

Supporting Information to:

## Determination of the Propagation Rate Coefficient of Acrylonitrile

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### Experimental

#### *Materials*

Acrylonitrile (Acros,  $\geq 99\%$ ) was percolated over a column of basic alumina to remove the inhibitor. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%) and propylene carbonate (Aldrich,  $\geq 99\%$ ) were used as received.

#### *Pulsed Laser Polymerization*

Solutions of acrylonitrile in propylene carbonate solution ( $\sim 5 \text{ mol}\cdot\text{L}^{-1}$ ) containing variable concentrations of DMPA (ranging from 1 to  $20\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) were transferred into sample vials (containing about 0.3 mL of reaction solution each) and sealed with rubber septa. Oxygen was removed by purging the samples with nitrogen for about 2 min. The sample vial was subsequently placed into a stainless steel sample holder that was temperature controlled by a thermostat (VWR 1196D). The temperature was measured directly at the sample. The samples were allowed to

equilibrate in temperature for close to 3 minutes and were subsequently initiated by laser pulsing at constant repetition rates of up to 500 Hz. Laser initiation was achieved by a Xantos XS-500 operated at 351 nm. The laser beam, which was adjusted to an energy of close to 2.5 mJ/pulse hitting the sample, was redirected to illuminate the vial from the bottom. After polymerization, hydroquinone/methanol solution was added to the samples to prevent further reactions. Methanol and the carbonate were then removed in a vacuum oven at 60 °C to obtain the pure polymer. Typically, about 2-3 mg of polymer are recovered (corresponding to monomer conversions of approximately 1-2%) and the full sample is subjected to SEC analysis in concentrations of about 2 mg·mL<sup>-1</sup>.

#### *Molecular weight determination*

For the determination of molecular weight distributions (MWD) obtained from PLP, a Varian PL50 system, comprising an auto injector, a Polymer Laboratories 5.0 µm bead-size guard column, followed by three linear PL columns (PLgel 5 µm MIXED-C) and a differential refractive index detector using DMAc/0.03 % LiBr as the eluent at 50 °C with a flow rate of 1 mL·min<sup>-1</sup> was used. The SEC system was calibrated using narrow polystyrene standards ranging from 160 to 6·10<sup>6</sup> g mol<sup>-1</sup>. The resulting molecular weight distributions have been recalibrated employing literature Mark-Houwink parameters for polyacrylonitrile ( $K = 27.4 \cdot 10^{-5} \text{ dL} \cdot \text{g}^{-1}$  and  $a = 0.764$ )<sup>1</sup> and for polystyrene ( $K = 12.1 \cdot 10^{-5} \text{ dL} \cdot \text{g}^{-1}$  and  $a = 0.69$ ).<sup>2</sup>

**Table S1** Collated experimental results from PLP-SEC of AN under variation of initiator concentration and pulse frequency ( $n$  denotes the number of laser pulses applied and  $\nu$  is the pulse repetition rate)

