Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information (ESI) for:

Benchtop Flow-NMR for Rapid Online Monitoring of RAFT and Free Radical Polymerisation in Batch and Continuous Reactors

Stephen T. Knox, Sam Parkinson, Raphael Stone and Nicholas J. Warren*

School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, Leeds, West Yorkshire, LS2 9JT

^{1}H NMR spectroscopy

Low field (or "benchtop") NMR spectra were recorded using a Magritek Spinsolve 60 Ultra. "High-field" spectra were recorded using a Bruker 400 MHz spectrometer.

For the low field instrument, single offline "sampled" measurements were collected using a standard routine – a 7 µs excitation pulse and a spectral width of 5 kHz (32,768 points) was applied, with an acquisition time of 6.5 s and a repetition time of 15 s. For the flow rate experiment all spectra were obtained using a 7 µs excitation pulse and a spectral width of 5 kHz (32,768 points) with an acquisition time of 3.2 s and a repetition time of 7 s. The 'PRESAT' samples used a presaturation solvent suppression routine via a 1s saturation pulse at 4.79 ppm of -65 dB. NMR kinetic profiles were collected using the same presaturation solvent suppression routine (7 µs excitation pulse, spectral width of 5 kHz (32,768 points), acquisition time of 3.2 s, repetition time of 7 s and a 1s saturation pulse at 4.79 ppm of -65 dB)

For the high field instrument, single offline "sampled" measurements were collected using a standard routine.

All NMR data processing was performed using MestreReNova 12.0. Phase correction was applied using a combination of the baseline optimization and minimum entropy routines, and baseline correction using a polynomial fit (3rd order). Integrals were then measured for each spectrum.

Comparison of high-field and benchtop NMR spectrometers

Clear differences between the spectra obtained from a high field (400 MHz) spectrometer and a lower field benchtop (60 MHz) spectrometer are observed, resulting from the difference in magnet strength - the 60 MHz instrument shows both increased peak line width broadening and J values. Therefore, a kinetic study was performed with sampling from a batch polymerisation where the samples were analysed using both spectrometers (Figure SI1). Clearly the resolution obtained by the lower-field spectrometer remains sufficient to obtain a good measure of conversion.

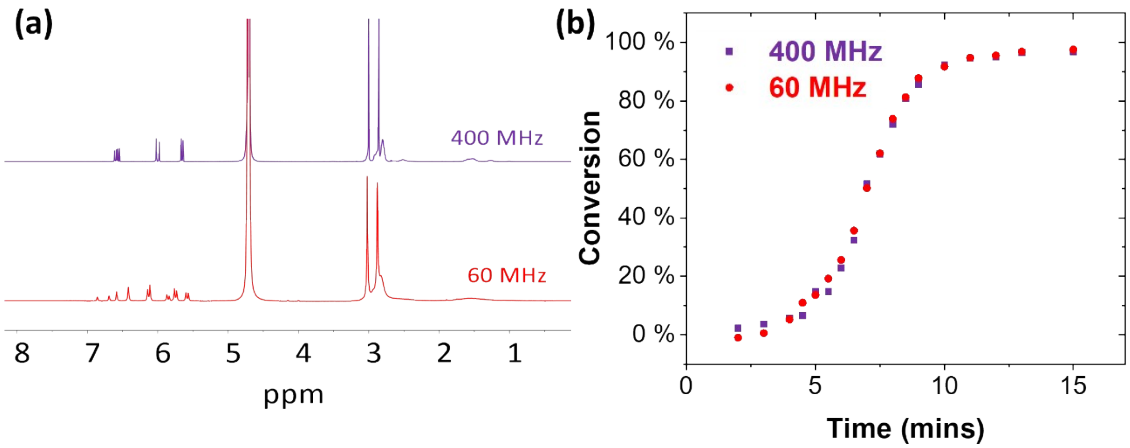

Figure SI1. ***(a)*** *Comparison of spectra obtained from a 400 MHz instrument and a 60 MHz instrument at approx. 50 % conversion for the RAFT polymerisation of DMAm.* ***(b)*** *Conversion with time for the polymerisation at 85 °C as measured by both instruments. All samples are approx. 7.5 % w/w solids.*

Comparison of hydrogenated and deuterated solvent (H_2O vs. D_2O)

Three time points were sampled through a batch RAFT polymerisation of DMAm at 80 °C. This sample was then diluted with water with a varied degree of deuteration to 7.5 % w/w and NMR spectra recorded, and conversion calculated from the method laid out above.

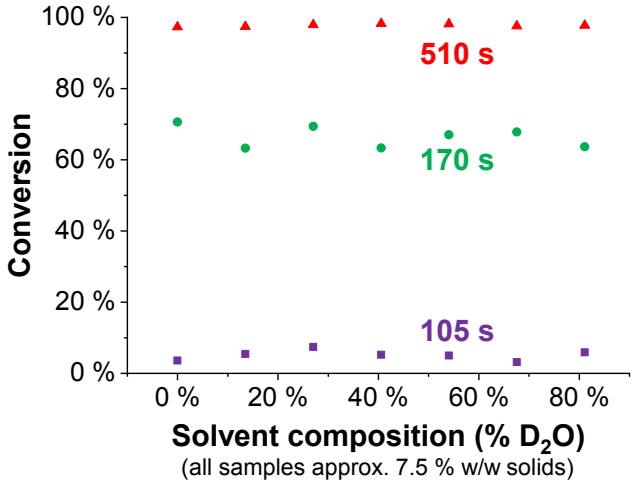

Figure SI2. Conversion for three samples, taken at 105 s, 170 s and 510 s for the RAFT polymerisation of dimethylacrylamide, in water of varying degree of deuteration.

