**Supporting Information**

# A COMPARISON OF THE SOLUTION RADICAL PROPAGATION KINETICS OF PARTIALLY WATER-MISCIBLE NON-FUNCTIONAL ACRYLATES TO ACRYLIC ACID

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Curve smoothing was performed on the 1st derivative ($\frac{\mathrm{d}w(\log M)}{\mathrm{d}\log M}$) plots calculated from the RI and LS molar mass distributions collected at Queen's University using finite differences (equation S1) to reduce the noise and unambiguously identify the location of the maxima, as shown in **Figure S1**.

$$\frac{\mathrm{d}w(\log M)_k}{\mathrm{d}\log M_k} = \frac{w(\log M)_k - w(\log M)_{k+j}}{\log M_k - \log M_{k+j}} \tag{S1}$$

Index $k$ represents the data slice and $\log M_k$ and $w(\log M)_k$ are the corresponding $\log M$ and $w(\log M)$ values. The value of the step size $j$ is selected to significantly reduce the noise without losing the features of the distribution. Typically, $j \approx$ 7-10 was chosen for the distributions collected from the Waters RI detector, which provided 300-600 slices of data. The Wyatt Instruments LS detector provided ~600 slices of data and a typical value chosen for $j \approx$ 30-40.

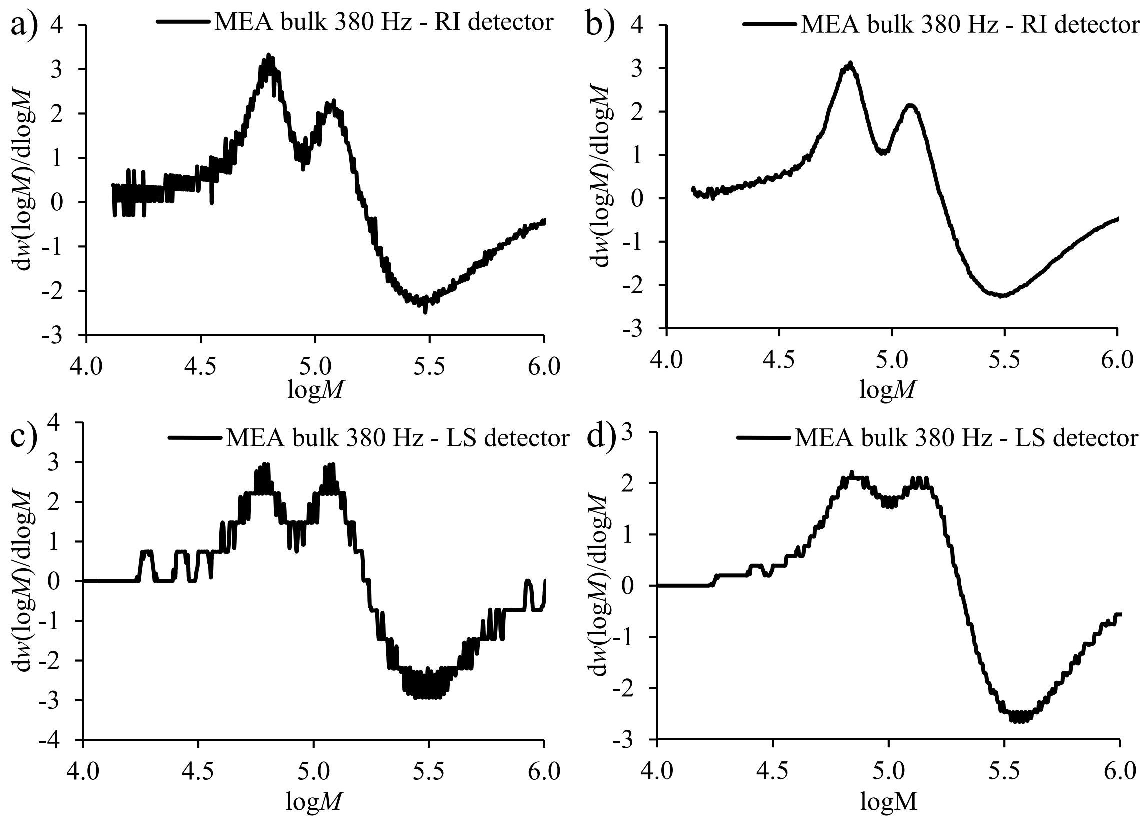


**Figure S1. First derivative plots calculated using the MMD bulk MEA at 380 Hz (a) before and (b) after curve smoothing procedure using data from the RI detector and (c) before and (d) after curve smoothing procedure using data from the LS detector.**

**Table S1. Density correlations for monomers and solvents, with $T$ in °C. Ideal mixing of monomer and solvents was assumed for the calculation of the overall density of the solution.**

| Solvents/Monomer | $\rho$ (g·cm$^{-3}$) | References |
|---|---|---|
| MA | $0.9774 \cdot \exp(-0.001260T)$ | 1 |
| MEA | $1.0247 - 0.000835T^{a}$ | 2 |
| AA | $1.0731 - 1.0826 \cdot 10^{-3}T - 7.2379 \cdot 10^{-7}T^{2}$ | 3 |
| MeOH | $0.8110 - 0.001000T^{b}$ | 4 |
| BuOH | $0.8398 - 0.001190T$ | 5 |
| EtOH | $0.8070 - 0.000877T^{c}$ | 6 |
| $H_2O$ | $1.0087 - 0.000400T^{d}$ | 7 |
| DMF | $1.235026 - 0.000972T$ | 5 |

[a]MEA density correlation assumes the temperature dependence is identical to butyl acrylate with the y-intercept selected such that $\rho_{MEA}$=1.008 g/cm$^3$ (Sigma-Aldrich) at 20 °C. [b]MeOH density correlation obtained from linear regression of $\rho_{MeOH}$ data between 25-50 °C. [c]EtOH density correlation obtained from linear regression of $\rho_{EtOH}$ data between 15-55 °C. [d]$H_2O$ density correlation obtained from linear regression based of $\rho_{H_2O}$ data between 17-82 °C.

**Table S2. A comparison of MEA $k_p$ values calculated from SEC analysis of PLP-generated polymer MMDs using refractive index (RI) and multiangle light scattering (LS) detectors. Δ is the percent difference between values estimates from RI and LS detection according to ($k_{p1}$ RI−$k_{p1}$ LS)/($k_{p1}$ RI). All samples generated at 30 °C using 5 mmol·L$^{-1}$ DMPA initiator, with $w_{MEA}$ the weight fraction of MEA in solution and $\alpha_{MeOH}$ the weight fraction of MeOH (balance $H_2O$) in the solvent.**

| $w_{MEA}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ RI | $k_{p1} \cdot 10^{-3}$ RI (L·mol$^{-1}$·s$^{-1}$) | log$M_1$ LS | $M_1/M_2$ LS | $k_{p1} \cdot 10^{-3}$ LS (L·mol$^{-1}$·s$^{-1}$) | Δ (%) |
|---|---|---|---|---|---|---|---|---|
| **Bulk** | | | | | | | | |
| 1.00 | 380 | 4.847 | 0.486 | 26.7 | 4.812 | 0.452 | 24.7 | 7.74 |
| **$\alpha_{MeOH}$=0.70** | | | | | | | | |
| 0.83 | 300 | 4.879 | 0.538 | 28.4 | 4.886 | 0.546 | 28.9 | −1.62 |
| 0.83 | 400 | 4.776 | 0.513 | 29.9 | 4.799 | 0.470 | 31.5 | −5.44 |
| **$\alpha_{MeOH}$=0.44** | | | | | | | | |
| 0.82 | 400 | 4.816 | 0.509 | 32.7 | 4.821 | 0.513 | 33.1 | −1.16 |
| 0.14 | 300 | 4.529 | 0.558 | 81.2 | 4.528 | 0.561 | 81.0 | 0.23 |
| 0.14 | 350 | 4.463 | 0.535 | 81.3 | 4.457 | 0.528 | 80.2 | 1.37 |

**Figure S2. Droplets observed in 26 wt% MEA at $\alpha_{MeOH}$ = 0.20 with 6 mmol·L$^{-1}$ DMPA. The MEA system became immiscible when DMPA was added to reaction mixtures with a high water content (e.g., 5 wt% MEA in water, 13 and 26 wt% MEA at $\alpha_{MeOH}$ = 0.20).**

**Table S3. $k_p$ values for bulk MEA at 30 °C using DMPA as initiator.**

| $C_{Initiator}$ (mmol·L$^{-1}$) | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|
| 5.0 | 380 | 4.799 | 0.570 | 23.9 | |
| 5.0 | 480 | 4.670 | 0.494 | 22.5 | |
| 5.0 | 380 | 4.792 | 0.505 | 23.5 | |
| 5.0 | 480 | 4.680 | 0.469 | 23.0 | |
| 5.0 | 380 | 4.847 | 0.486 | 26.7 | |
| 5.0 | 480 | 4.755 | 0.442 | 27.3 | |
| 5.0 | 380 | 4.827 | 0.541 | 25.3 | |
| 5.0 | 380 | 4.813 | 0.558 | 24.5 | |
| 5.0 | 480 | 4.747 | 0.518 | 26.6 | |
| 5.0 | 480 | 4.754 | 0.540 | 27.0 | |
| 5.0 | 380 | - | 0.563 | 22.8 | [8] |
| 5.0 | 480 | - | 0.516 | 24.5 | [8] |
| 7.0 | 380 | - | 0.502 | 23.5 | [8] |
| 7.0 | 480 | - | 0.570 | 24.5 | [8] |

