Supporting Information to:

Determination of the Propagation Rate Coefficient of Acrylonitrile

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Experimental

Materials

Acrylonitrile (Acros, ≥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, ≥99 %) were used as received.

Pulsed Laser Polymerization

Solutions of acrylonitrile in propylene carbonate solution (~5 $mol \cdot L^{-1}$) containing variable concentrations of DMPA (ranging from 1 to $20 \cdot 10^{-3}$ $mol \cdot L^{-1}$) 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 $mg \cdot mL^{-1}$.

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 $mL \cdot min^{-1}$ was used. The SEC system was calibrated using narrow polystyrene standards ranging from 160 to $6 \cdot 10^6$ g mol^{-1}. The resulting molecular weight distributions have been recalibrated employing literature Mark-Houwink parameters for polyacrylonitrile ($K = 27.4 \cdot 10^{-5}$ $dL \cdot g^{-1}$ and $a = 0.764$)[1] and for polystyrene ($K = 12.1 \cdot 10^{-5}$ $dL \cdot g^{-1}$ and $a = 0.69$).[2]

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 ν is the pulse repetition rate)

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

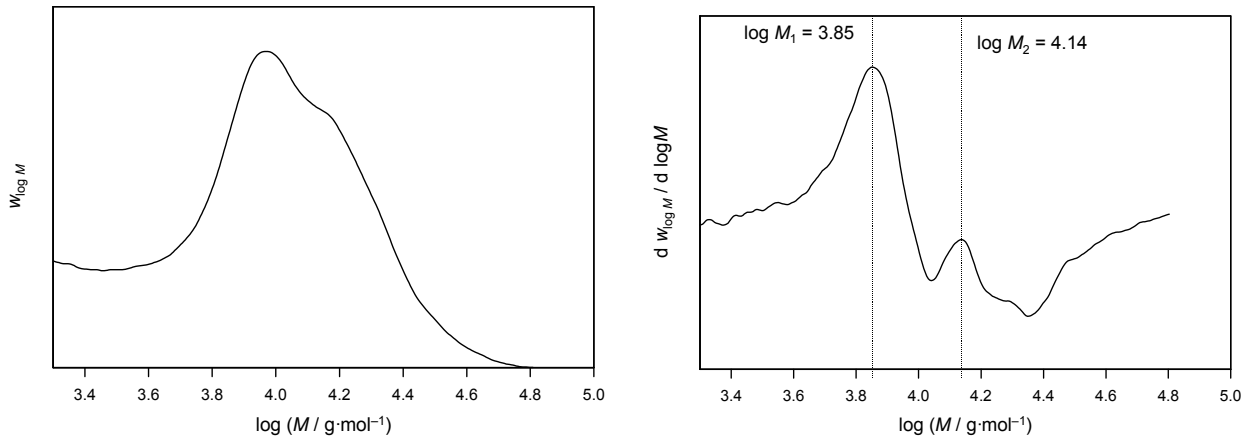
Table S2 Collated experimental results from PLP-SEC of AN with $c_{monomer} = 5.29$ mol·L^{-1}, $c_{DMPA} = 5.3 \cdot 10^{-3}$mol·L^{-1} at a pulse repetition rate of 500 Hz (*n* denotes the number of laser pulses applied)

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

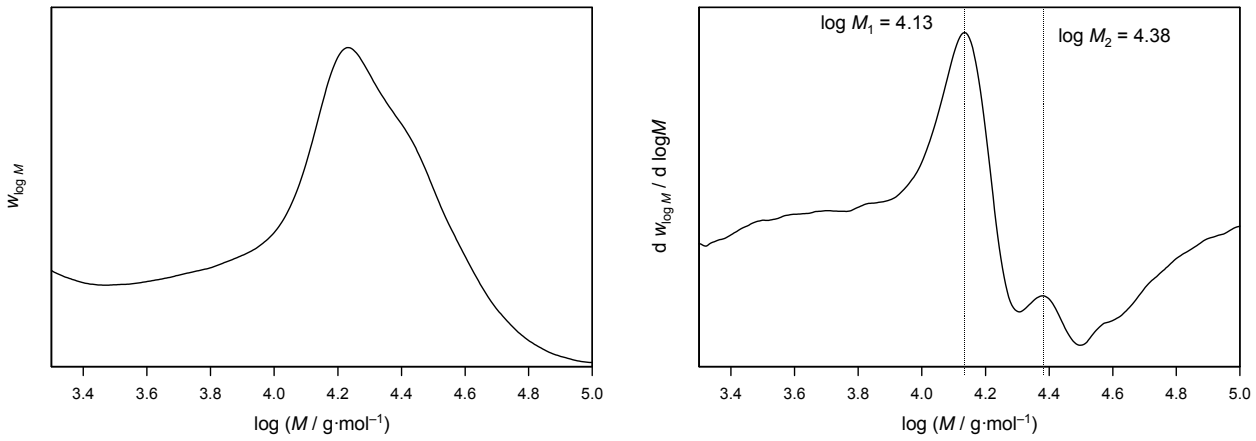
Selected examples for PLP distributions and their derivatives

