

Evaluating Polymerization Kinetics Using Microrheology

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Samples for calibration

Table S1. Properties of the poly(dimethylacrylamide) polymers used in calibration measurements to determine the Mark-Houwink constants (eq 5), such as the degree of polymerization (DP) expected from the molar equivalent of monomer relative to the chain transfer agent, n_{eq} , the DP from proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy, the molecular weight, M , expected from the n_{eq} , the number-average molecular weight, M_n , from size-exclusion chromatography (SEC), the dispersity, \mathcal{D} , also from SEC, and the yield.

DP (expected)	DP ($^1\text{H-NMR}$)	M (expected; kg/mol)	M_n (SEC; kg/mol)	\mathcal{D} (SEC)	Yield (%)
50	56	5.0	4.4	1.16	82
75	75	7.4	8.5	1.17	67
100	94	9.9	10.8	1.19	85
140	148	13.9	14.7	1.23	80
175	172	17.3	18.1	1.25	85
200	206	19.8	20.2	1.27	77
300	317	29.7	22.3	1.31	86
400	411	39.7	42.6	1.32	86
500	513	49.6	50.2	1.32	86

For calibration to determine the Mark-Houwink constants (eq 5), polymer samples with different viscosity-averaged molecular weights, M_v , were prepared by varying the molar equivalent of monomer relative to the chain transfer agent, n_{eq} , from 50 to 500. The resulting degree of polymerization (DP) and molecular weights were then confirmed from experimental measurements, where the DP was estimated from proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy data using

$$DP = \frac{\frac{I_{2CH3}}{6} + \frac{I_{CH2}}{2}}{2} \quad (\text{S1})$$

where I_{2CH3} and I_{CH2} are the integrations of the two methyl groups (3.15–2.64 ppm) and the methylene group (1.80–0.95 ppm), respectively, on the poly(dimethylacrylamide) backbone.

Table S1 shows the experimental values of the DP from $^1\text{H-NMR}$, the number-averaged molecular weight, M_n , from size-exclusion chromatography (SEC), the dispersity, \mathcal{D} , also from SEC, and the yield, in comparison with the expected values of the DP and molecular weight from n_{eq} . The experimental DP and M_n values were consistent with their corresponding expected values, differing only by factors of 0.9–1.1 and 0.8–1.1, respectively. In addition, \mathcal{D} values remained low and within the range of 1.16–1.32, while the yields were 67–86 %.

Newtonian rheology of poly(dimethylacrylamide) solutions

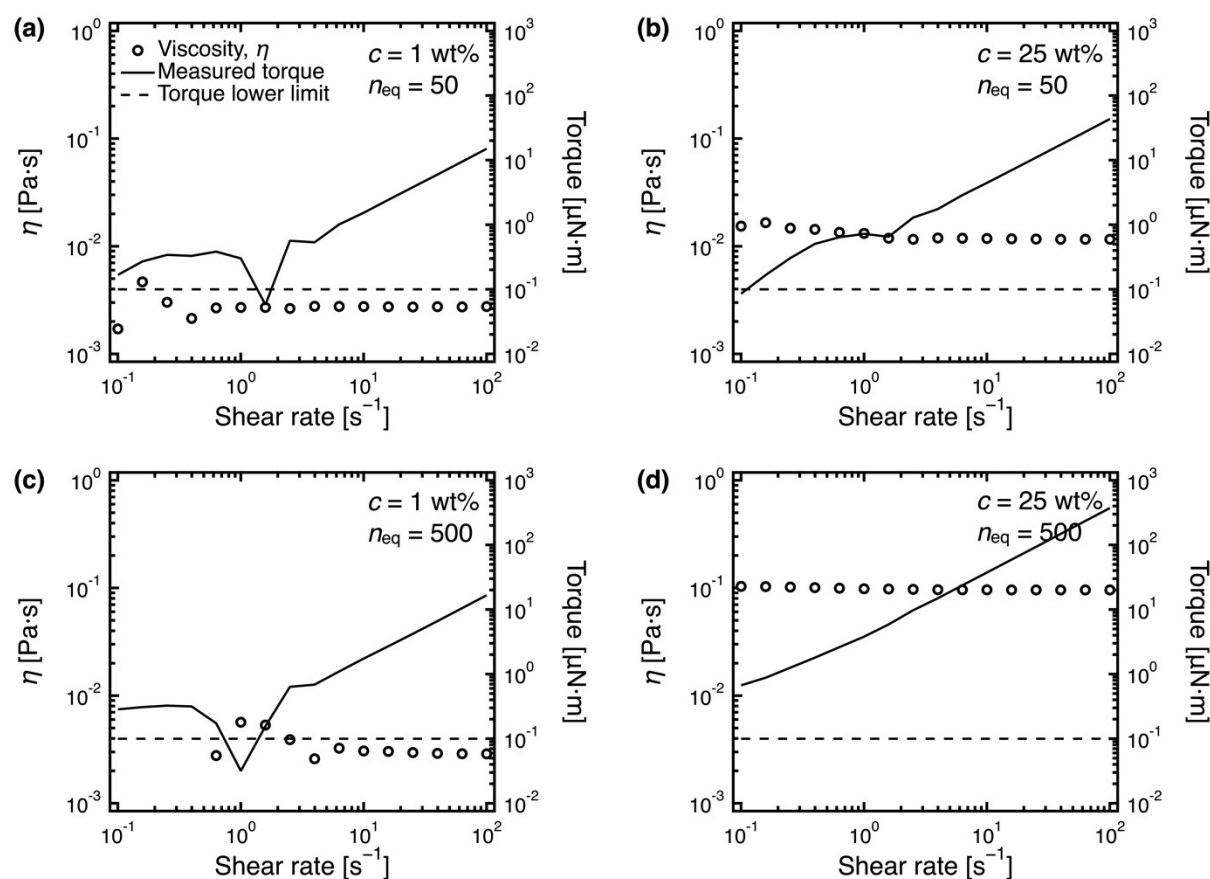


Figure S1. Solution viscosity, η , (empty circles) and torque (solid line) measured using bulk rheology as a function of shear rate at different polymer concentrations, c , and molar equivalents of monomer relative to the chain transfer agent, n_{eq} : (a) $c = 1$ wt%, $n_{eq} = 50$; (b) $c = 25$ wt%, $n_{eq} = 50$; (c) $c = 1$ wt%, $n_{eq} = 500$; (d) $c = 25$ wt%, $n_{eq} = 500$. The dashed line represents the lower limit of the torque resolution of the rheometer.

Figure S1 shows the solution viscosity, η , measured using bulk rheology as a function of shear rate at the polymer concentrations, c , of 1 wt% and 25 wt%, and molar equivalents of monomer relative to the chain transfer agent, n_{eq} , of 50 and 500 or DP of 44 and 506, respectively. The lower limit of the torque resolution of the rheometer is indicated by the dashed line in **Figure S1**. Beyond this limit, the viscosity was independent of the shear rate in all cases, confirming the Newtonian behavior of the samples. Since the values of c and DP in **Figure S1** generally encompass the range of c and DP of the samples for calibration with $c = 4$ wt% and DP = 44 to 506, and the kinetically evolving samples undergoing polymerization with $c = 1.2$ to 23.1 wt% and DP = 21 to 234, these samples are expected to behave as Newtonian fluids as well.