**Table S4.** $k_p$ **values for MEA at 30 °C determined from PLP experiments conducted in MeOH and MeOH/$H_2O$ mixtures. Experiments used DMPA as initiator unless otherwise indicated ([a]D1173 initiator).** $w_{MEA}$ **and** $v_{MEA}$ **are weight and volume fraction of monomer in solution, respectively, and** $\alpha_{MeOH}$ **is the weight fraction of MeOH (balance $H_2O$) in the solvent. Some MMDs were transformed with the parameter γ in order to reveal PLP structure according to a technique described in another work.[9] [b]Polymer precipitated out of PLP solution after pulsing.**

| $w_{MEA}$ | $v_{MEA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $\alpha_{MeOH}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot 10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|---|
| 0.84 | 0.80 | 5.0 | 1.00 | 250 | 4.897 | 0.556 | 24.7 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 300 | 4.827 | 0.522 | 25.2 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 350 | 4.776 | 0.526 | 26.2 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 250 | 4.870 | 0.570 | 23.2 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 300 | 4.820 | 0.540 | 24.8 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 350 | 4.765 | 0.545 | 25.5 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 250 | 4.680 | 0.541 | 24.0 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 300 | 4.603 | 0.547 | 24.1 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 250 | 4.733 | 0.561 | 27.1 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 300 | 4.664 | 0.540 | 27.8 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 250 | 4.469 | 0.558 | 29.6 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 300 | 4.405 | 0.564 | 30.6 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 250 | 4.506 | 0.539 | 32.2 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 300 | 4.437 | 0.560 | 33.0 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 150 | 4.353 | 0.535 | 27.2 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 150 | 4.428 | 0.485 | 32.3 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 200 | 4.289 | 0.540 | 31.3 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 250 | 4.200 | 0.546 | 31.8 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 300 | 4.030 | 0.472 | 25.8 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 350 | 4.009 | 0.504 | 28.7 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 150 | 4.400 | 0.497 | 30.3 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 200 | 4.301 | 0.530 | 32.1 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 250 | 4.225 | 0.546 | 33.7 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 300 | 4.137 | 0.528 | 33.0 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 350 | 4.067 | 0.507 | 32.8 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 150 | 4.443 | 0.494 | 33.4 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 200 | 4.331 | 0.533 | 34.4 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 250 | 4.245 | 0.545 | 35.4 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 300 | 4.161 | 0.523 | 35.0 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 350 | 4.094 | 0.503 | 34.9 | |
| 0.83 | 0.80 | 5.0 | 0.70 | 300 | 4.879 | 0.538 | 28.4 | |
| 0.83 | 0.80 | 5.0 | 0.70 | 350 | 4.830 | 0.513 | 29.6 | |
| 0.83 | 0.80 | 5.0 | 0.70 | 400 | 4.776 | 0.513 | 29.9 | |
| 0.54 | 0.50 | 5.0 | 0.70 | 250 | 4.786 | 0.558 | 30.6 | |
| 0.54 | 0.50 | 5.0 | 0.70 | 300 | 4.664 | 0.500 | 27.7 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.29 | 0.25 | 5.0 | 0.70 | 250 | 4.569 | 0.548 | 37.1 | |
| 0.29 | 0.25 | 5.0 | 0.70 | 300 | 4.535 | 0.597 | 41.2 | |
| 0.29 | 0.25 | 5.0 | 0.70 | 200 | 4.603 | 0.434 | 32.1 | [a] |
| 0.29 | 0.25 | 5.0 | 0.70 | 250 | 4.553 | 0.498 | 35.8 | [a] |
| 0.29 | 0.25 | 5.0 | 0.70 | 300 | 4.507 | 0.541 | 38.6 | [a] |
| 0.15 | 0.13 | 5.0 | 0.70 | 250 | 4.407 | 0.538 | 51.2 | |
| 0.15 | 0.13 | 5.0 | 0.70 | 300 | 4.330 | 0.548 | 51.4 | |
| 0.15 | 0.13 | 5.0 | 0.70 | 350 | 4.277 | 0.545 | 53.1 | |
| 0.15 | 0.13 | 5.0 | 0.70 | 200 | 4.444 | 0.540 | 44.6 | [a] |
| 0.15 | 0.13 | 5.0 | 0.70 | 250 | 4.369 | 0.553 | 46.9 | [a] |
| 0.15 | 0.13 | 5.0 | 0.70 | 300 | 4.304 | 0.564 | 48.4 | [a] |
| 0.82 | 0.80 | 5.0 | 0.44 | 300 | 4.936 | 0.550 | 32.4 | |
| 0.82 | 0.80 | 5.0 | 0.44 | 400 | 4.816 | 0.509 | 32.7 | |
| 0.53 | 0.50 | 5.0 | 0.44 | 250 | 4.868 | 0.590 | 36.9 | |
| 0.53 | 0.50 | 5.0 | 0.44 | 300 | 4.803 | 0.556 | 38.1 | |
| 0.53 | 0.50 | 5.0 | 0.44 | 350 | 4.762 | 0.509 | 40.5 | |
| 0.27 | 0.25 | 5.0 | 0.44 | 250 | 4.823 | 0.527 | 66.6 | |
| 0.27 | 0.25 | 5.0 | 0.44 | 300 | 4.762 | 0.492 | 69.4 | |
| 0.27 | 0.25 | 5.0 | 0.44 | 350 | 4.722 | 0.552 | 73.8 | |
| 0.27 | 0.25 | 5.0 | 0.44 | 250 | 4.825 | 0.531 | 66.9 | [a] |
| 0.27 | 0.25 | 5.0 | 0.44 | 300 | 4.759 | 0.541 | 68.9 | [a] |
| 0.27 | 0.25 | 5.0 | 0.44 | 350 | 4.687 | 0.536 | 68.1 | [a] |
| 0.22 | 0.20 | 5.0 | 0.44 | 300 | 4.709 | 0.508 | 76.1 | |
| 0.22 | 0.20 | 5.0 | 0.44 | 300 | 4.706 | 0.526 | 75.6 | |
| 0.22 | 0.20 | 5.0 | 0.44 | 250 | 4.777 | 0.495 | 74.2 | |
| 0.22 | 0.20 | 5.0 | 0.44 | 250 | 4.770 | 0.488 | 73.1 | |
| 0.14 | 0.13 | 5.0 | 0.44 | 250 | 4.590 | 0.562 | 77.8 | |
| 0.14 | 0.13 | 5.0 | 0.44 | 300 | 4.529 | 0.558 | 81.2 | |
| 0.14 | 0.13 | 5.0 | 0.44 | 350 | 4.463 | 0.535 | 81.3 | |
| 0.14 | 0.13 | 5.0 | 0.44 | 200 | 4.636 | 0.535 | 69.2 | [a] |
| 0.14 | 0.13 | 5.0 | 0.44 | 250 | 4.553 | 0.546 | 71.5 | [a] |
| 0.14 | 0.13 | 5.0 | 0.44 | 300 | 4.492 | 0.545 | 74.5 | [a] |
| 0.52 | 0.50 | 0.0 | 0.20 | immiscible at room temperature (RT) | | | | |
| 0.26 | 0.25 | 5.0 | 0.20 | immiscible when DMPA added at RT | | | | |
| 0.26 | 0.25 | 6.5 | 0.20 | 250 | 4.947 | 0.532 | 88.4 | [a,b], $\gamma = -1$ |
| 0.26 | 0.25 | 6.5 | 0.20 | 300 | 4.865 | 0.498 | 87.8 | [a,b], $\gamma = -0.5$ |
| 0.26 | 0.25 | 6.5 | 0.20 | 350 | 4.782 | 0.476 | 84.6 | [a,b] |
| 0.26 | 0.25 | 6.5 | 0.20 | 400 | 4.759 | 0.493 | 91.7 | [a,b], $\gamma = -0.5$ |
| 0.26 | 0.25 | 5.0 | 0.20 | 325 | 4.753 | 0.450 | 73.5 | [a,b] |
| 0.26 | 0.25 | 5.0 | 0.20 | 375 | 4.668 | 0.447 | 69.8 | [a,b] |
| 0.26 | 0.25 | 6.5 | 0.20 | 250 | 4.901 | 0.524 | 79.5 | [a,b] |
| 0.26 | 0.25 | 6.5 | 0.20 | 300 | 4.813 | 0.497 | 77.9 | [a,b] |
| 0.26 | 0.25 | 6.5 | 0.20 | 350 | 4.749 | 0.485 | 78.4 | [a,b] |
| 0.26 | 0.25 | 5.0 | 0.20 | 250 | 4.901 | 0.535 | 79.5 | [a,b] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.26 | 0.25 | 5.0 | 0.20 | 300 | 4.813 | 0.508 | 77.9 | a,b |
| 0.26 | 0.25 | 5.0 | 0.20 | 350 | 4.767 | 0.497 | 81.8 | a,b |
| 0.13 | 0.13 | 4.0 | 0.20 | Immiscible when DMPA added at RT | | | | |
| 0.13 | 0.13 | 5.0 | 0.20 | 150 | 4.912 | 0.455 | 97.8 | a,b, $\gamma = -1.3$ |
| 0.13 | 0.13 | 5.0 | 0.20 | 200 | 4.788 | 0.438 | 98.1 | a,b, $\gamma = -0.9$ |
| 0.13 | 0.13 | 6.5 | 0.20 | 250 | 4.786 | 0.480 | 122.0 | a,b, $\gamma = -1.1$ |
| 0.13 | 0.13 | 5.0 | 0.20 | 250 | 4.788 | 0.465 | 122.6 | a,b, $\gamma = -1.9$ |
| 0.13 | 0.13 | 5.0 | 0.20 | 225 | 4.845 | 0.480 | 125.8 | a,b, $\gamma = -1.6$ |
| 0.13 | 0.13 | 5.0 | 0.20 | 275 | 4.774 | 0.491 | 130.5 | a,b, $\gamma = -1.8$ |