| $T / ^\circ\text{C}$ | $n$  | $\nu$      | $c_M /$<br>$\text{mol}\cdot\text{L}^{-1}$ | $c_{\text{DMPA}} /$<br>$\text{mol}\cdot\text{L}^{-1}$ | $L_1$  | $L_2$ | $k_{p,1} /$<br>$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ | $k_{p,2} /$<br>$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ | $k_{p,1} /$<br>$k_{p,2}$ |
|----------------------|------|------------|---|---|--------|-------|---|---|--------------------------|
| 50.1                 | 1500 | 500        | 5.29                                      | <b>0.021</b>  | 59.62  | 122.2 | <b>5633</b>   | 5777  | 0.98                     |
| 50.0                 | 2000 | 500        | 5.29                                      | <b>0.021</b>  | 61.81  | 115.7 | <b>5840</b>   | 5470  | 1.07                     |
| 50.0                 | 2000 | 500        | 5.29                                      | <b>0.010</b>  | 60.96  | 115.7 | <b>5760</b>   | 5470  | 1.05                     |
| 50.0                 | 2000 | 500        | 5.29                                      | <b>0.010</b>  | 59.62  | 117.0 | <b>5633</b>   | 5530  | 1.02                     |
| 50.0                 | 2000 | 500        | 5.96                                      | <b>0.0053</b>   | 66.65  | 123.6 | <b>5593</b>   | 5187  | 1.08                     |
| 49.9                 | 2000 | 500        | 5.29                                      | <b>0.0053</b>   | 58.08  | 108.6 | <b>5488</b>   | 5134  | 1.07                     |
| 50.0                 | 2000 | 500        | 5.29                                      | <b>0.0021</b>   | 59.62  | 112.0 | <b>5633</b>   | 5293  | 1.06                     |
| 50.0                 | 3000 | 500        | 5.29                                      | <b>0.0021</b>   | 60.96  | 114.5 | <b>5760</b>   | 5410  | 1.06                     |
| 49.9                 | 2000 | <b>500</b> | 5.29                                      | 0.0053  | 58.08  | 108.6 | <b>5488</b>   | 5134  | 1.07                     |
| 50.0                 | 2000 | <b>400</b> | 5.96                                      | 0.0053  | 80.51  | 140.8 | <b>5404</b>   | 4729  | 1.14                     |
| 50.0                 | 2000 | <b>300</b> | 5.96                                      | 0.0053  | 108.42 | 186.7 | <b>5458</b>   | 4702  | 1.16                     |
| 50.0                 | 2000 | <b>200</b> | 5.96                                      | 0.0053  | 147.15 | 258.5 | <b>4939</b>   | 4339  | 1.14                     |
| 50.0                 | 2000 | <b>100</b> | 5.96                                      | 0.0053  | 250.24 | --    | <b>4200</b>   | --  | --                       |
| 50.0                 | 1000 | <b>100</b> | 5.96                                      | 0.0053  | 244.87 | 419.1 | <b>4109</b>   | 3517  | 1.17                     |

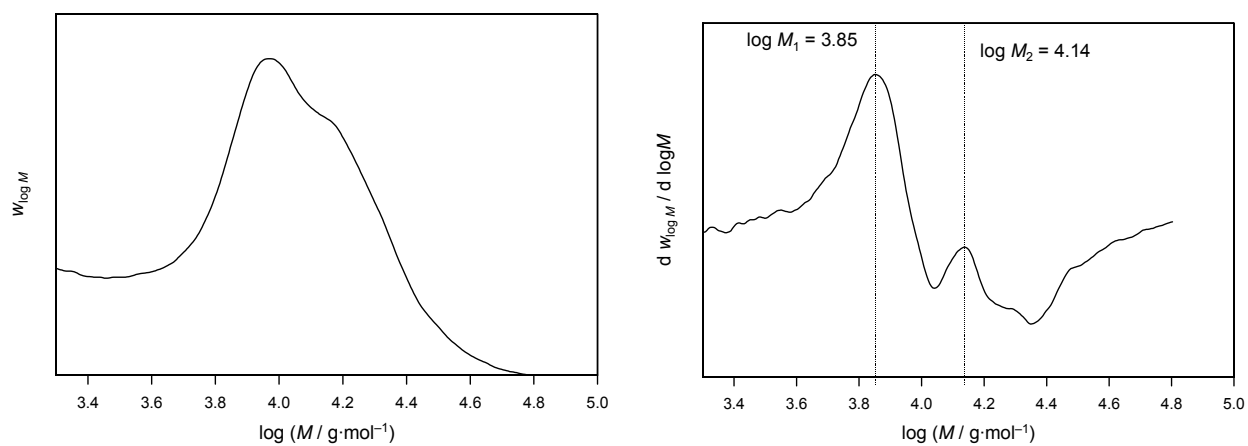
**Table S2** Collated experimental results from PLP-SEC of AN with  $c_{\text{monomer}} = 5.29 \text{ mol}\cdot\text{L}^{-1}$ ,  $c_{\text{DMPA}} = 5.3\cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  at a pulse repetition rate of 500 Hz ( $n$  denotes the number of laser pulses applied)