Mean-squared displacement from DDM microrheology

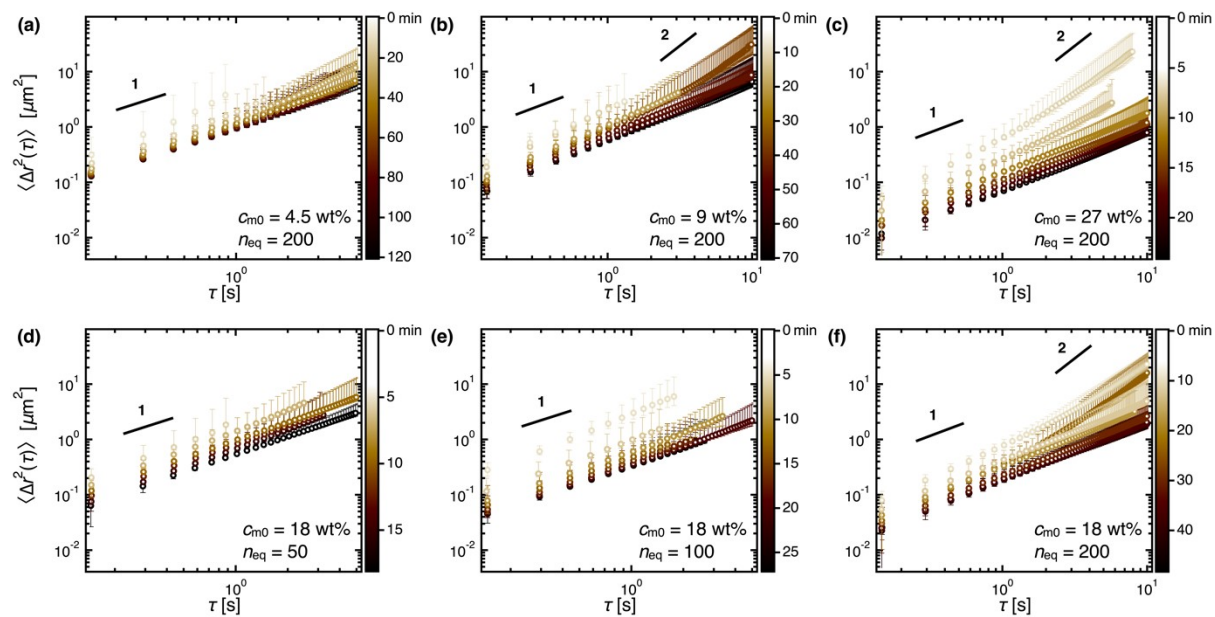


Figure S2. Mean-squared displacement, $\langle \Delta r^2(\tau) \rangle$, as a function of lag time, τ , at various times after initiation of the polymerization represented by the color bar and at various (a–c) initial monomer concentrations, C_{m0} , and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations after ensemble averaging using the differential dynamic microscopy (DDM) analysis.¹

Validation of viscosity from DDM microrheology

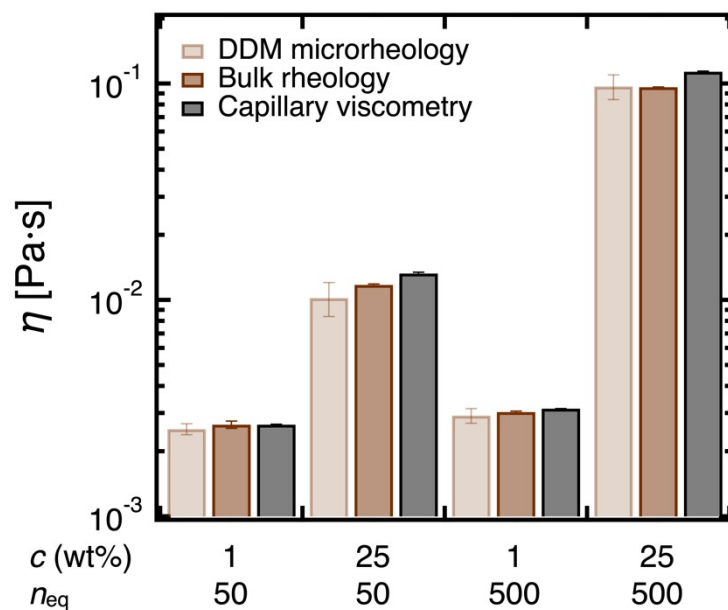


Figure S3. Solution viscosity, η , at the polymer concentrations, c , of 1 wt% and 25 wt% and molar equivalents of monomer relative to the chain transfer agent, n_{eq} , of 50 and 500 determined from differential dynamic microscopy (DDM) microrheology, bulk rheology at the shear rate of 10 s^{-1} , and capillary viscometry. The error bars represent standard deviations of three replicate measurements.