**Table S5. $k_p$ values for MEA at 30 °C determined from individual PLP experiments conducted in EtOH and EtOH/$H_2O$ mixtures. Experiments used DMPA as initiator unless otherwise indicated ([a]D1173 initiator). $w_{MEA}$ and $v_{MEA}$ are weight and volume fraction of monomer in solution, respectively, and $\alpha_{EtOH}$ is the weight fraction of EtOH (balance $H_2O$) in the solvent.**

| $w_{MEA}$ | $v_{MEA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $\alpha_{EtOH}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|---|
| 0.84 | 0.80 | 5.0 | 1.00 | 300 | 4.780 | 0.531 | 22.6 | |
| 0.84 | 0.80 | 5.0 | 1.00 | 400 | 4.688 | 0.518 | 24.4 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 300 | 4.635 | 0.561 | 25.9 | |
| 0.56 | 0.50 | 5.0 | 1.00 | 400 | 4.534 | 0.553 | 27.4 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 300 | 4.426 | 0.552 | 32.1 | |
| 0.30 | 0.25 | 5.0 | 1.00 | 400 | 4.320 | 0.550 | 33.5 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 300 | 4.206 | 0.564 | 38.7 | |
| 0.15 | 0.13 | 5.0 | 1.00 | 400 | 4.067 | 0.516 | 37.4 | |
| 0.83 | 0.80 | 5.0 | 0.70 | 300 | 4.834 | 0.596 | 25.6 | |
| 0.83 | 0.80 | 5.0 | 0.70 | 400 | 4.735 | 0.556 | 27.2 | |
| 0.55 | 0.50 | 5.0 | 0.70 | 300 | 4.725 | 0.519 | 31.9 | |
| 0.55 | 0.50 | 5.0 | 0.70 | 400 | 4.625 | 0.578 | 33.8 | |
| 0.29 | 0.25 | 5.0 | 0.70 | 300 | 4.509 | 0.566 | 38.8 | |
| 0.29 | 0.25 | 5.0 | 0.70 | 400 | 4.400 | 0.565 | 40.2 | |
| 0.29 | 0.25 | 5.0 | 0.70 | 250 | 4.522 | 0.499 | 33.3 | a |
| 0.29 | 0.25 | 5.0 | 0.70 | 300 | 4.474 | 0.509 | 35.8 | a |
| 0.15 | 0.13 | 5.0 | 0.70 | 300 | 4.265 | 0.570 | 44.2 | |
| 0.15 | 0.13 | 5.0 | 0.70 | 250 | 4.344 | 0.571 | 44.2 | a |
| 0.15 | 0.13 | 5.0 | 0.70 | 300 | 4.280 | 0.577 | 45.8 | a |
| 0.15 | 0.13 | 5.0 | 0.70 | 400 | 4.149 | 0.546 | 45.2 | a |

**Table S6.** $k_p$ **values for MEA at 30 °C determined from individual PLP experiments conducted in BuOH with DMPA initiator.** $w_{MEA}$ **and** $v_{MEA}$ **are weight and volume fraction of monomer in solution, respectively.** [b]**Polymer precipitated out of PLP solution after pulsing.**

| $w_{MEA}$ | $v_{MEA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| 0.55 | 0.50 | 5.0 | 300 | 4.632 | 0.553 | 25.8 | |
| 0.55 | 0.50 | 5.0 | 400 | 4.523 | 0.560 | 26.8 | |
| 0.55 | 0.50 | 5.0 | 300 | 4.731 | 0.530 | 32.1 | |
| 0.55 | 0.50 | 5.0 | 400 | 4.631 | 0.561 | 33.9 | |
| 0.55 | 0.50 | 5.0 | 380 | - | 0.573 | 31.9 | Taken from ref [8] |
| 0.55 | 0.50 | 5.0 | 480 | - | 0.557 | 33.3 | Taken from ref [8] |
| 0.55 | 0.50 | 5.0 | 300 | 4.708 | 0.551 | 30.6 | |
| 0.55 | 0.50 | 5.0 | 400 | 4.607 | 0.567 | 32.3 | |
| 0.55 | 0.50 | 5.0 | 380 | 4.616 | 0.556 | 31.4 | |
| 0.55 | 0.50 | 5.0 | 480 | 4.535 | 0.560 | 32.9 | |
| 0.29 | 0.25 | 5.0 | 300 | 4.457 | 0.560 | 34.5 | |
| 0.29 | 0.25 | 5.0 | 400 | 4.330 | 0.556 | 34.4 | |
| 0.29 | 0.25 | 5.0 | 300 | 4.486 | 0.558 | 36.7 | |
| 0.29 | 0.25 | 5.0 | 400 | 4.398 | 0.557 | 39.9 | |
| 0.15 | 0.13 | 5.0 | 400 | 4.115 | 0.489 | 41.9 | [b] |
| 0.15 | 0.13 | 5.0 | 450 | 4.108 | 0.507 | 46.4 | [b] |
| 0.15 | 0.13 | 5.0 | 500 | 4.078 | 0.505 | 48.2 | [b] |
| 0.15 | 0.13 | 5.0 | 400 | 4.134 | 0.528 | 43.5 | [b] |
| 0.15 | 0.13 | 5.0 | 450 | 4.105 | 0.506 | 45.8 | [b] |
| 0.15 | 0.13 | 5.0 | 500 | 4.054 | 0.483 | 45.2 | [b] |
| 0.15 | 0.13 | 5.0 | 400 | 4.127 | 0.538 | 43.1 | [b] |
| 0.15 | 0.13 | 5.0 | 450 | 4.072 | 0.509 | 42.7 | [b] |
| 0.15 | 0.13 | 5.0 | 500 | 4.060 | 0.528 | 46.2 | [b] |

**Table S7.** $k_p$ **values for MEA at 30 °C determined from individual PLP experiments conducted in** $H_2O$ **(**[a]**D1173 initiator was used).** $w_{MEA}$ **and** $v_{MEA}$ **are weight and volume fraction of monomer in solution.** [b]**Polymer precipitated out of PLP solution after pulsing. Some MMDs were transformed with the parameter** $\gamma$ **in order to reveal PLP structure according to a technique described in another work.**[9]

| $w_{MEA}$ | $v_{MEA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| 0.05 | 0.05 | 5.0 | Immiscible with DMPA at room temperature | | | | |
| 0.05 | 0.05 | 5.0 | 300 | 4.507 | 0.455 | 192.1 | [a,b], $\gamma = -1.0$ |
| 0.05 | 0.05 | 5.0 | 350 | 4.477 | 0.538 | 209.2 | [a,b], $\gamma = -1.4$ |
| 0.05 | 0.05 | 5.0 | 250 | 4.547 | 0.474 | 175.5 | [a,b], $\gamma = -1.3$ |
| 0.05 | 0.05 | 5.0 | 250 | 4.607 | 0.500 | 201.5 | [a,b], $\gamma = -1.3$ |

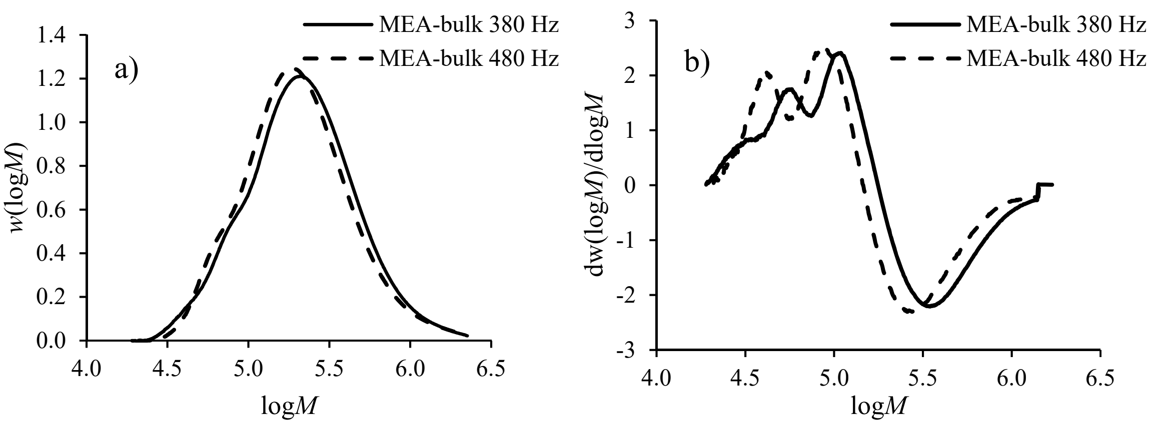


**Figure S3. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for bulk MEA at 30 °C at 380 Hz and 480 Hz with 5 mmol·L$^{-1}$ DMPA.**

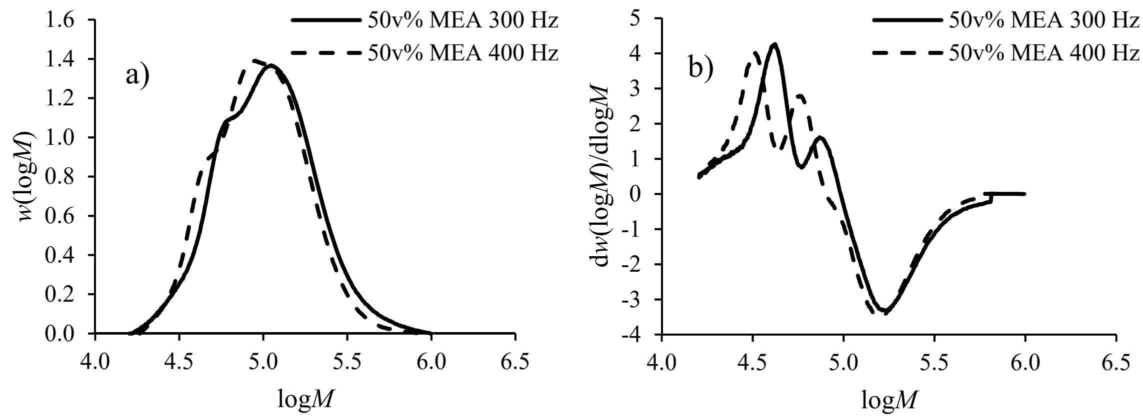


**Figure S4. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for 50 v% MEA in BuOH at 30 °C at 300 Hz and 400 Hz with 5 mmol·L$^{-1}$ DMPA.**