| $T / ^\circ\text{C}$ | $n$  | $L_1$ | $L_2$  | $k_{p,1} /$<br>$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ | $k_{p,2} /$<br>$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ | $k_{p,1} / k_{p,2}$ |
|----------------------|------|-------|--------|---|---|---------------------|
| <b>3.6</b>           | 3000 | 24.28 | --     | <b>2294</b>   | --  | --                  |
| <b>2.6</b>           | 5000 | 23.53 | --     | <b>2223</b>   | --  | --                  |
| <b>9.9</b>           | 5000 | 28.10 | --     | <b>2655</b>   | --  | --                  |
| <b>11</b>            | 4000 | 28.99 | --     | <b>2740</b>   | --  | --                  |
| <b>20.6</b>          | 4000 | 34.60 | --     | <b>3269</b>   | --  | --                  |
| <b>20.7</b>          | 4000 | 33.19 | --     | <b>3136</b>   | --  | --                  |
| <b>30</b>            | 4000 | 40.84 | 71.50  | <b>3859</b>   | 3378  | 1.14                |
| <b>30</b>            | 3000 | 41.27 | --     | <b>3899</b>   | --  | --                  |
| <b>40.1</b>          | 3000 | 47.70 | 83.59  | <b>4507</b>   | 3949  | 1.14                |
| <b>40.1</b>          | 2500 | 48.20 | 83.59  | <b>4554</b>   | 3949  | 1.15                |
| <b>49.9</b>          | 2000 | 58.08 | 108.68 | <b>5488</b>   | 5134  | 1.07                |
| <b>60.1</b>          | 2000 | 74.54 | 132.95 | <b>7042</b>   | 6281  | 1.12                |
| <b>60.2</b>          | 1500 | 73.00 | 128.77 | <b>6897</b>   | 6083  | 1.13                |
| <b>70.3</b>          | 1000 | 90.89 | 156.12 | <b>8588</b>   | 7375  | 1.16                |
| <b>70.6</b>          | 800  | 92.82 | 159.52 | <b>8770</b>   | 7536  | 1.16                |
| <b>76.1</b>          | 700  | 99.90 | --     | <b>9438</b>   | --  | --                  |
| <b>76.8</b>          | 800  | 91.85 | 156.12 | <b>8678</b>   | 7375  | 1.18                |

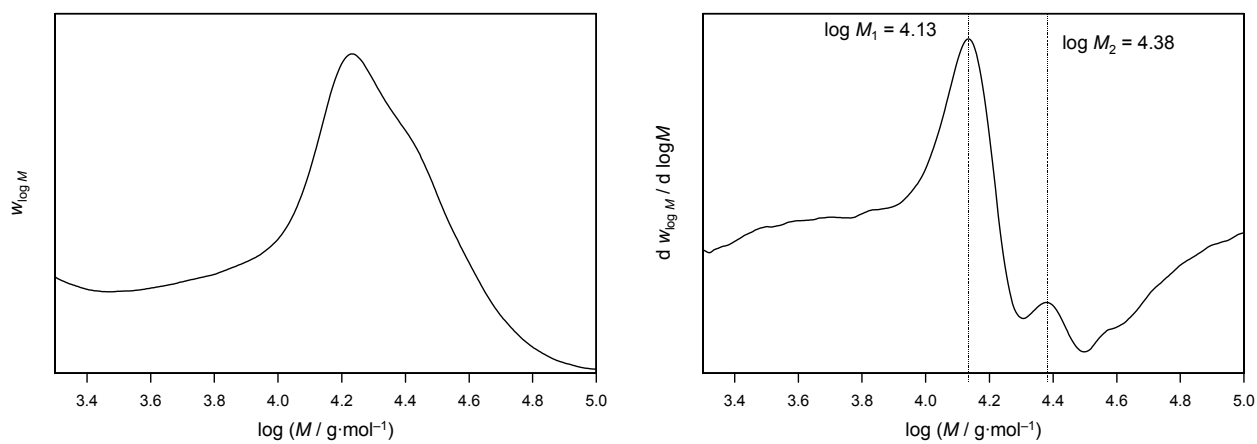
### Selected examples for PLP distributions and their derivatives