Viscosity from mean-squared displacement and intermediate scattering function

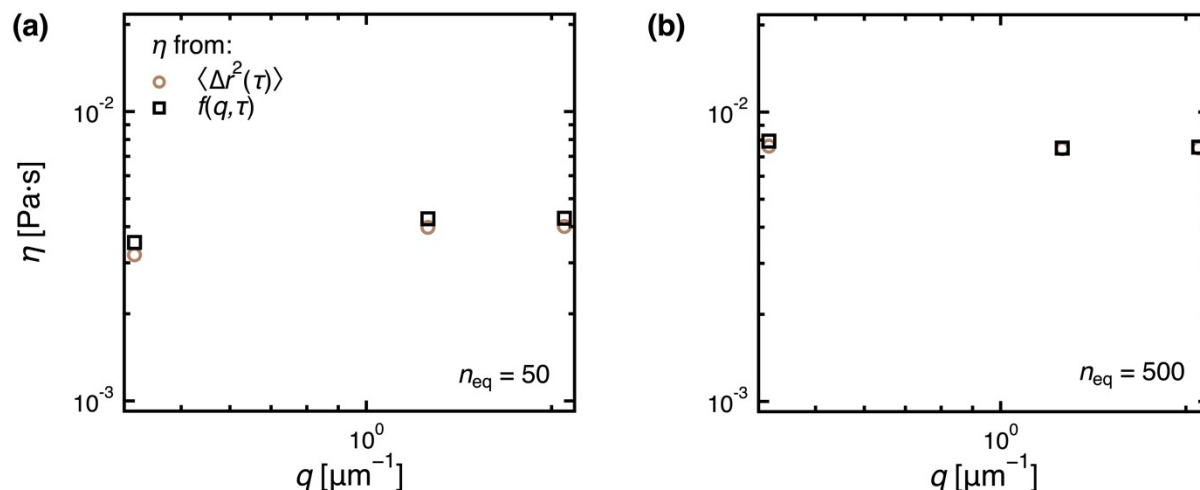
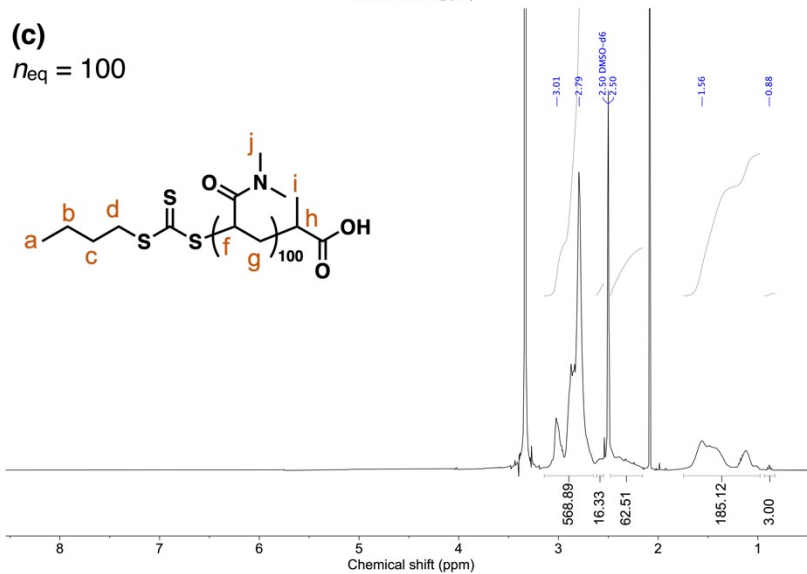
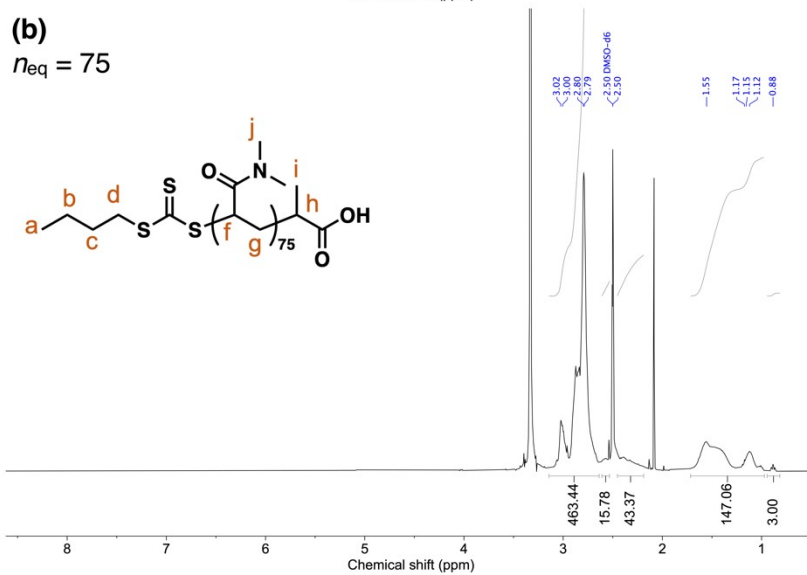
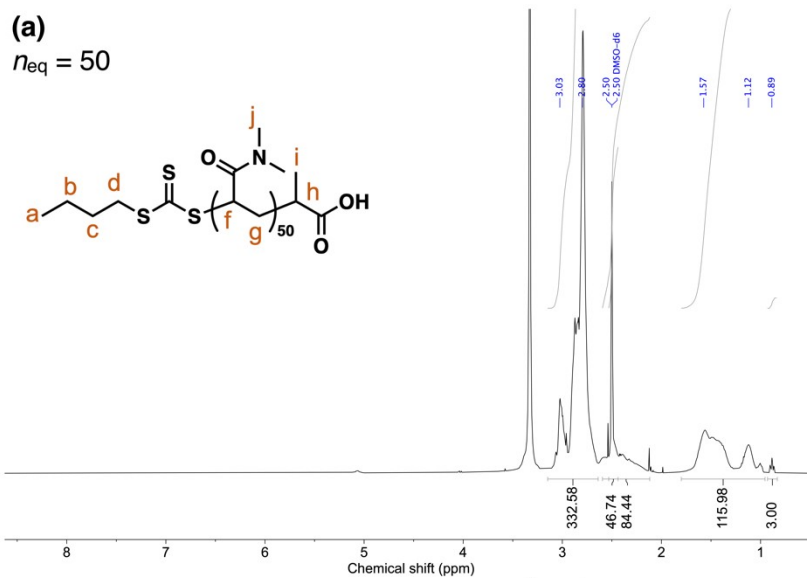
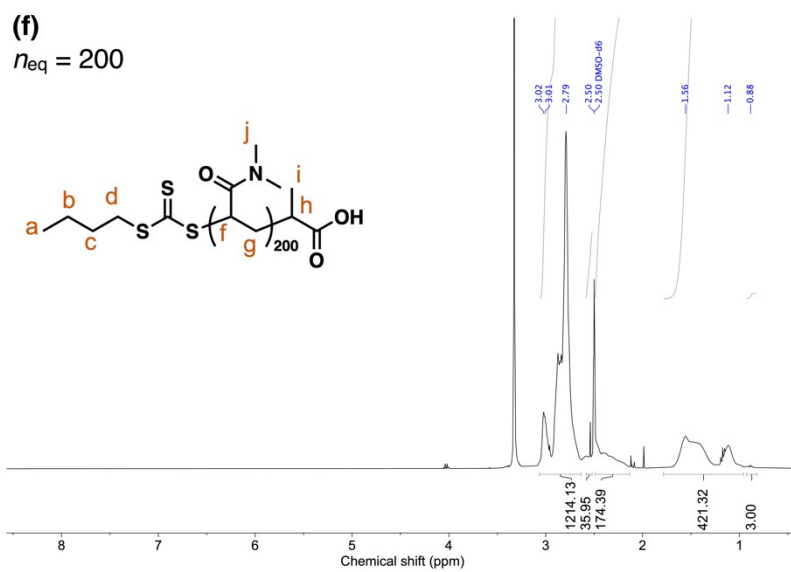
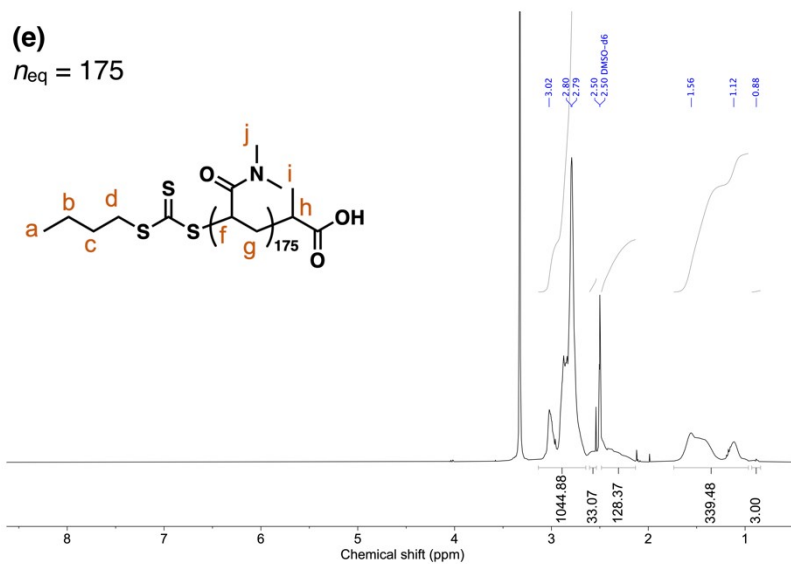
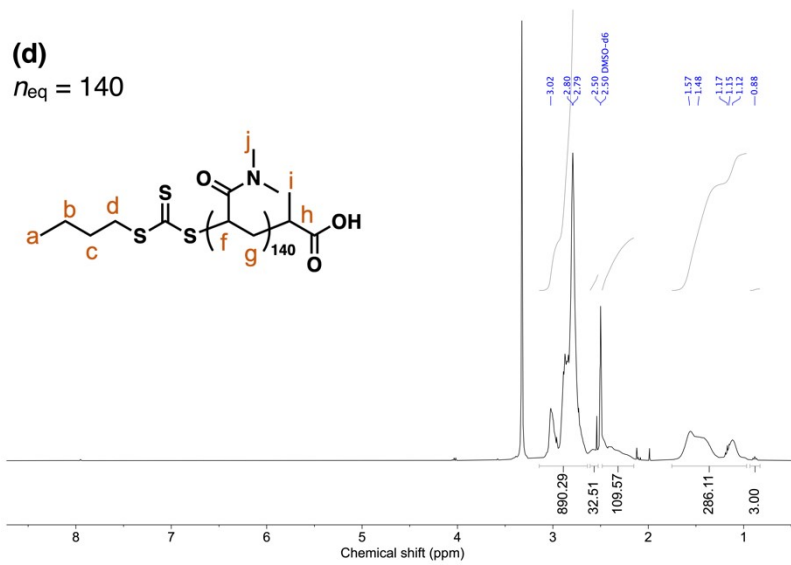