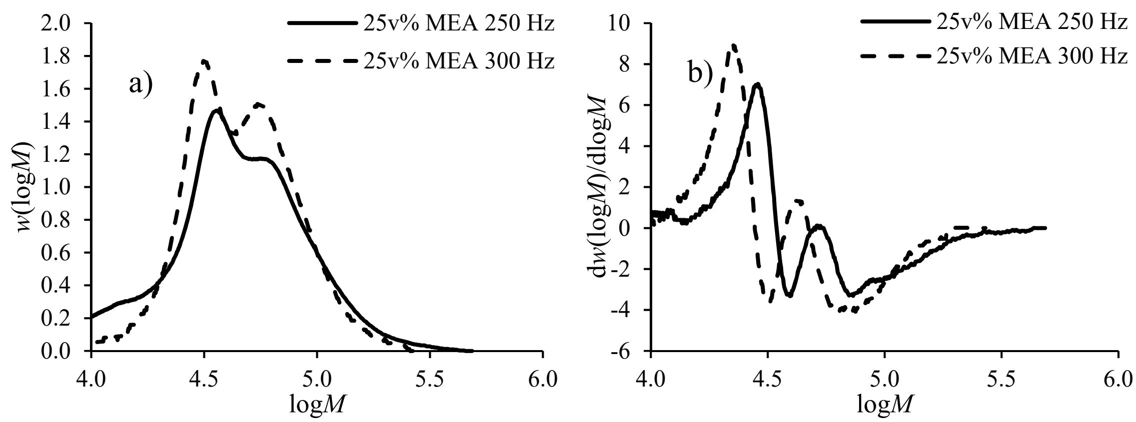


**Figure S5. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for 25 v% MEA in MeOH at 30 °C at 300 Hz and 400 Hz with 5 mmol·L$^{-1}$ DMPA.**

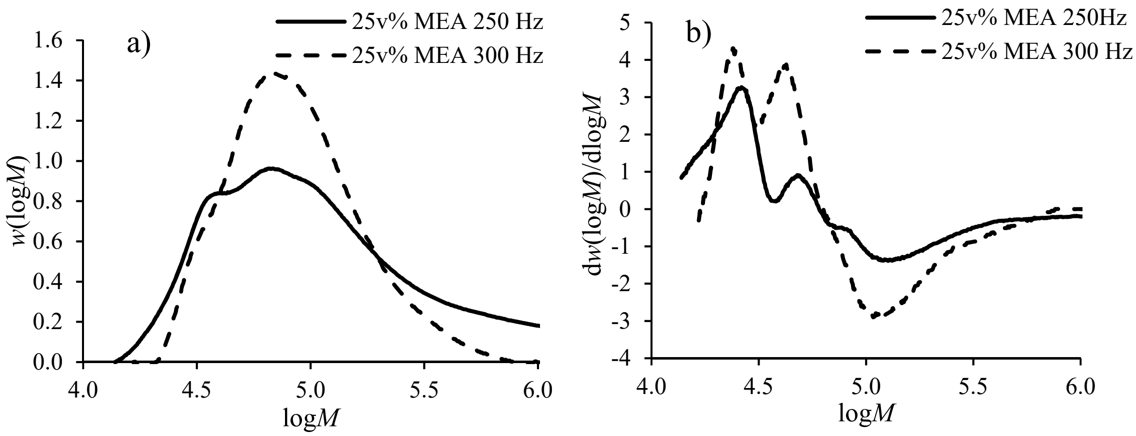


**Figure S6. (a) $w(\log M)$ molar mass distribution and (b) differential $w(\log M)$ distribution for 25 v% MEA in 75v:25v MeOH:$H_2O$ at 30 °C at 250 Hz and 300 Hz 5 mmol·L$^{-1}$ DMPA.**

**Table S8. A comparison of mean $k_p$ values ($k_p^{mean}$) of MEA from PLP experiments at 30 °C using two different photoinitiators, DMPA and D1173, at identical conditions (see Table S4 and Table S5 for details). The absolute difference |Δ| (%) is calculated as $100\cdot(k_{p,\text{ DMPA}}^{mean} - k_{p,\text{ D1173}}^{mean})/k_{p,\text{ DMPA}}^{mean}$. $w_{MEA}$ and $v_{MEA}$ are weight and volume fraction of monomer in solution, respectively, and $\alpha_x$ is the weight fraction of alcohol $x$ (balance $H_2O$) in the solvent.**

| $w_{MEA}$ | $v_{MEA}$ | Solvent | $\alpha_x$ | $k_{p,\text{ DMPA}}^{mean}\cdot 10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | $k_{p,\text{ D1173}}^{mean}\cdot 10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | \|Δ\| (%) |
|---|---|---|---|---|---|---|
| 0.29 | 0.25 | MeOH/$H_2O$ | 0.70 | 39.2 | 35.5 | 9.3 |
| 0.15 | 0.13 | MeOH/$H_2O$ | 0.70 | 51.9 | 46.6 | 10.2 |
| 0.27 | 0.25 | MeOH/$H_2O$ | 0.44 | 69.9 | 68.0 | 2.8 |
| 0.14 | 0.13 | MeOH/$H_2O$ | 0.44 | 80.1 | 71.8 | 10.4 |
| 0.29 | 0.25 | EtOH/$H_2O$ | 0.70 | 39.5 | 34.5 | 12.6 |
| 0.15 | 0.13 | EtOH/$H_2O$ | 0.70 | 44.2 | 45.1 | 1.9 |

**Table S9.** $k_p$ **values for MA determined from PLP experiments conducted in EtOH and EtOH/$H_2O$ mixtures at 30 °C. Experiments used D1173 as initiator unless otherwise indicated ([a]DMPA initiator).** $w_{MA}$ **and** $v_{MA}$ **are weight and volume fraction of monomer in solution, respectively, and** $\alpha_{EtOH}$ **is the weight fraction of EtOH (balance $H_2O$) in the solvent.**

| $w_{MA}$ | $v_{MA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $\alpha_{EtOH}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|---|
| 0.55 | 0.50 | 5.0 | 1.00 | 200 | 4.620 | 0.471 | 17.7 | a |
| 0.55 | 0.50 | 5.0 | 1.00 | 300 | 4.470 | 0.515 | 18.8 | a |
| 0.55 | 0.50 | 5.0 | 1.00 | 300 | 4.480 | 0.504 | 19.2 | a |
| 0.55 | 0.50 | 5.0 | 1.00 | 400 | 4.359 | 0.513 | 19.4 | a |
| 0.55 | 0.50 | 5.0 | 1.00 | 400 | 4.369 | 0.538 | 19.9 | a |
| 0.55 | 0.50 | 5.0 | 1.00 | 500 | 4.285 | 0.536 | 20.5 | a |
| 0.50 | 0.45 | 5.0 | 1.00 | 300 | 4.565 | 0.468 | 25.7 | |
| 0.50 | 0.45 | 5.0 | 1.00 | 400 | 4.426 | 0.511 | 24.9 | |
| 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.279 | 0.552 | 22.2 | |
| 0.20 | 0.17 | 5.0 | 1.00 | 300 | 4.195 | 0.566 | 28.8 | |
| 0.20 | 0.17 | 5.0 | 1.00 | 400 | 4.067 | 0.578 | 28.6 | |
| 0.20 | 0.17 | 5.0 | 1.00 | 500 | 3.985 | 0.528 | 29.6 | |
| 0.10 | 0.08 | 5.0 | 1.00 | 200 | 4.094 | 0.509 | 30.7 | |
| 0.10 | 0.08 | 5.0 | 1.00 | 300 | 3.918 | 0.474 | 30.7 | |
| 0.10 | 0.08 | 5.0 | 1.00 | 400 | 3.819 | 0.500 | 32.6 | |
| 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.745 | 0.560 | 34.3 | |
| 0.50 | 0.47 | 5.0 | 0.75 | 200 | 4.804 | 0.481 | 28.9 | |
| 0.50 | 0.47 | 5.0 | 0.75 | 300 | 4.652 | 0.476 | 30.5 | |
| 0.50 | 0.47 | 5.0 | 0.75 | 400 | 4.539 | 0.514 | 31.4 | |
| 0.50 | 0.47 | 5.0 | 0.75 | 500 | 4.445 | 0.509 | 31.6 | |
| 0.20 | 0.18 | 5.0 | 0.75 | 300 | 4.311 | 0.548 | 36.0 | |
| 0.20 | 0.18 | 5.0 | 0.75 | 400 | 4.215 | 0.558 | 38.5 | |
| 0.20 | 0.18 | 5.0 | 0.75 | 500 | 4.13 | 0.566 | 39.6 | |
| 0.10 | 0.09 | 5.0 | 0.75 | 300 | 4.041 | 0.548 | 39.1 | |
| 0.10 | 0.09 | 5.0 | 0.75 | 400 | 3.947 | 0.522 | 42.0 | |
| 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.876 | 0.526 | 44.6 | |
| 0.50 | 0.48 | 5.0 | 0.50 | 300 | 4.684 | 0.441 | 31.8 | |
| 0.50 | 0.48 | 5.0 | 0.50 | 400 | 4.582 | 0.467 | 33.5 | |
| 0.50 | 0.48 | 5.0 | 0.50 | 500 | 4.504 | 0.522 | 35.0 | |
| 0.20 | 0.19 | 5.0 | 0.50 | 400 | 4.356 | 0.458 | 50.8 | |
| 0.20 | 0.19 | 5.0 | 0.50 | 500 | 4.285 | 0.543 | 53.9 | |
| 0.10 | 0.09 | 5.0 | 0.50 | 300 | 4.251 | 0.509 | 60.1 | |
| 0.10 | 0.09 | 5.0 | 0.50 | 400 | 4.150 | 0.573 | 63.5 | |
| 0.10 | 0.09 | 5.0 | 0.50 | 500 | 4.031 | 0.500 | 60.4 | |
| 0.05 | 0.04 | 5.0 | 0.50 | 400 | 3.909 | 0.525 | 73.2 | |
| 0.05 | 0.04 | 5.0 | 0.50 | 500 | 3.831 | 0.439 | 76.5 | |
| 0.10 | 0.10 | 5.0 | 0.25 | 300 | 4.562 | 0.435 | 115.9 | |
| 0.10 | 0.10 | 5.0 | 0.25 | 400 | 4.458 | 0.491 | 121.6 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.10 | 0.10 | 5.0 | 0.25 | 500 | 4.362 | 0.472 | 121.9 | |
| 0.05 | 0.05 | 5.0 | 0.25 | 400 | 4.234 | 0.451 | 145.7 | |
| 0.05 | 0.05 | 5.0 | 0.25 | 500 | 4.120 | 0.495 | 140.1 | |