(molecular weights given are based on direct polystyrene calibration, for recalibrated values see Tables S1 and S2)

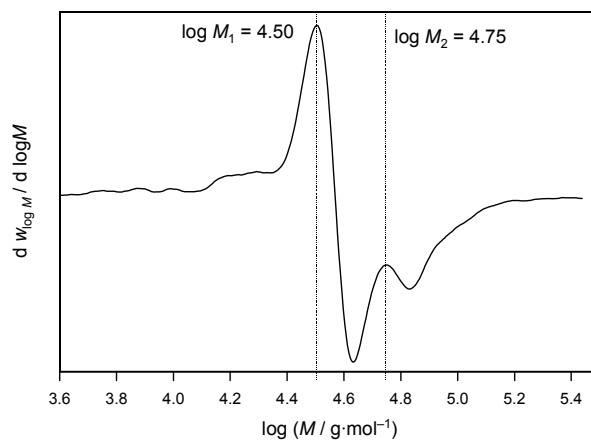
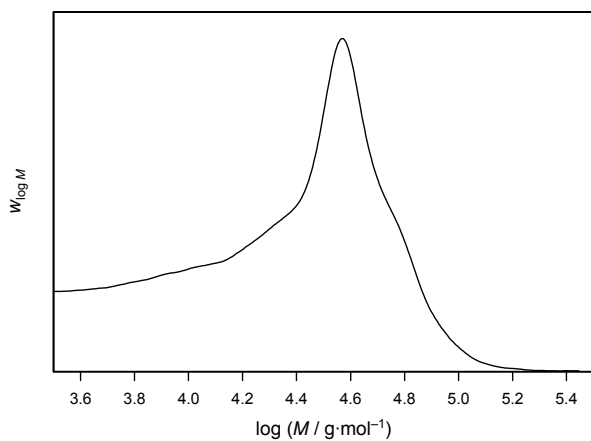
Frequency variation, 50 °C, 500 Hz



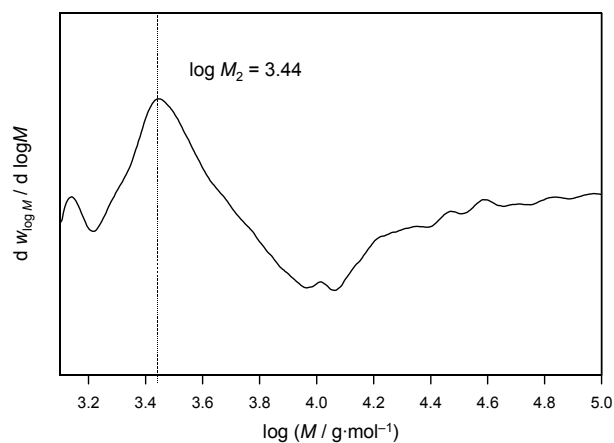
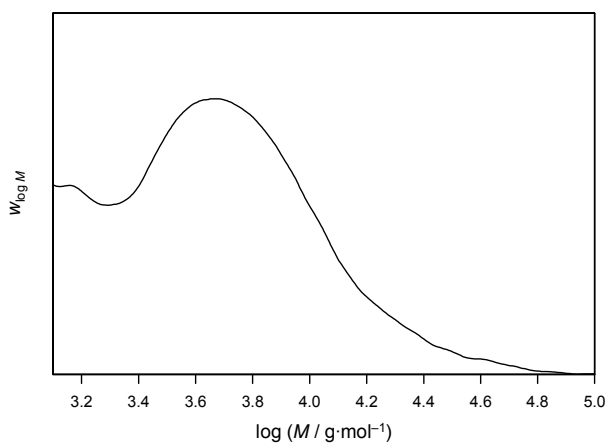
Frequency variation, 50 °C, 300 Hz