Figure S4. Solution viscosity, η , as a function of wave vector, q , at molar equivalents of monomer relative to the chain transfer agent, n_{eq} , of (a) 50 and (b) 500. The η values were determined from the mean-squared displacement, $\langle \Delta r^2(\tau) \rangle$, (circles) by using eqs 3 and 4, and from the intermediate scattering function, $f(q, \tau)$, (squares) by fitting with the exponential function $f(q, \tau) = \exp(-2Dq^2\tau)$ then using the diffusion coefficient, D , to calculate η (eq 4). The error bars represent standard deviations of the best-fit curves which are smaller than the data markers themselves.

Spectra from NMR spectroscopy





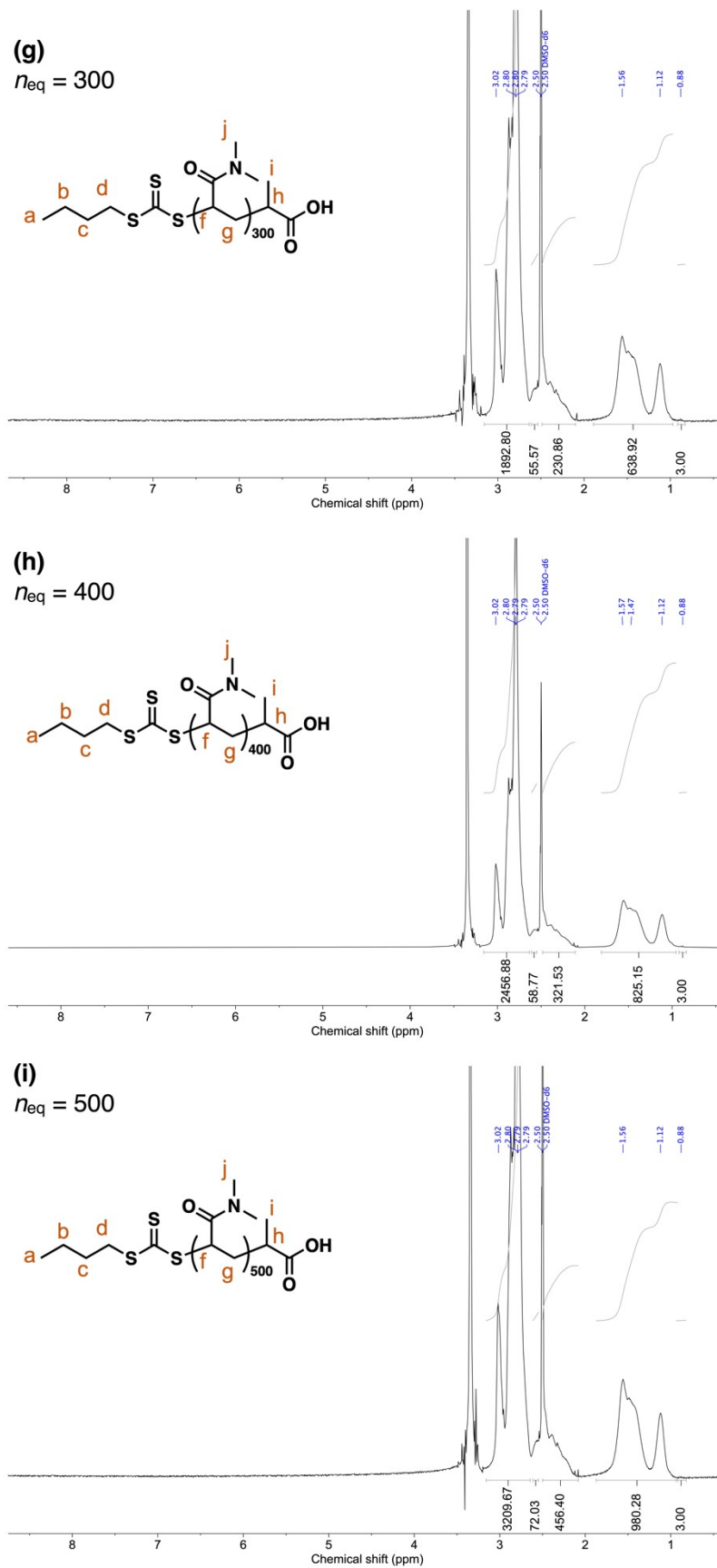


Figure S5. Representative spectra from proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy measurements of poly(dimethylacrylamide) in DMSO-d_6 at various molar equivalents of monomer relative to the chain transfer agent, n_{eq} , and after polymerization for 16 h.

Chromatograms from SEC

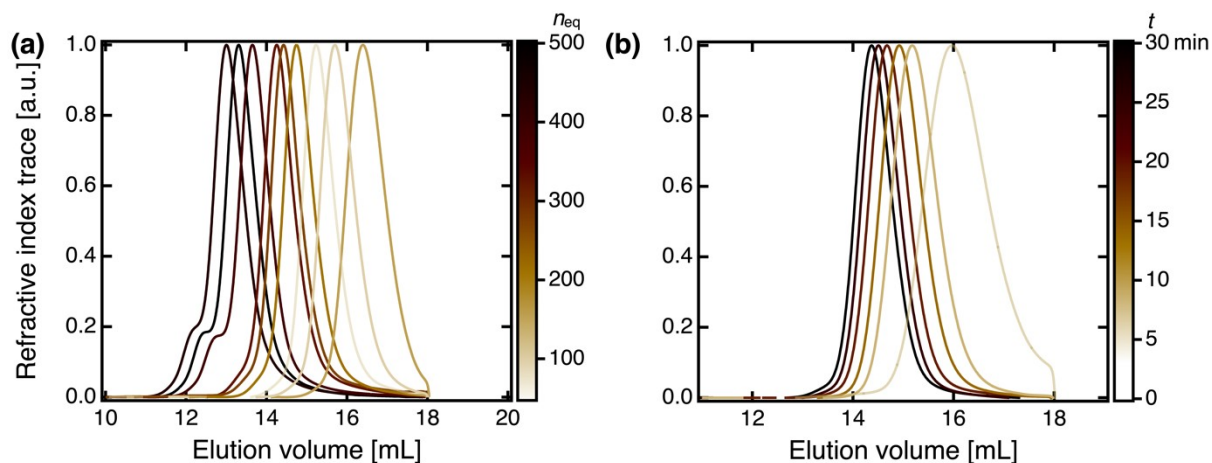


Figure S6. Representative chromatograms from size-exclusion chromatography (SEC) measurements of poly(dimethylacrylamide) (a) at various molar equivalents of monomer relative to the chain transfer agent, n_{eq} , represented by the color bar and after polymerization for 16 h; and (b) at initial monomer concentration, c_{m0} , of 18 wt%, n_{eq} of 200, and various times, t , after initiation of the polymerization represented by the color bar.