**Table S10.** **$k_p$ values for MA at 40-60 °C determined from PLP experiments conducted in EtOH and EtOH/$H_2O$ mixtures using DMPA as initiator unless otherwise stated ([a]D1173) initiator). $w_{MA}$ and $v_{MA}$ are weight and volume fraction of monomer in solution, respectively, and $\alpha_{EtOH}$ is the weight fraction of EtOH (balance $H_2O$) in the solvent.**

| $T$ (°C) | $w_{MA}$ | $v_{MA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $\alpha_{EtOH}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 0.55 | 0.50 | 5.0 | 1.00 | 300 | 4.545 | 0.491 | 22.6 | |
| 40 | 0.55 | 0.50 | 5.0 | 1.00 | 300 | 4.535 | 0.493 | 22.1 | |
| 40 | 0.55 | 0.50 | 5.0 | 1.00 | 400 | 4.440 | 0.520 | 23.7 | |
| 40 | 0.55 | 0.50 | 5.0 | 1.00 | 400 | 4.430 | 0.522 | 23.1 | |
| 40 | 0.55 | 0.50 | 5.0 | 1.00 | 500 | 4.350 | 0.525 | 24.0 | |
| 40 | 0.10 | 0.08 | 5.0 | 1.00 | 400 | 3.829 | 0.440 | 34.0 | a |
| 40 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.768 | 0.484 | 37.0 | a |
| 40 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.750 | 0.513 | 35.5 | a |
| 50 | 0.55 | 0.50 | 5.0 | 1.00 | 300 | 4.563 | 0.422 | 23.8 | |
| 50 | 0.55 | 0.50 | 5.0 | 1.00 | 400 | 4.467 | 0.513 | 25.5 | |
| 50 | 0.55 | 0.50 | 5.0 | 1.00 | 500 | 4.401 | 0.532 | 27.4 | |
| 50 | 0.10 | 0.08 | 5.0 | 1.00 | 400 | 3.888 | 0.463 | 39.4 | a |
| 50 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.797 | 0.428 | 40.0 | a |
| 50 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.786 | 0.428 | 39.0 | a |
| 60 | 0.55 | 0.50 | 5.0 | 1.00 | 500 | 4.427 | 0.505 | 29.4 | |
| 60 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.805 | 0.450 | 41.2 | a |
| 60 | 0.10 | 0.08 | 5.0 | 1.00 | 500 | 3.808 | 0.442 | 41.4 | a |
| 40 | 0.10 | 0.09 | 5.0 | 0.75 | 400 | 3.975 | 0.562 | 45.0 | a |
| 40 | 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.893 | 0.489 | 46.6 | a |
| 40 | 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.890 | 0.433 | 46.4 | a |
| 50 | 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.918 | 0.442 | 49.8 | a |
| 50 | 0.10 | 0.09 | 5.0 | 0.75 | 400 | 4.000 | 0.420 | 48.2 | a |
| 60 | 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.929 | 0.450 | 51.6 | a |
| 60 | 0.10 | 0.09 | 5.0 | 0.75 | 500 | 3.915 | 0.530 | 50.0 | a |
| 40 | 0.53 | 0.50 | 5.0 | 0.70 | 300 | 4.630 | 0.468 | 27.4 | |
| 40 | 0.53 | 0.50 | 5.0 | 0.70 | 400 | 4.531 | 0.498 | 29.1 | |
| 40 | 0.53 | 0.50 | 5.0 | 0.70 | 500 | 4.437 | 0.526 | 29.3 | |
| 40 | 0.10 | 0.09 | 5.0 | 0.50 | 400 | 4.172 | 0.494 | 67.5 | a |
| 40 | 0.10 | 0.09 | 5.0 | 0.50 | 500 | 4.078 | 0.506 | 67.9 | a |
| 50 | 0.10 | 0.09 | 5.0 | 0.50 | 400 | 4.222 | 0.526 | 76.4 | a |
| 50 | 0.10 | 0.09 | 5.0 | 0.50 | 500 | 4.137 | 0.535 | 78.5 | a |
| 60 | 0.10 | 0.09 | 5.0 | 0.50 | 400 | 4.246 | 0.443 | 81.4 | a |
| 60 | 0.10 | 0.09 | 5.0 | 0.50 | 500 | 4.16 | 0.564 | 83.5 | a |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 0.10 | 0.10 | 5.0 | 0.25 | 400 | 4.461 | 0.478 | 123.1 | [a] |
| 40 | 0.10 | 0.10 | 5.0 | 0.25 | 500 | 4.374 | 0.446 | 126.0 | [a] |
| 50 | 0.10 | 0.10 | 5.0 | 0.25 | 500 | 4.504 | 0.540 | 136.8 | [a] |
| 50 | 0.10 | 0.10 | 5.0 | 0.25 | 400 | 4.390 | 0.512 | 131.5 | [a] |

**Table S11. $k_p$ values for MA at various temperatures determined from PLP experiments conducted in MeOH and MeOH/$H_2O$ mixtures. Experiments used DMPA as initiator. $w_{MA}$ and $v_{MA}$ are weight and volume fraction of monomer in solution, respectively, and $\alpha_{MeOH}$ is the weight fraction of MeOH (balance $H_2O$) in the solvent.**

| $T$ (°C) | $w_{MA}$ | $v_{MA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $\alpha_{MeOH}$ | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 3 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.274 | 0.54 | 10.7 |
| 3 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.272 | 0.54 | 10.7 |
| 3 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 3.946 | 0.47 | 10.1 |
| 3 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 3.945 | 0.47 | 10.0 |
| 3 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.344 | 0.55 | 12.4 |
| 3 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.341 | 0.55 | 12.3 |
| 3 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.069 | 0.51 | 13.2 |
| 3 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.068 | 0.51 | 13.1 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.360 | 0.55 | 13.3 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.347 | 0.55 | 12.9 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.347 | 0.55 | 12.9 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.360 | 0.55 | 13.3 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.081 | 0.49 | 13.9 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.076 | 0.49 | 13.8 |
| 15 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.096 | 0.49 | 14.4 |
| 15 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.442 | 0.55 | 15.8 |
| 15 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.442 | 0.55 | 15.8 |
| 15 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.194 | 0.53 | 17.8 |
| 15 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.191 | 0.53 | 17.7 |
| 25 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.474 | 0.54 | 17.5 |
| 25 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.463 | 0.54 | 17.0 |
| 25 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.181 | 0.53 | 17.7 |
| 25 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.183 | 0.53 | 17.8 |
| 25 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.558 | 0.55 | 20.8 |
| 25 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.553 | 0.55 | 20.6 |
| 25 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.292 | 0.55 | 22.5 |
| 25 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.302 | 0.54 | 23.0 |
| 40 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.564 | 0.55 | 22.0 |
| 40 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.565 | 0.56 | 22.0 |
| 40 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.263 | 0.55 | 21.9 |
| 40 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.261 | 0.55 | 21.8 |
| 40 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.658 | 0.55 | 26.8 |
| 40 | 0.50 | 0.46 | 5.0 | 0.80 | 250 | 4.658 | 0.55 | 26.8 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 40 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.410 | 0.56 | 30.2 |
| 40 | 0.50 | 0.46 | 5.0 | 0.80 | 500 | 4.412 | 0.56 | 30.3 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.631 | 0.53 | 25.9 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.627 | 0.55 | 25.6 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.629 | 0.57 | 25.8 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.631 | 0.56 | 25.9 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.621 | 0.54 | 25.4 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.624 | 0.52 | 25.6 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.404 | 0.58 | 30.6 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.403 | 0.58 | 30.5 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.415 | 0.58 | 31.4 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.417 | 0.58 | 31.6 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.418 | 0.58 | 31.7 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.414 | 0.57 | 31.4 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.398 | 0.57 | 30.2 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.406 | 0.57 | 30.8 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.409 | 0.58 | 31.2 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.409 | 0.58 | 31.2 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.565 | – | 22.3 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 250 | 4.567 | 0.51 | 22.4 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.346 | 0.57 | 26.9 |
| 50 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.344 | 0.57 | 26.8 |
| 50 | 0.50 | 0.46 | 5.0 | 0.75 | 250 | 4.700 | 0.56 | 29.9 |
| 50 | 0.50 | 0.46 | 5.0 | 0.75 | 250 | 4.699 | 0.56 | 29.9 |
| 50 | 0.50 | 0.46 | 5.0 | 0.75 | 500 | 4.475 | 0.58 | 35.6 |
| 50 | 0.50 | 0.46 | 5.0 | 0.75 | 500 | 4.470 | 0.58 | 35.1 |
| 60 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.386 | 0.61 | 29.9 |
| 60 | 0.50 | 0.45 | 5.0 | 1.00 | 500 | 4.389 | 0.60 | 30.1 |
| 60 | 0.50 | 0.46 | 5.0 | 0.75 | 500 | 4.527 | 0.63 | 40.6 |
| 60 | 0.50 | 0.46 | 5.0 | 0.75 | 500 | 4.524 | 0.62 | 40.3 |