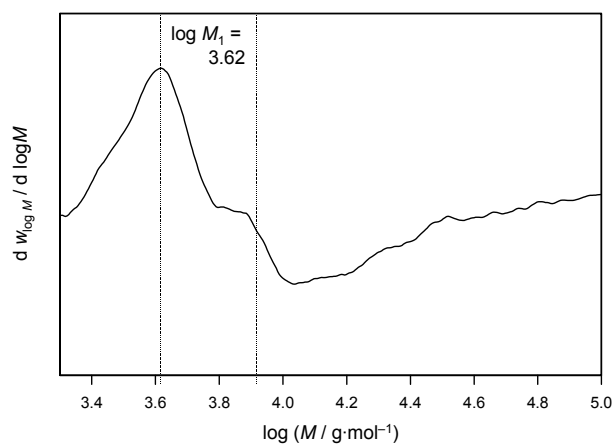
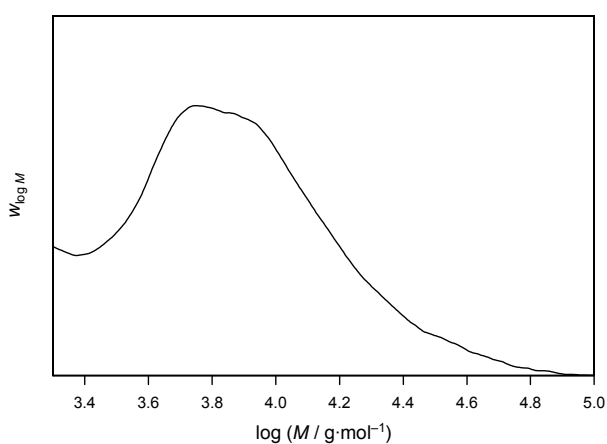
Frequency variation, 50 °C, 100 Hz



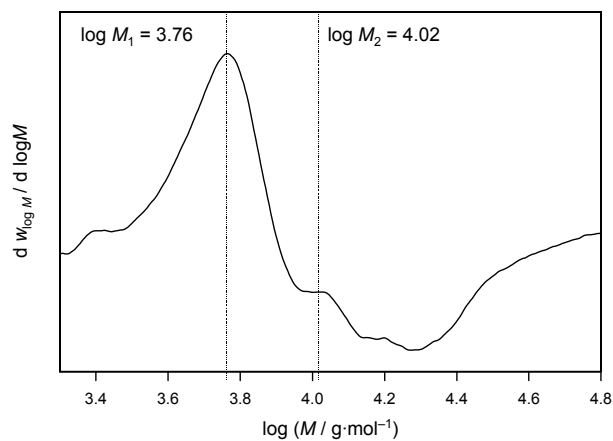
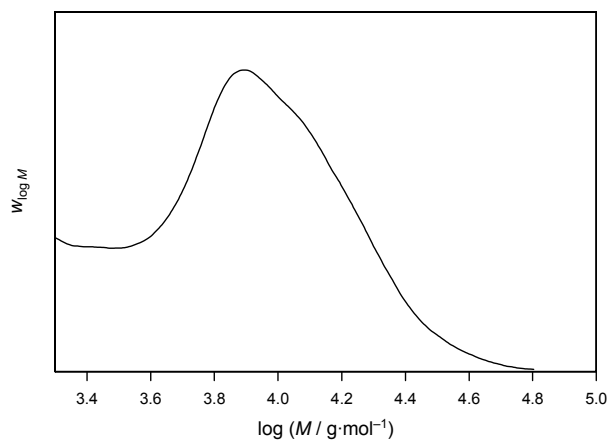
Temperature variation, 2 °C, 500 Hz