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

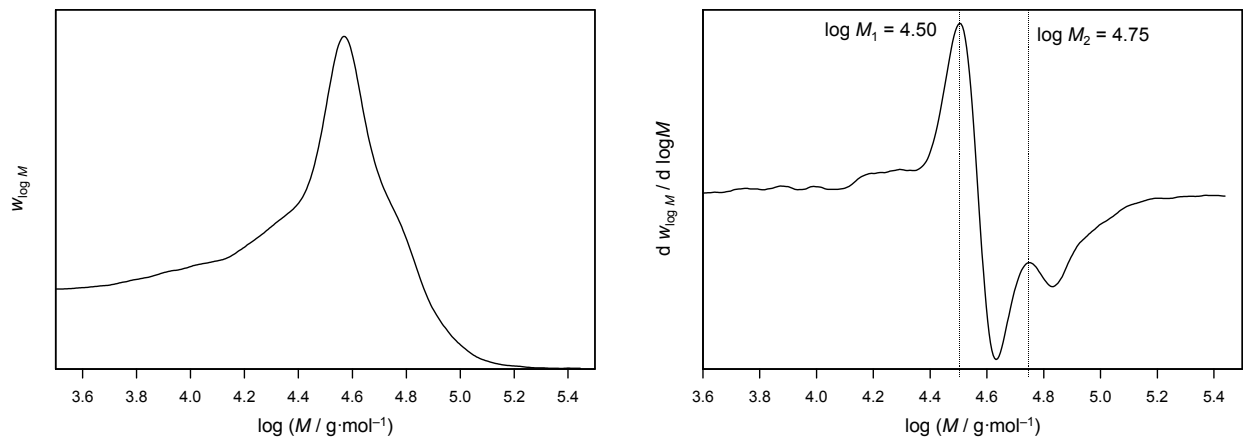
Frequency variation, 50 °C, 500 Hz



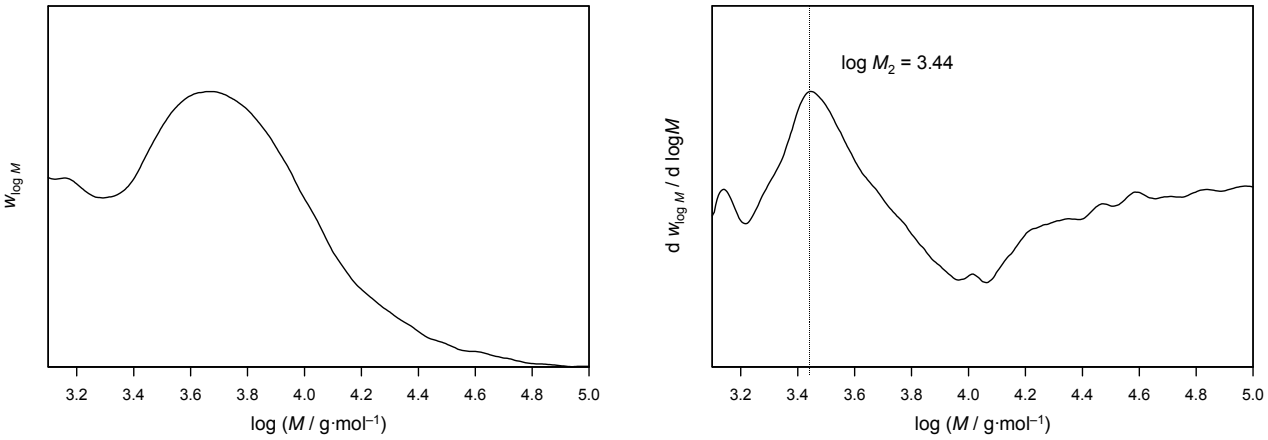
Frequency variation, 50 °C, 300 Hz



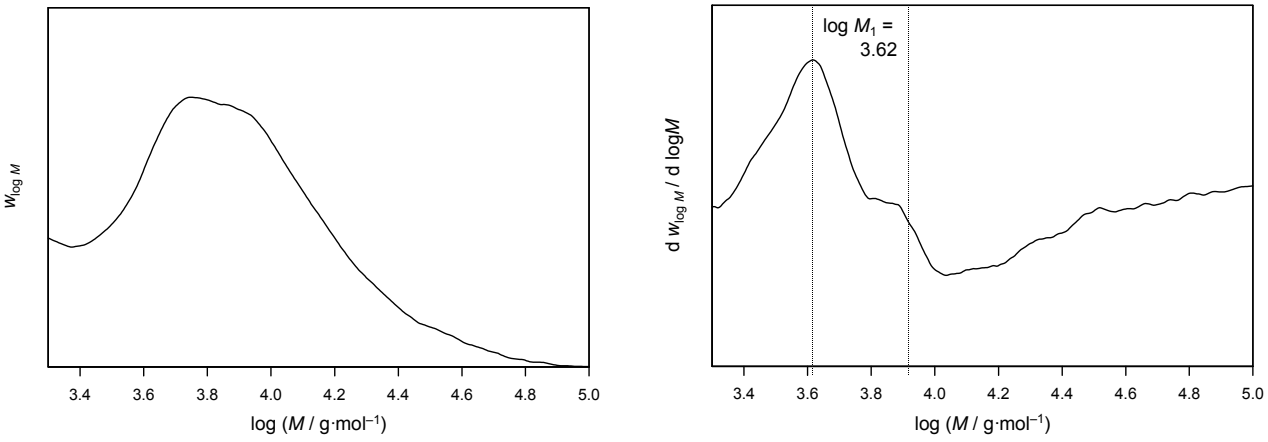
Frequency variation, 50 °C, 100 Hz