**Table S12. $k_p$ values for MA at various temperatures determined from PLP experiments conducted in $H_2O$ using D1173 as initiator. $w_{MA}$ and $v_{MA}$ are weight and volume fraction of monomer in solution.**

| $T$ (°C) | $w_{MA}$ | $v_{MA}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $f$ (Hz) | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 30 | 0.05 | 0.05 | 5.0 | 300 | 4.532 | 0.501 | 214.9 |
| 30 | 0.05 | 0.05 | 5.0 | 400 | 4.406 | 0.495 | 214.4 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.315 | 0.497 | 217.5 |
| 30 | 0.05 | 0.05 | 5.0 | 150 | 4.816 | 0.419 | 212.6 |
| 30 | 0.05 | 0.05 | 5.0 | 200 | 4.726 | 0.410 | 230.4 |
| 30 | 0.05 | 0.05 | 5.0 | 300 | 4.573 | 0.511 | 243.0 |
| 30 | 0.05 | 0.05 | 5.0 | 400 | 4.442 | 0.489 | 239.6 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.365 | 0.508 | 250.9 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.364 | 0.504 | 237.9 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.371 | 0.506 | 241.7 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.385 | 0.490 | 249.9 |
| 30 | 0.05 | 0.05 | 5.0 | 500 | 4.383 | 0.495 | 248.8 |
| 30 | 0.04 | 0.04 | 5.0 | 500 | 4.263 | 0.491 | 236.8 |
| 30 | 0.04 | 0.04 | 5.0 | 500 | 4.273 | 0.490 | 242.3 |
| 30 | 0.04 | 0.04 | 5.0 | 500 | 4.259 | 0.494 | 232.9 |
| 30 | 0.04 | 0.04 | 5.0 | 500 | 4.259 | 0.498 | 232.9 |
| 30 | 0.03 | 0.03 | 5.0 | 500 | 4.140 | 0.472 | 240.6 |
| 30 | 0.03 | 0.03 | 5.0 | 500 | 4.136 | 0.472 | 238.4 |
| 30 | 0.03 | 0.03 | 5.0 | 500 | 4.141 | 0.476 | 242.1 |
| 30 | 0.03 | 0.03 | 5.0 | 500 | 4.143 | 0.476 | 243.3 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.932 | 0.457 | 236.5 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.932 | 0.458 | 236.5 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.952 | 0.456 | 232.9 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.956 | 0.460 | 235.1 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.989 | 0.457 | 243.9 |
| 30 | 0.02 | 0.02 | 5.0 | 500 | 3.989 | 0.448 | 243.9 |
| 40 | 0.05 | 0.05 | 5.0 | 300 | 4.570 | 0.462 | 235.6 |
| 40 | 0.05 | 0.05 | 5.0 | 400 | 4.471 | 0.500 | 250.1 |
| 40 | 0.05 | 0.05 | 5.0 | 500 | 4.384 | 0.521 | 255.8 |
| 50 | 0.05 | 0.05 | 5.0 | 300 | 4.588 | 0.411 | 246.8 |
| 50 | 0.05 | 0.05 | 5.0 | 400 | 4.491 | 0.473 | 263.2 |
| 50 | 0.05 | 0.05 | 5.0 | 500 | 4.384 | 0.479 | 257.2 |

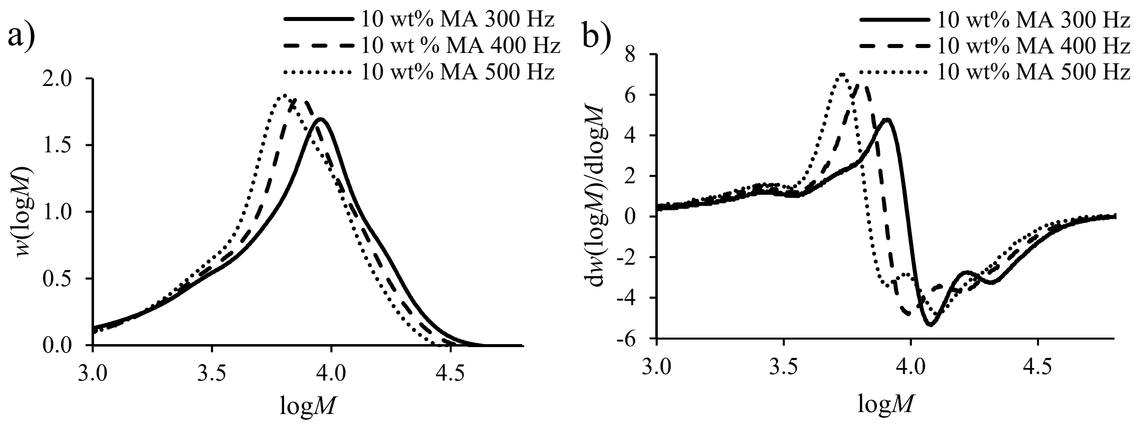


**Figure S7. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for 10 wt % MA in EtOH at 30 °C at 300 Hz, 200 Hz and 400 Hz with 5 mmol·L$^{-1}$ D1173.**

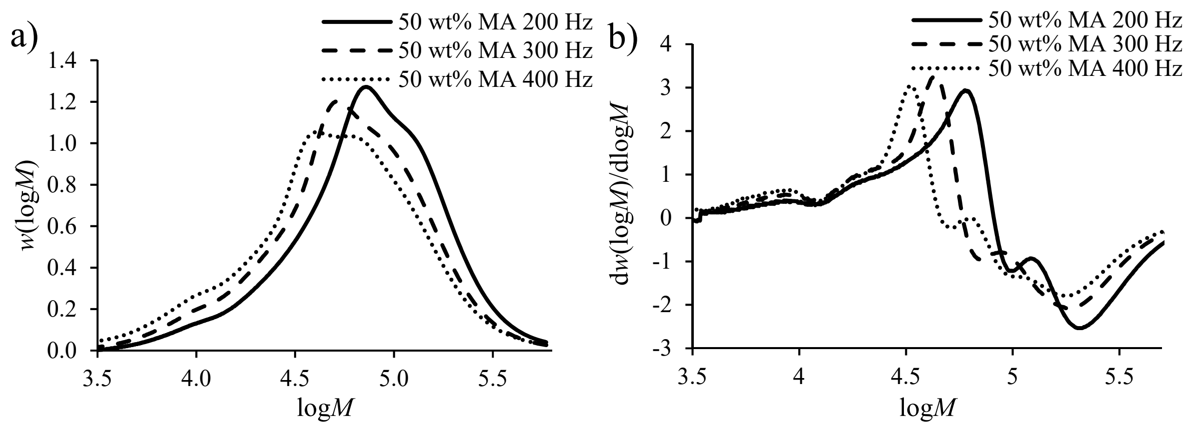


**Figure S8. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for 50 wt % MA, $\alpha_{EtOH}$ = 0.75 at 30 °C at 200 Hz, 300 Hz, 400 Hz and 500 Hz with 5 mmol·L$^{-1}$ D1173.**

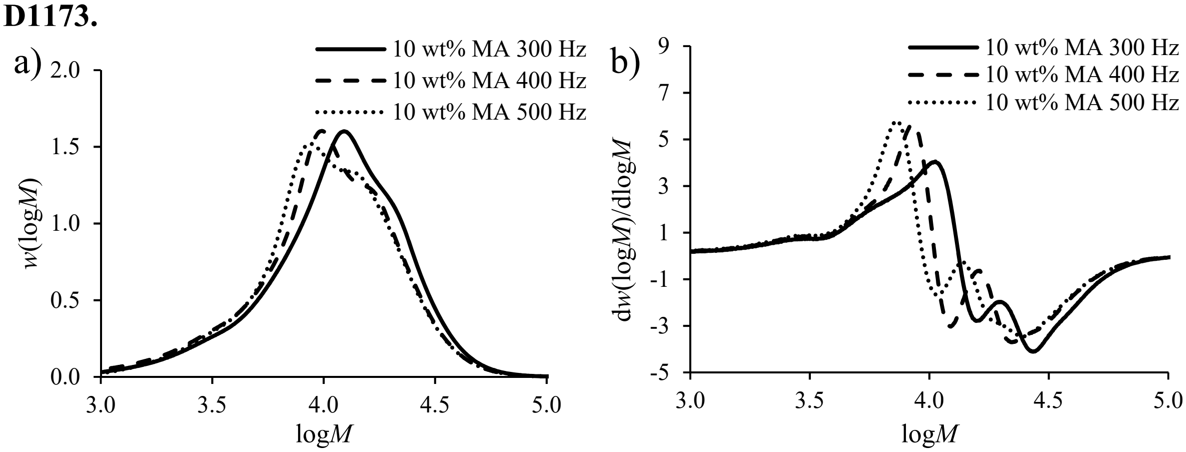


**Figure S9. (a) *w*(log*M*) molar mass distribution and (b) differential *w*(log*M*) distribution for 10 wt % MA, $\alpha_{EtOH}$ = 0.75) at 30 °C at 300 Hz, 400 Hz and 500 Hz with 5 mmol·L$^{-1}$ D1173.**

**Table S13. Arrhenius parameters determined from fitting of MA $k_p$ results.**

| | $A \cdot 10^{-7}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | $E_A$ ($kJ \cdot mol^{-1}$) | $k_p \cdot 10^{-3}$ (30 °C) ($L \cdot mol^{-1} \cdot s^{-1}$) | % increase from bulk $k_p$ |
|---|---|---|---|---|
| bulk (IUPAC)[1] | 1.41 | 17.3 | 14.7 | |
| $w_{MA}$=0.55, $\alpha_{EtOH}$=1.00 and $w_{MA}$=0.50, $\alpha_{MeOH}$=1.00 (combined fit) | 0.24±0.27 | 12.1±3.1 | 19.3 | 30 |
| $w_{MA}$=0.53, $\alpha_{EtOH}$=0.75 and $w_{MA}$=0.50, $\alpha_{MeOH}$=0.80 (combined fit) | 0.60±1.07 | 13.9±4.7 | 24.1 | 60 |

**Table S14. Best-fit values of *C*, with 95% confidence intervals, at 30 °C from functional representation of $k_p^{MEA}\left(\frac{L}{mol \cdot s}\right) = k_{p,\,bulk}^{MEA}[A+(1-A)\cdot \exp(-C \cdot w_{sol})]$, with $A$ = 0. Note: $\alpha_x$ is the weight fraction of alcohol in the solvent where *x* being the solvent identity.**

| Solvent | $\alpha_x$ | $C$ |
|---|---|---|
| MeOH | 1.00 | −0.292±0.104 |
| MeOH/$H_2O$ | 0.70 | −0.696±0.209 |
| MeOH/$H_2O$ | 0.44 | −1.348±0.113 |
| MeOH/$H_2O$ | 0.20 | −1.730±0.244 |
| EtOH | 1.00 | −0.435±0.173 |
| EtOH/$H_2O$ | 0.70 | −0.647±0.091 |
| BuOH | 1.00 | −0.642±0.130 |

