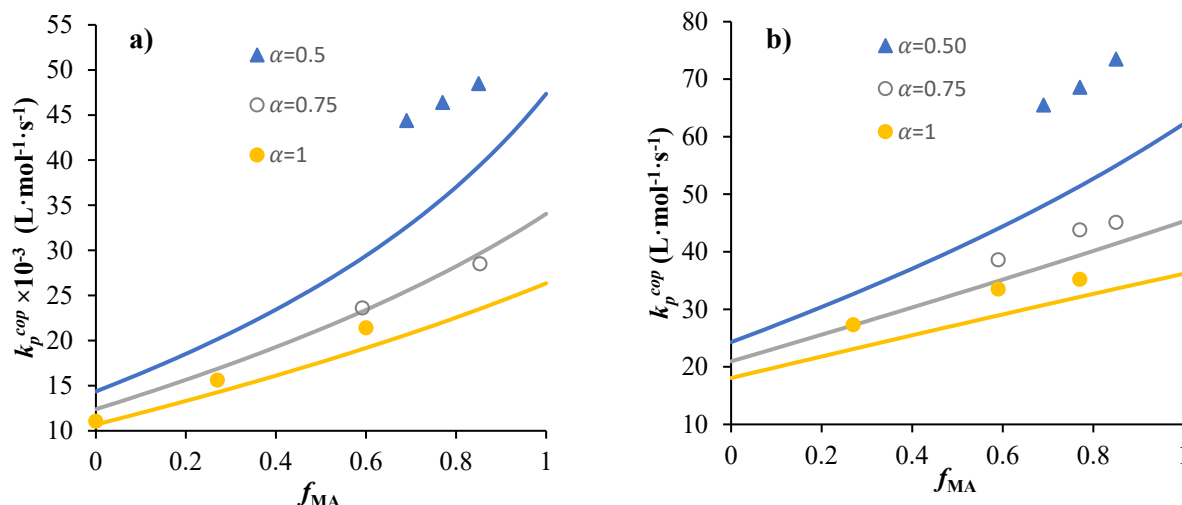


Figure S4 Experimental values of $k_{p,cop}$ determined by PLP-SEC (points) compared to terminal model predictions (lines) with varying wt fraction of ethanol (α_{EtOH}) in EtOH/H₂O solvent mixtures as a function of MA molar composition (f_{MA}) of the MA-tBuAAm comonomer mixture with $w_{mon} = 0.30$ at (a) 30 °C and (b) 60 °C.

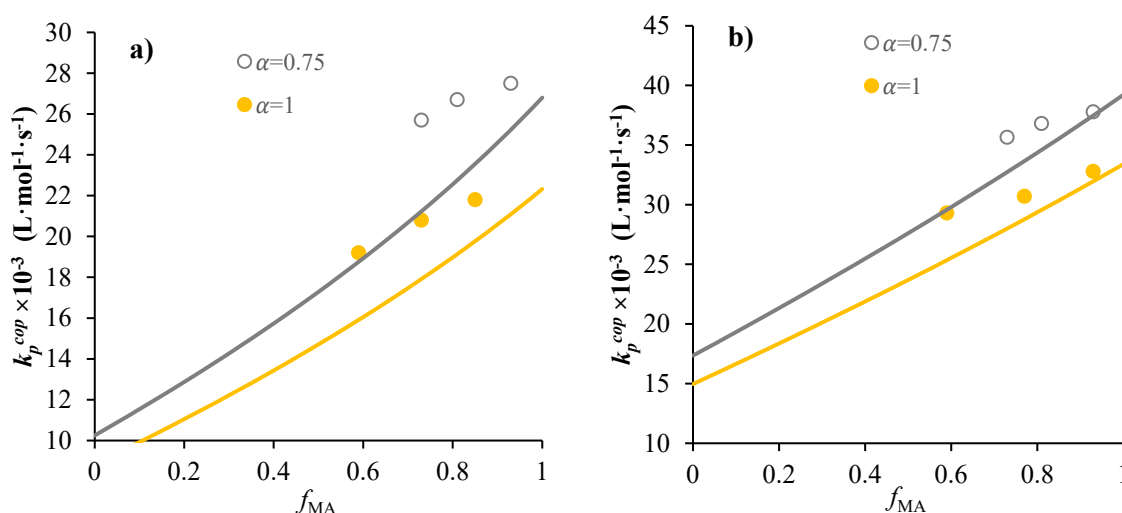


Figure S5 Experimental values of $k_{p,cop}$ determined by PLP-SEC (points) compared to terminal model predictions (lines) with varying wt fraction of ethanol (α_{EtOH}) in EtOH/H₂O solvent mixtures as a function of MA molar composition (f_{MA}) of the MA-tBuAAm comonomer mixture with $w_{mon} = 0.50$ at (a) 30 °C and (b) 60 °C.