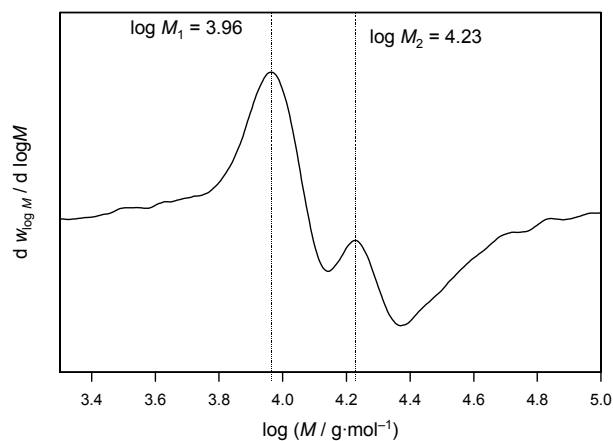
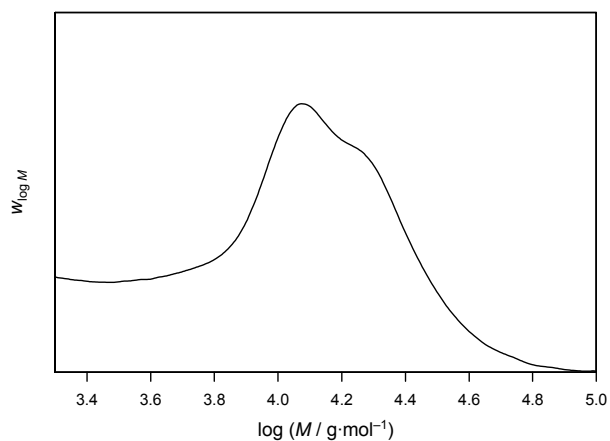
Temperature variation, 21 °C, 500 Hz



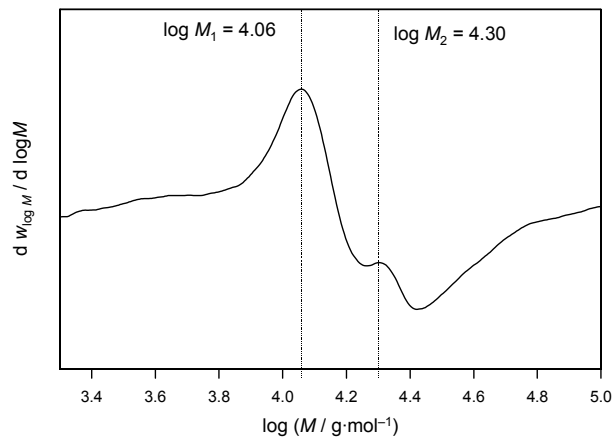
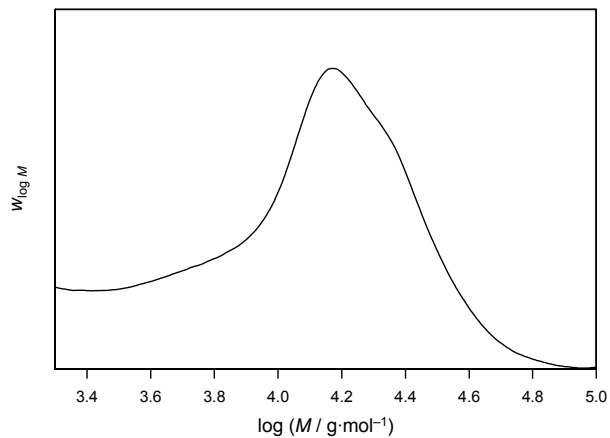
Temperature variation, 41 °C, 500 Hz



Temperature variation, 60 °C, 500 Hz



Temperature variation, 77 °C, 500 Hz



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- [<sup>1</sup>] (a) Y. Fujisaki, H. Kobayashi, *Chem High Polym*, 1962, **19**, 81; (b) J. Brandrup, E. H. Immergut, E. A. Grulke, *Polymer Handbook 4<sup>th</sup> edition*, John Wiley and Sons, New York, 1999.
- [<sup>2</sup>] C. C. Walker, *J. Polym. Sci. A. Polym. Chem.*, 1988, **26**, 1649-1657.