**Table S15. Best-fit values of *C*, with 95% confidence intervals, from functional representation of $k_p^{MA}\left(\frac{L}{mol \cdot s}\right) = k_{p,\,bulk}^{MA}[A+(1-A)\cdot \exp(-C \cdot w_{sol})]$, with $A$ = 0 at different temperatures.**

| Solvent | $\alpha_{EtOH}$ | $C$ (30 °C) | $C$ (40 °C) | $C$ (50 °C) | $C$ (60 °C) |
|---|---|---|---|---|---|
| EtOH | 1.00 | −0.863±0.084 | −0.714±0.267 | −0.593±0.325 | −0.426±0.332 |
| EtOH/$H_2O$ | 0.75 | −1.205±0.150 | −1.033 | −0.876 | −0.700 |
| EtOH/$H_2O$ | 0.70 | – | −0.947 | −0.830 | – |
| EtOH/$H_2O$ | 0.50 | −1.656±0.086 | −1.462 | −1.383 | −1.238 |
| EtOH/$H_2O$ | 0.25 | −2.378±0.094 | −2.140 | −1.994 | – |
| $H_2O$ | 0.00 | −2.890±0.037 | −2.741±0.007 | −2.568 | – |

**Table S16. Best-fit values of *A* and *C*, with 95% confidence intervals, from functional representation of $k_p^{AA}\left(\frac{\mathrm{L}}{\mathrm{mol{\cdot}s}}\right)=k_{p,\,bulk}^{AA}[A+(1-A)\cdot\exp(-C{\cdot}w_{sol})]$, at 25 °C, with $C=-2.5$.**

| Solvent | $\alpha_x$ | *A* |
|---|---|---|
| EtOH | 1.00 | 1.077±0.017 |
| EtOH/$H_2O$ | 0.44 | 0.947±0.017 |
| EtOH/$H_2O$ | 0.00 | 0.627±0.058 |

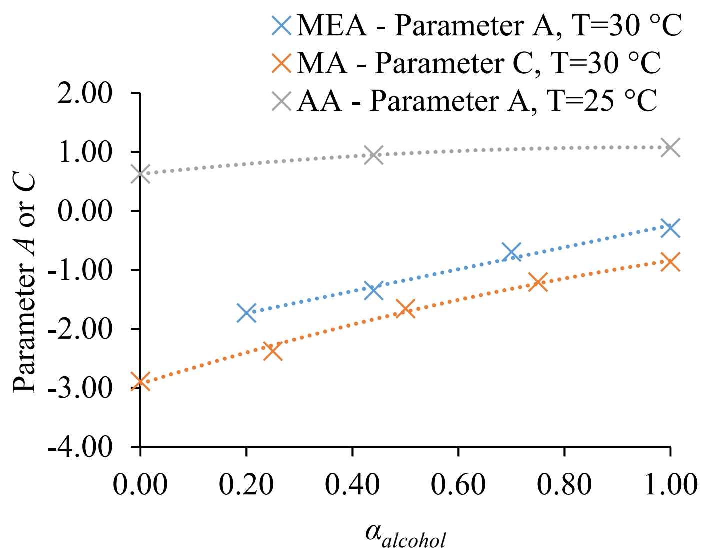


**Figure S10. Parameter *A* and *C* from fitting of $k_p$ expression to PLP data as a function of $\alpha_{alcohol}$ (balance $H_2O$) for MA (EtOH), MEA (MeOH) and AA (EtOH). Note: $A=0$ for MEA and MA, and $C=-2.5$ for AA.**

**Table S17.** $k_p$ **values for AA determined from PLP experiments conducted in EtOH/$H_2O$ solutions. Experiments used DMPA as initiator unless otherwise indicated ([a]LiTPO initiator). Experiments were conducted at 25 °C unless otherwise indicated ([b]20 °C).** $N_p$ **is the number of pulses performed on the sample,** $w_{AA}$ **is weight fraction of monomer in solution and** $\alpha_{EtOH}$ **is the weight fraction of EtOH (balance $H_2O$) in the solvent. Note: the fit in Figure 8 at** $\alpha_{EtOH} = 0$**, uses a combination of previously published data (**$w_{AA}$ **= 0.20, 0.40 at 25 °C)[10] and data determined in this current work,** $w_{AA}$ **= 0.05, 0.10 at 25 °C, and** $w_{AA}$ **= 0.76 at 20 °C adjusted to 25 °C assuming AA** $E_A$ **at** $w_{AA}$ **= 0.40 (12.2 kJ·mol⁻¹).[10]**