Dispersities from SEC

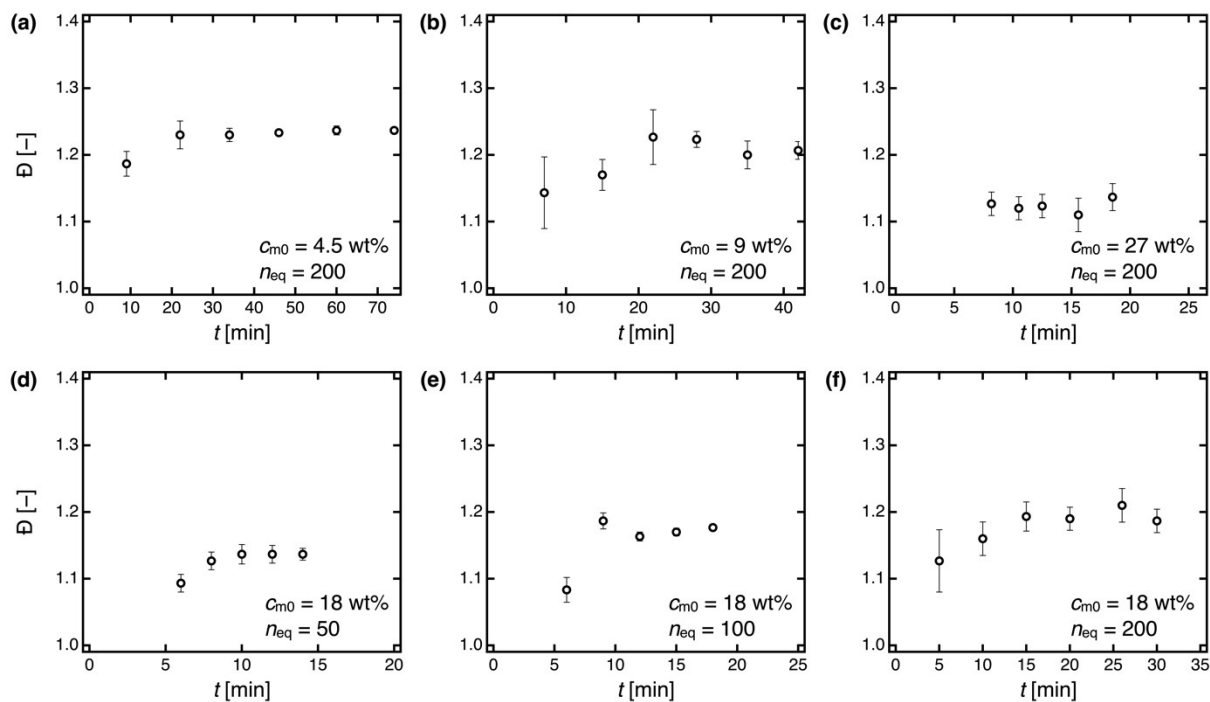


Figure S7. Dispersity, \mathcal{D} , measured using SEC as a function of polymerization time, t , at various (a–c) initial monomer concentrations, c_{m0} , and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations of six replicate measurements. The dispersities remained low and within the range of 1.1–1.2 during polymerization of all samples demonstrating the controlled RAFT polymerization.

Reaction conversions from NMR spectroscopy

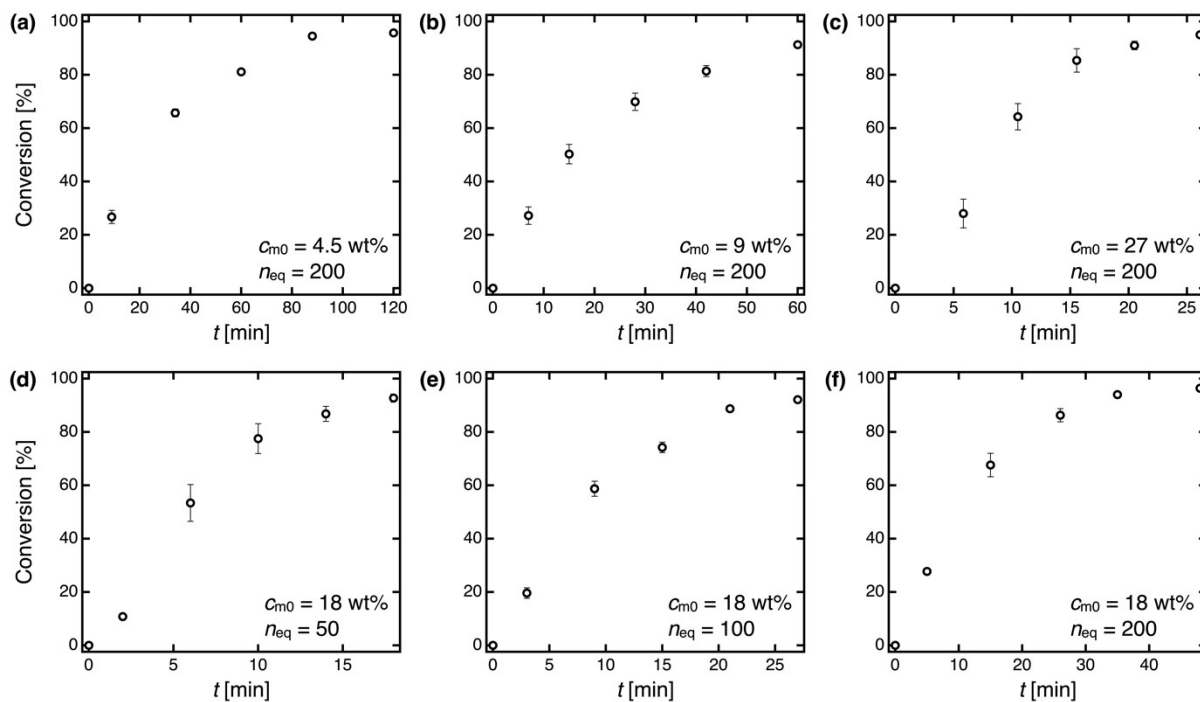


Figure S8. Reaction conversion measured using NMR as a function of polymerization time, t , at various (a–c) initial monomer concentrations, C_{m0} , and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations of six replicate measurements. The conversions were as high as 91–97% for the samples at C_{m0} of 4.5–27.0 wt% and n_{eq} of 50–200, further demonstrating the controlled reaction in RAFT polymerization producing polymers with predetermined molecular weights.²