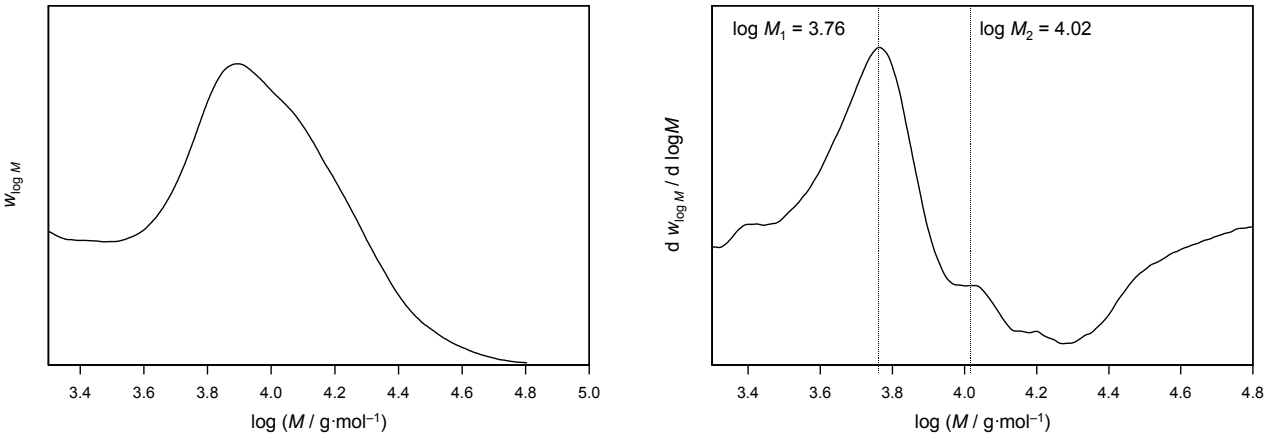
Temperature variation, 2 °C, 500 Hz



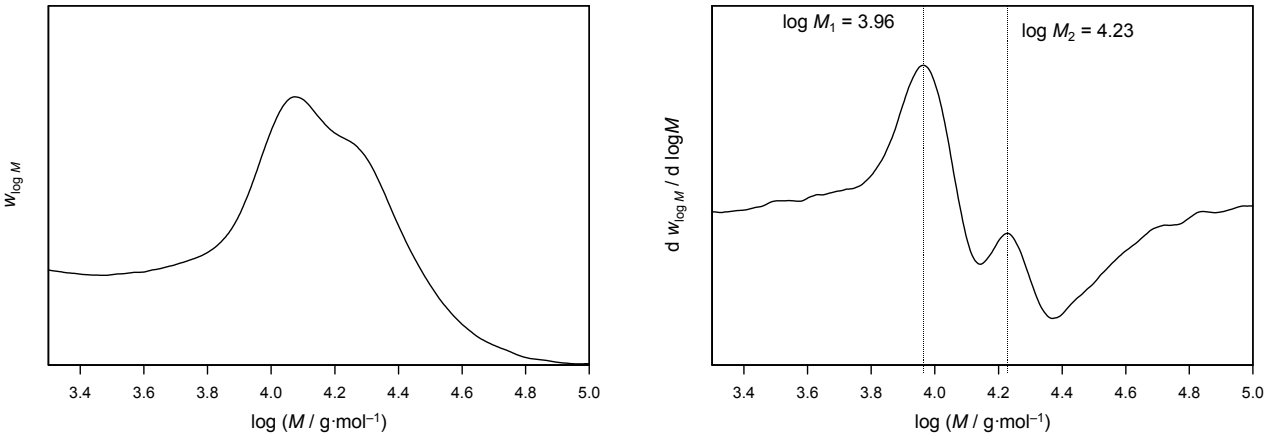
Temperature variation, 21 °C, 500 Hz



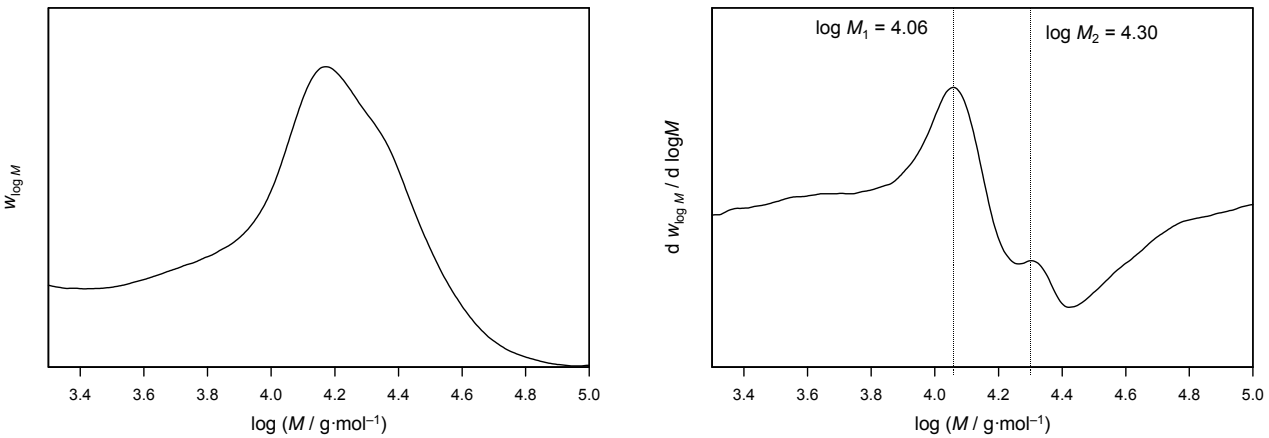
Temperature variation, 41 °C, 500 Hz



Temperature variation, 60 °C, 500 Hz



Temperature variation, 77 °C, 500 Hz



[1] (a) Y. Fujisaki, H. Kobayashi, *Chem High Polym,* 1962, **19**, 81; (b) J. Brandrup, E. H. Immergut, E. A. Grulke, *Polymer Handbook 4th edition*, John Wiley and Sons, New York, 1999.

[2] C. C. Walker, *J. Polym. Sci. A. Polym. Chem*., 1988, **26**, 1649-1657.