| $w_{AA}$ | Solvent | $\alpha_{EtOH}$ | $C_{Initiator}$ (mmol·L$^{-1}$) | $f$ (Hz) | $N_p$ | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|---|---|
| 0.84 | EtOH | 1.00 | 5.0 | 250 | 25 | 5.104 | - | 29.4 | |
| | | | 5.0 | 250 | 25 | 5.099 | - | 29.0 | |
| | | | 5.0 | 250 | 50 | 5.113 | - | 30.1 | |
| | | | 5.0 | 250 | 50 | 5.110 | - | 29.9 | |
| | | | 5.0 | 500 | 50 | 4.810 | 0.53 | 29.9 | |
| | | | 5.0 | 500 | 50 | 4.812 | 0.53 | 30.1 | |
| | | | 5.0 | 500 | 100 | 4.839 | 0.53 | 32.0 | |
| | | | 5.0 | 500 | 100 | 4.833 | 0.53 | 31.6 | |
| 0.65 | EtOH | 1.00 | 5.0 | 250 | 100 | 4.957 | 0.59 | 28.6 | |
| | | | 5.0 | 250 | 100 | 4.960 | 0.60 | 28.8 | |
| | | | 5.0 | 250 | 200 | 4.988 | 0.67 | 31.1 | |
| | | | 5.0 | 250 | 200 | 4.988 | - | 31.1 | |
| | | | 5.0 | 500 | 200 | 4.685 | 0.52 | 30.9 | |
| | | | 5.0 | 500 | 200 | 4.685 | 0.53 | 30.9 | |
| | | | 5.0 | 500 | 300 | 4.730 | 0.55 | 34.6 | |
| | | | 5.0 | 500 | 300 | 4.722 | 0.54 | 33.9 | |
| 0.45 | EtOH | 1.00 | 5.0 | 250 | 100 | 4.681 | 0.54 | 23.1 | |
| | | | 5.0 | 250 | 100 | 4.680 | 0.54 | 23.1 | |
| | | | 5.0 | 250 | 200 | 4.684 | 0.54 | 23.3 | |
| | | | 5.0 | 250 | 200 | 4.689 | 0.55 | 23.6 | |
| | | | 5.0 | 500 | 100 | 4.318 | 0.45 | 20.0 | |
| | | | 5.0 | 500 | 100 | 4.323 | 0.45 | 20.2 | |
| | | | 5.0 | 500 | 200 | 4.344 | 0.46 | 21.4 | |
| | | | 5.0 | 500 | 200 | 4.345 | 0.46 | 21.5 | |
| 0.20 | EtOH | 1.00 | 5.0 | 250 | 150 | 4.068 | 0.45 | 13.9 | |
| | | | 5.0 | 250 | 150 | 4.064 | 0.44 | 13.7 | |
| | | | 5.0 | 250 | 300 | 4.065 | 0.45 | 13.9 | |
| | | | 5.0 | 250 | 300 | 4.066 | 0.45 | 13.9 | |
| | | | 5.0 | 500 | 150 | 3.700 | 0.41 | 11.9 | |
| | | | 5.0 | 500 | 150 | 3.703 | 0.41 | 12.0 | |
| | | | 5.0 | 500 | 300 | 3.711 | 0.42 | 12.3 | |
| | | | 5.0 | 500 | 300 | 3.706 | 0.42 | 12.1 | |
| 0.06 | EtOH | 1.00 | 5.0 | 200 | 300 | 3.483 | 0.41 | 9.5 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 5.0 | 200 | 300 | 3.482 | 0.42 | 9.5 | |
| | | | 5.0 | 200 | 600 | 3.472 | - | 9.3 | |
| | | | 5.0 | 200 | 600 | 3.471 | - | 9.3 | |
| | | | 5.0 | 400 | 300 | 3.308 | - | 12.6 | |
| | | | 5.0 | 400 | 300 | 3.318 | - | 12.9 | |
| | | | 5.0 | 400 | 600 | 3.346 | - | 13.9 | |
| | | | 5.0 | 400 | 600 | 3.347 | - | 13.9 | |
| 0.79 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 25 | 5.136 | - | 34.4 | |
| | | | 5.0 | 250 | 25 | 5.137 | - | 34.4 | |
| | | | 5.0 | 250 | 50 | 5.144 | - | 35.1 | |
| | | | 5.0 | 250 | 50 | 5.147 | - | 35.4 | |
| | | | 5.0 | 500 | 50 | 4.849 | 0.52 | 35.5 | |
| | | | 5.0 | 500 | 50 | 4.838 | 0.51 | 34.6 | |
| | | | 5.0 | 500 | 100 | 4.875 | 0.52 | 37.9 | |
| | | | 5.0 | 500 | 100 | 4.890 | 0.53 | 39.3 | |
| 0.59 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 50 | 5.056 | 0.62 | 39.5 | |
| | | | 5.0 | 250 | 50 | 5.057 | 0.63 | 39.6 | |
| | | | 5.0 | 250 | 100 | 5.076 | - | 41.7 | |
| | | | 5.0 | 250 | 100 | 5.074 | - | 41.5 | |
| | | | 5.0 | 500 | 50 | 4.749 | 0.51 | 38.9 | |
| | | | 5.0 | 500 | 50 | 4.749 | 0.50 | 38.9 | |
| | | | 5.0 | 500 | 100 | 4.760 | 0.50 | 40.0 | |
| | | | 5.0 | 500 | 100 | 4.763 | 0.51 | 40.3 | |
| 0.40 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 50 | 4.915 | 0.56 | 44.1 | |
| | | | 5.0 | 250 | 50 | 4.913 | 0.56 | 43.9 | |
| | | | 5.0 | 250 | 100 | 4.926 | 0.57 | 45.5 | |
| | | | 5.0 | 250 | 100 | 4.926 | 0.56 | 45.5 | |
| | | | 5.0 | 500 | 50 | 4.600 | 0.50 | 42.6 | |
| | | | 5.0 | 500 | 50 | 4.598 | 0.49 | 42.4 | |
| | | | 5.0 | 500 | 100 | 4.612 | 0.49 | 44.1 | |
| | | | 5.0 | 500 | 100 | 4.613 | 0.50 | 44.2 | |
| 0.20 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 150 | 4.636 | 0.53 | 47.5 | |
| | | | 5.0 | 250 | 150 | 4.644 | 0.54 | 48.4 | |
| | | | 5.0 | 250 | 200 | 4.658 | 0.54 | 50.3 | |
| | | | 5.0 | 250 | 200 | 4.652 | 0.53 | 49.6 | |
| | | | 5.0 | 500 | 150 | 4.298 | 0.45 | 43.7 | |
| | | | 5.0 | 500 | 150 | 4.298 | 0.46 | 43.7 | |
| | | | 5.0 | 500 | 200 | 4.298 | 0.46 | 43.8 | |
| | | | 5.0 | 500 | 200 | 4.299 | 0.45 | 43.9 | |
| 0.11 | EtOH/ $H_2O$ | 0.44 | 3.0 | 250 | 150 | 4.425 | 0.50 | 54.0 | [a] |
| | | | 3.0 | 250 | 150 | 4.425 | 0.51 | 54.0 | [a] |
| | | | 3.0 | 250 | 300 | 4.432 | 0.51 | 56.2 | [a] |
| | | | 3.0 | 250 | 300 | 4.431 | 0.50 | 56.1 | [a] |
| | | | 3.0 | 500 | 150 | 4.081 | 0.44 | 48.8 | [a] |
| | | | 3.0 | 500 | 150 | 4.075 | 0.43 | 48.1 | [a] |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 3.0 | 500 | 300 | 4.078 | 0.43 | 49.4 | a |
| | | | 3.0 | 500 | 300 | 4.079 | 0.44 | 49.5 | a |
| 0.10 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 150 | 4.334 | 0.50 | 46.6 | |
| | | | 5.0 | 250 | 150 | 4.340 | 0.49 | 47.3 | |
| | | | 5.0 | 250 | 300 | 4.316 | 0.49 | 45.6 | |
| | | | 5.0 | 250 | 300 | 4.321 | 0.49 | 46.1 | |
| | | | 5.0 | 500 | 150 | 3.971 | 0.44 | 40.2 | |
| | | | 5.0 | 500 | 150 | 3.967 | 0.42 | 39.8 | |
| | | | 5.0 | 500 | 300 | 3.974 | 0.44 | 41.0 | |
| | | | 5.0 | 500 | 300 | 3.970 | 0.44 | 40.6 | |
| 0.06 | EtOH/ $H_2O$ | 0.44 | 3.0 | 250 | 150 | 4.126 | 0.49 | 53.2 | a |
| | | | 3.0 | 250 | 150 | 4.106 | 0.47 | 50.8 | a |
| | | | 3.0 | 250 | 300 | 4.083 | 0.47 | 49.2 | a |
| | | | 3.0 | 250 | 300 | 4.082 | 0.47 | 49.1 | a |
| | | | 3.0 | 500 | 150 | 3.762 | 0.46 | 45.9 | a |
| | | | 3.0 | 500 | 150 | 3.751 | 0.45 | 44.7 | a |
| | | | 3.0 | 500 | 300 | 3.734 | 0.45 | 43.8 | a |
| | | | 3.0 | 500 | 300 | 3.732 | 0.44 | 43.6 | a |
| 0.05 | EtOH/ $H_2O$ | 0.44 | 5.0 | 250 | 150 | 3.975 | 0.43 | 41.4 | |
| | | | 5.0 | 250 | 150 | 3.980 | 0.44 | 41.9 | |
| | | | 5.0 | 250 | 300 | 3.954 | 0.44 | 39.8 | |
| | | | 5.0 | 250 | 300 | 3.956 | 0.44 | 40.0 | |
| | | | 5.0 | 500 | 150 | 3.623 | 0.42 | 36.9 | |
| | | | 5.0 | 500 | 150 | 3.629 | 0.43 | 37.4 | |
| | | | 5.0 | 500 | 300 | 3.606 | 0.42 | 35.6 | |
| | | | 5.0 | 500 | 300 | 3.625 | 0.44 | 37.2 | |
| 0.76 | $H_2O$ | 0.00 | 2.0 | 250 | 25 | 5.216 | 0.62 | 40.0 | b |
| | | | 2.0 | 250 | 25 | 5.213 | 0.64 | 39.7 | b |
| | | | 2.0 | 250 | 50 | 5.218 | 0.61 | 40.2 | b |
| | | | 2.0 | 250 | 50 | 5.218 | 0.62 | 40.2 | b |
| | | | 2.0 | 500 | 25 | 4.899 | 0.43 | 38.6 | b |
| | | | 2.0 | 500 | 25 | 4.909 | 0.46 | 39.5 | b |
| | | | 5.0 | 250 | 25 | 5.217 | 0.62 | 40.2 | b |
| | | | 5.0 | 250 | 25 | 5.215 | 0.62 | 40.0 | b |
| | | | 5.0 | 250 | 25 | 5.219 | 0.62 | 40.4 | b |
| | | | 5.0 | 250 | 25 | 5.217 | 0.62 | 40.2 | b |
| | | | 5.0 | 250 | 50 | 5.244 | 0.65 | 43.0 | b |
| | | | 5.0 | 250 | 50 | 5.243 | 0.65 | 42.9 | b |
| | | | 5.0 | 250 | 50 | 5.217 | 0.63 | 40.2 | b |
| | | | 5.0 | 250 | 50 | 5.219 | 0.63 | 40.3 | b |
| | | | 5.0 | 500 | 25 | 4.884 | 0.46 | 37.4 | b |
| | | | 5.0 | 500 | 25 | 4.891 | 0.46 | 38.0 | b |
| | | | 5.0 | 500 | 25 | 4.887 | 0.46 | 37.6 | b |
| | | | 5.0 | 500 | 25 | 4.890 | 0.46 | 37.9 | b |
| | | | 5.0 | 500 | 50 | 4.896 | 0.46 | 38.4 | b |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 5.0 | 500 | 50 | 4.896 | 0.47 | 38.4 | b |
| | | | 5.0 | 500 | 50 | 4.904 | 0.46 | 39.2 | b |
| | | | 5.0 | 500 | 50 | 4.909 | 0.46 | 39.6 | b |
| | | | 5.0 | 500 | 100 | 4.940 | 0.46 | 42.9 | b |
| | | | 5.0 | 500 | 100 | 4.943 | 0.47 | 43.2 | b |
| | | | 5.0 | 500 | 200 | 5.034 | 0.53 | 53.8 | b |
| 0.10 | $H_2O$ | 0.00 | 3.0 | 250 | 50 | 4.806 | 0.61 | 125.8 | a |
| | | | 3.0 | 250 | 50 | 4.807 | 0.60 | 126.1 | a |
| | | | 3.0 | 250 | 150 | 4.812 | 0.60 | 131.5 | a |
| | | | 3.0 | 250 | 150 | 4.809 | 0.60 | 130.6 | a |
| | | | 3.0 | 500 | 50 | 4.484 | 0.53 | 119.7 | a |
| | | | 3.0 | 500 | 50 | 4.483 | 0.52 | 119.4 | a |
| | | | 3.0 | 500 | 150 | 4.488 | 0.54 | 123.5 | a |
| | | | 3.0 | 500 | 150 | 4.491 | 0.55 | 124.4 | a |
| 0.05 | $H_2O$ | 0.00 | 3.0 | 250 | 50 | 4.610 | 0.59 | 176.3 | a |
| | | | 3.0 | 250 | 50 | 4.611 | 0.50 | 176.6 | a |
| | | | 3.0 | 250 | 150 | 4.606 | 0.53 | 179.8 | a |
| | | | 3.0 | 250 | 150 | 4.597 | 0.52 | 176.2 | a |
| | | | 3.0 | 500 | 50 | 4.246 | 0.56 | 152.0 | a |
| | | | 3.0 | 500 | 50 | 4.251 | 0.56 | 153.8 | a |
| | | | 3.0 | 500 | 150 | 4.251 | 0.57 | 158.1 | a |
| | | | 3.0 | 500 | 150 | 4.249 | 0.58 | 157.3 | a |

**Table S18. $k_p$ values for AA determined from PLP experiments at $w_{AA}$ = 0.20 in DMF. Experiments used DMPA as initiator and were conducted at 25 °C. $N_p$ is the number of pulses performed on the sample and $C_{initiator}$ = 10 mmol·L$^{-1}$.**

| $f$ (Hz) | $N_p$ | log$M_1$ RI | $M_1/M_2$ | RI $k_{p1}\cdot10^{-3}$ (L·mol$^{-1}$·s$^{-1}$) |
|---|---|---|---|---|
| 250 | 300 | 4.096 | 0.42 | 12.5 |
| 250 | 300 | 4.099 | 0.42 | 12.6 |
| 250 | 300 | 4.103 | 0.42 | 12.7 |
| 250 | 600 | 4.104 | 0.47 | 12.8 |
| 250 | 600 | 4.104 | 0.43 | 12.9 |
| 250 | 600 | 4.103 | 0.42 | 12.8 |
| 500 | 300 | 3.733 | 0.41 | 10.9 |
| 500 | 300 | 3.736 | 0.40 | 10.9 |
| 500 | 300 | 3.735 | 0.40 | 10.9 |
| 500 | 600 | 3.745 | 0.41 | 11.2 |
| 500 | 600 | 3.746 | 0.40 | 11.2 |
| 500 | 600 | 3.742 | 0.4 | 11.1 |

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