Determination of rate constants

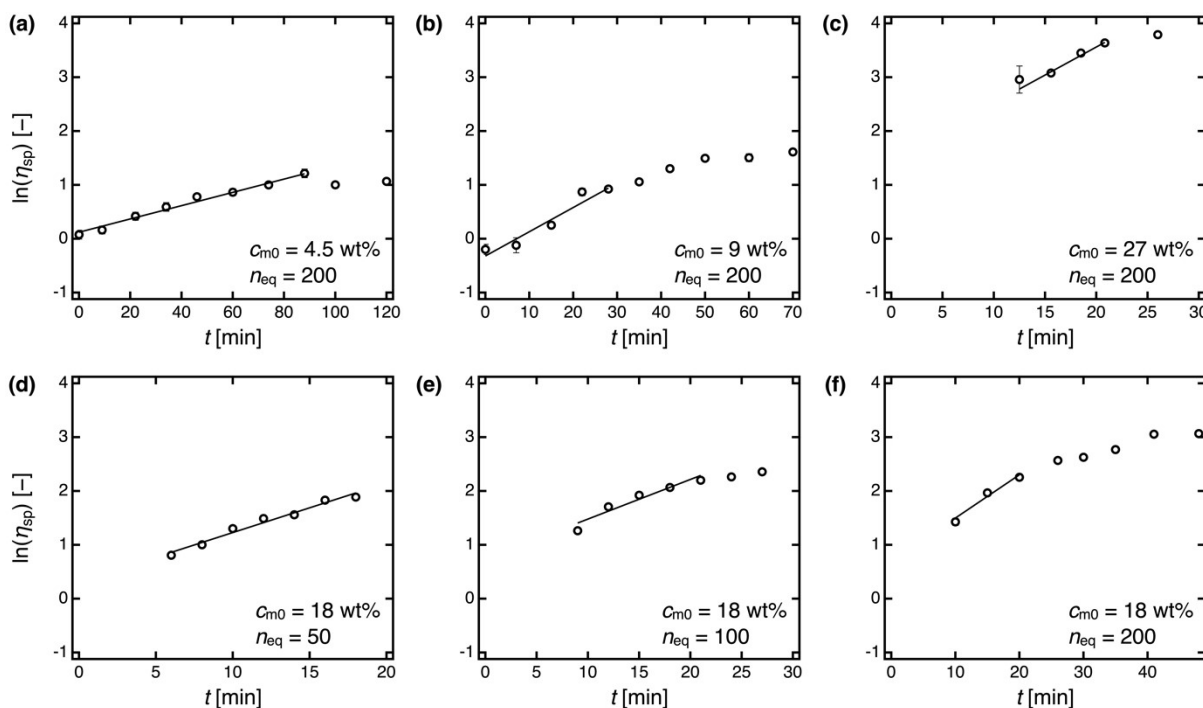


Figure S9. Natural logarithm of the specific viscosity, $\ln(\eta_{sp})$, as a function of polymerization time, t , at various (a–c) initial monomer concentrations, c_{m0} , and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations of six replicate measurements. The solid lines indicate the weighted linear fit.

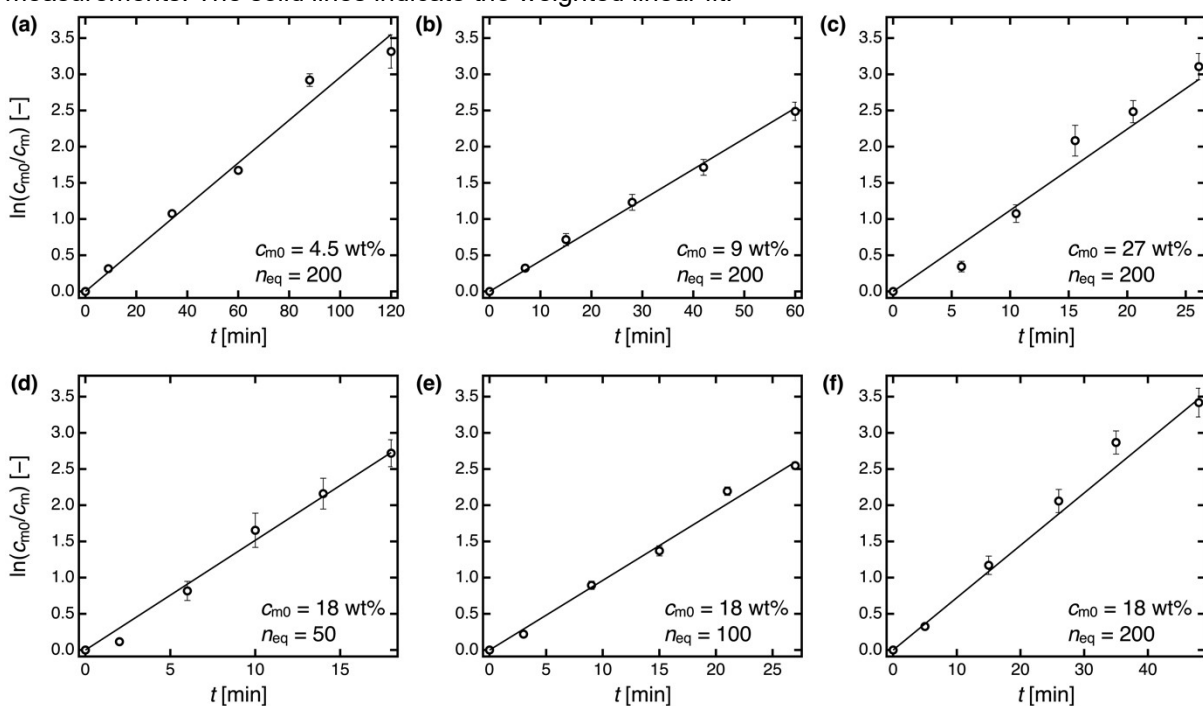


Figure S10. Natural logarithm of the monomer concentration, $\ln(c_{m0}/c_m)$ where c_{m0} and c_m are the initial and instantaneous concentrations of free monomer, respectively, as a function of polymerization time, t , at various (a–c) c_{m0} and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations of six replicate measurements. The solid lines indicate the weighted linear fit.

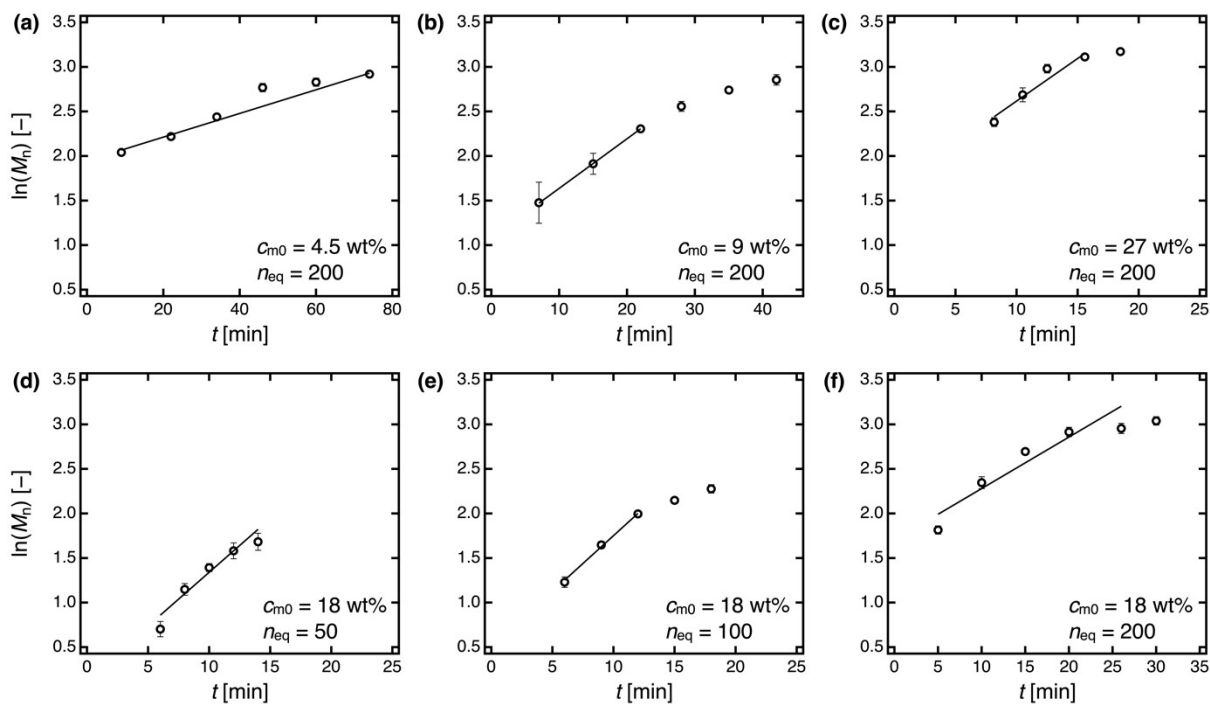


Figure S11. Natural logarithm of the number-average molecular weight, $\ln(M_n)$, as a function of polymerization time, t , at various (a–c) initial monomer concentrations, c_{m0} , and (d–f) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The error bars represent standard deviations of six replicate measurements. The solid lines indicate the weighted linear fit.

Goodness of linear fit

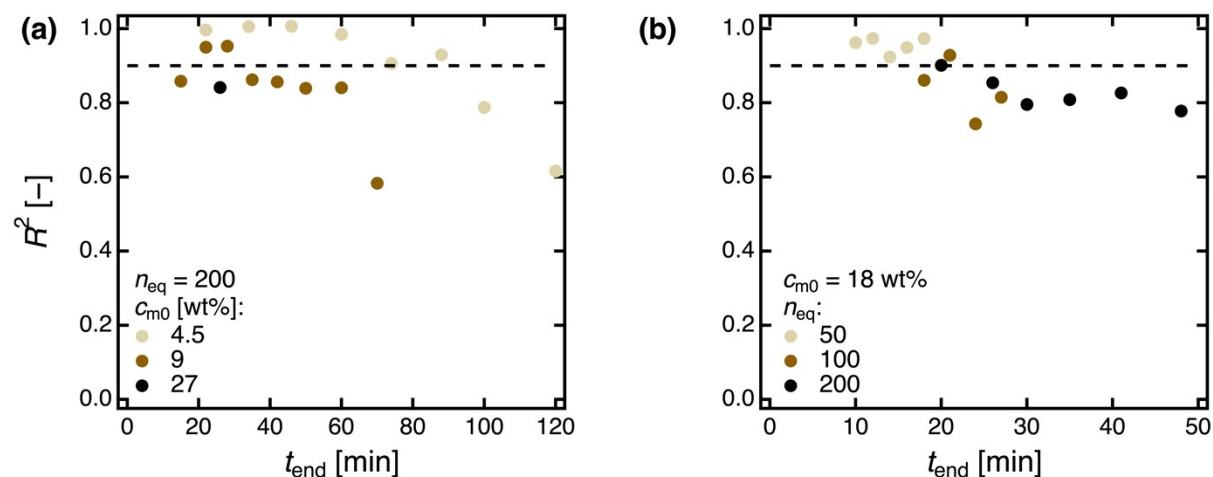


Figure S12. Coefficient of determination, R^2 , as a function of the ending time point, t_{end} , included in the linear fit of $\ln(\eta_{sp})$ vs t plots (**Figure S9**) at various (a) initial monomer concentrations, c_{m0} , and (b) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . Dashed lines indicate the lower threshold value of $R^2 = 0.9$ determining the range of time points included in the fit.

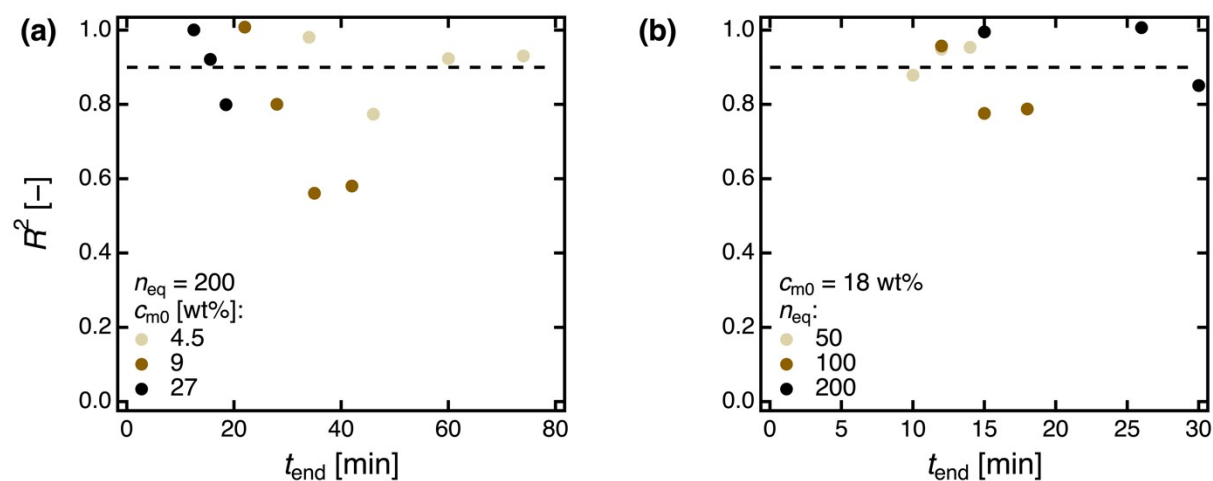


Figure S13. Coefficient of determination, R^2 , as a function of the ending time point, t_{end} , included in the linear fit of $\ln(M_n)$ vs t plots (**Figure S11**) at various (a) initial monomer concentrations, c_{m0} , and (b) molar equivalents of monomer relative to the chain transfer agent, n_{eq} . Dashed lines indicate the lower threshold value of $R^2 = 0.9$ determining the range of time points included in the fit.

Validation of Rao-Yaseen equation

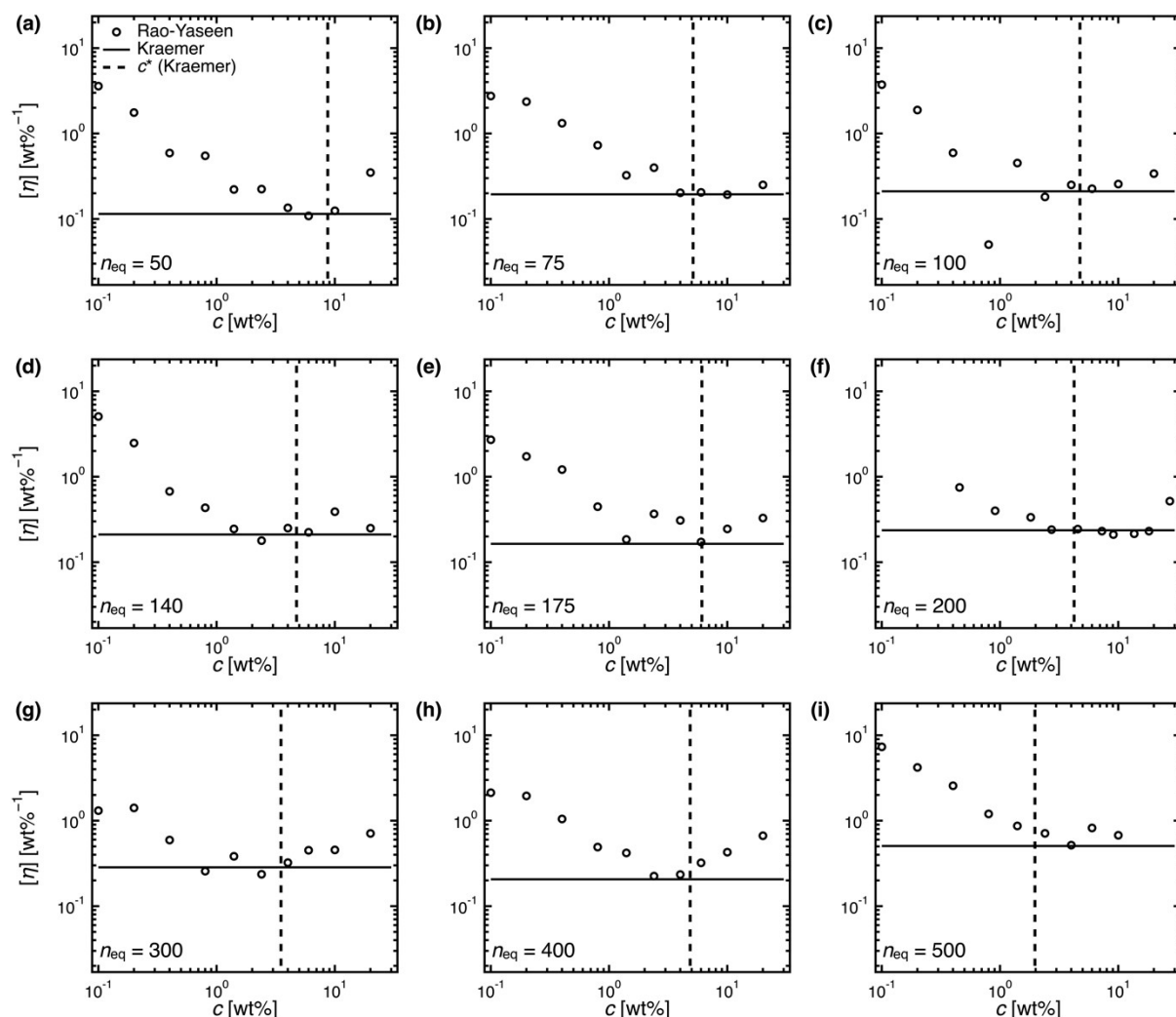


Figure S14. Intrinsic viscosity, $[\eta]$, estimated using the Rao-Yaseen³ (eq S2; empty circles) and Kraemer⁴ (eq S3; solid lines) equations as a function of polymer concentration, c , at various molar equivalents of monomer relative to the chain transfer agent, n_{eq} . The dashed lines represent the overlap concentration, $c^* = 1/[\eta]$, estimated using the Kraemer equation.

The Rao-Yaseen equation³ (eq S2) is a single-point method providing a simple, fast, and low-cost means to estimate the intrinsic viscosity, $[\eta]$, from the solution viscosity, η , measured at a single polymer concentration, c . The $[\eta]$ values estimated using this equation were compared with those estimated using the Kraemer equation⁴ (eq S3) which is the conventional and standard method to estimate $[\eta]$ from η measured at different values of c and then extrapolated to $c = 0$.

$$[\eta] = \frac{1}{2c}[\eta_{sp} + \ln(\eta_{rel})] \quad (\text{S2})$$

$$\frac{\ln(\eta_{rel})}{c} = [\eta] + (k_H - 1/2)[\eta]^2 c \quad (\text{S3})$$

where $\eta_{sp} = (\eta - \eta_s)/\eta_s$ is the specific viscosity, $\eta_{rel} = \eta/\eta_s$ is the relative viscosity, η_s is the viscosity of the pure solvent, and k_H is the Huggins coefficient.

Figure S14 shows $[\eta]$ estimated using the Rao-Yaseen and Kraemer equations as functions of c at various n_{eq} . Note that the upturn in $[\eta]$ at low c is attributed to the low sensitivity of DDM microrheology to detect the changes in η with c when the polymer concentration or, equivalently, the solution viscosity is low. Beyond this upturn, $[\eta]$ obtained from both equations showed good agreement with each other for the c range of about 4–20 wt% and the entire n_{eq} range. This validates the use of the Rao-Yaseen equation to quickly and accurately estimate $[\eta]$ at least within this range of c and n_{eq} . In addition, $[\eta]$ is ideally estimated in the dilute regime or below the overlap concentration⁴, c^* , shown as dashed lines in **Figure S14**. Considering the c^* and the c range of validity of the Rao-Yaseen equation, samples at 4 wt% were then measured to estimate $[\eta]$ at various M_v (**Figure 5**) to determine the Mark-Houwink constants.

In addition, the range of validity of the Rao-Yaseen equation of $c = 4$ to 20 wt% and $n_{eq} = 50$ to 500 or DP = 44 to 506 coincides well with the experimentally measured $c = 1.2$ to 23.1 wt% and DP = 21 to 234 during polymerization. Therefore, this validates the use of the Rao-Yaseen equation, along with the Mark-Houwink equation, to convert the time-dependent data during polymerization to the apparent viscosities and apparent molecular weights (**Figures 6-7**).

Expression for polymer concentration in terms of rate constant

The instantaneous polymer concentration, c , at a certain time, t , during the polymerization is expressed in terms of the rate constant, k , through a first-order rate equation confirmed from the NMR measurements (**Figure S10**),

$$-\frac{dc_m}{dt} = kc_m \quad (\text{S4})$$

Which is integrated,

$$-\int_{c_{m0}}^{c_m} \frac{dc_m}{c_m} = \int_{t_0}^t k dt \quad (\text{S5})$$

$$\frac{c_{m0}}{c_m} = e^{kt} \quad (\text{S6})$$

Where c_m is related to the instantaneous concentration of reacted monomer, $c_{m,r}$, by

$$c_m = c_{m0} - c_{m,r} \quad (\text{S7})$$

By substituting eq S7 into eq S6, an expression for $c_{m,r}$ is defined,

$$c_{m,r} = \frac{c_{m0}(e^{kt} - 1)}{e^{kt}} \quad (\text{S8})$$

$c_{m,r}$ is then related to c by

$$c = \frac{c_{m,r}}{DP} = c_{m,r} \frac{M_m}{M} \quad (\text{S9})$$

Where $DP = M/M_m$, M_m is the molecular weight of the monomer, and M is the instantaneous molecular weight of the polymer during polymerization. To avoid using M from SEC in estimating c , eq S9 is multiplied by M , effectively converting c in units of mol/L to cM in units of g/L which is further converted to wt% using the solution density, which is the concentration unit used in this work. Using eqs S8 and S9, an expression for c in terms of k , along with c_{m0} and M_m which are known beforehand, is derived,

$$cM = c_{m,r} M_m = \frac{c_{m0}(e^{kt} - 1)}{e^{kt}} M_m \quad (\text{S10})$$

References

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- (4) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press; 2003.