Flow rate experiment

Dimethylacrylamide in water (30 % w/w) was flowed through the NMR spectrometer using a glass flow cell or 1/8" PFA tubing. The flow rate was modified, and spectra recorded using two methods – a standard ^{1}H routine (2 scans, pulse angle 90 °, dwell time 200 µs, 3.2 s acquisition time, 7 s repetition time); and a solvent suppression routine with the same parameters and an initial presaturation pulse (saturation power -65 dB, saturation time 1s, 4.79 ppm). The relative integral (vs. a stationary scan) of the vinyl signal at 7.1-5.5 ppm was measured as flow rate was increased. Deviations from ideality (i.e. 1) are observed from 0.7 mL min^{-1} for the glass flow cell and 0.5 mL min^{-1} for the PFA tubing.

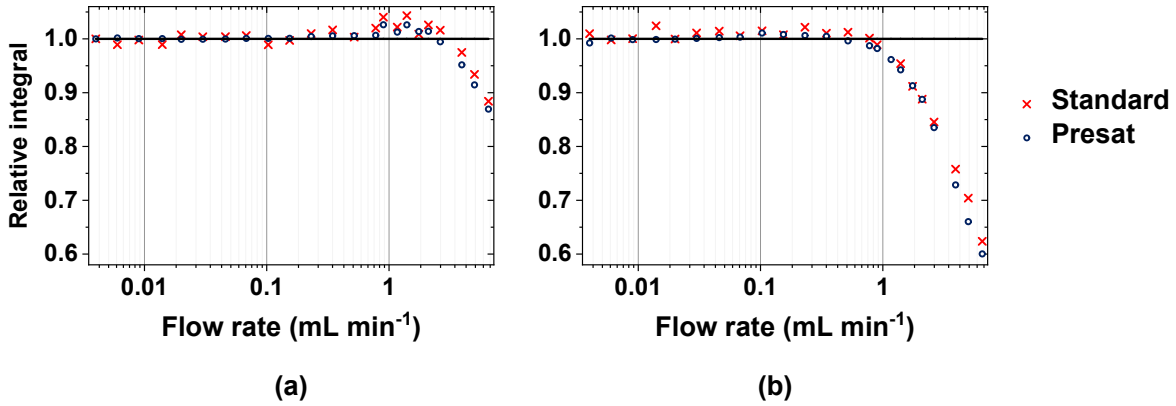

Figure SI3. Relative NMR signal intensities for the vinyl signal of DMAm (for a 30 % w/w solution in water) at varied flow rates by a standard ^{1}H NMR routine (red crosses) and a presaturation solvent suppression routine (blue circles), for (a) a glass flow cell and (b) PFA tubing.

Comparison of kinetics obtained using a glass flow cell and PFA tubing

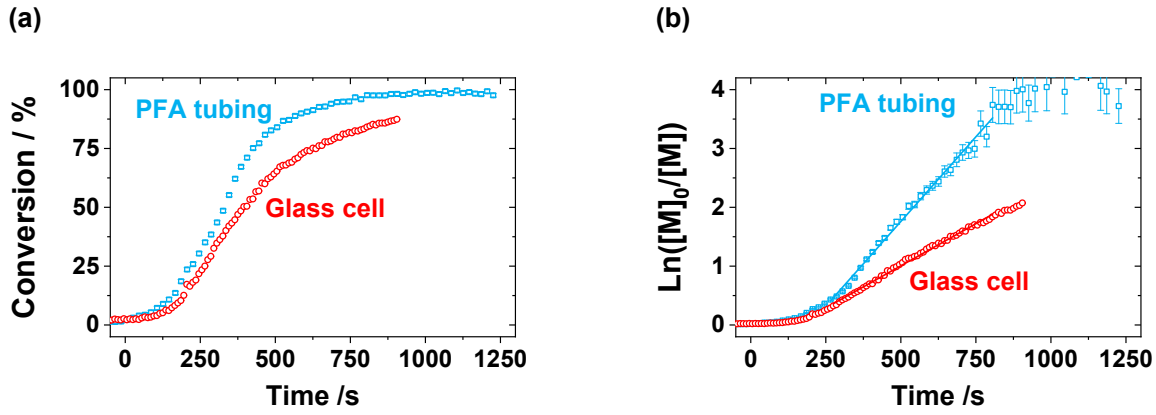

Figure SI4. (a) Conversion and (b) semi-logarithmic plot for the transient kinetic study of the polymerisation of dimethylacrylamide at 80 °C where the sampling was performed from a glass cell or from PFA tubing passed through the benchtop NMR spectrometer.

Calculation of conversion

Conversion (α), by definition, is the amount of monomer that has reacted – i.e. if there are no side reactions, "converted" into polymer. It can therefore be described mathematically by Equation 1.

$$\alpha = 1 - \frac{[M]}{[M]_0}$$

Equation 1. Conversion, where [M] is monomer concentration, and $[M]_0$ is concentration at time = 0.

Where there are no side reactions the initial monomer concentration can be replaced with the sum of the concentration of monomer and polymer (Equation 2).

$$\alpha = 1 - \frac{[M]}{[M] + [P]}$$

Equation 2. Conversion, where [M] is monomer concentration, and [P] is concentration of polymer.

Since NMR provides a measure of relative concentration of protons within the mixture it offers a route to investigation of conversion, though it at the very least requires a unique peak of one of the components (i.e. monomer or polymer). There are three options: (i) the preparation of samples of equal total concentration for the range of the kinetic study and use the concentration of monomer at t = 0 as per Equation 1 (and the monomer concentration at any time, t). Whilst the simplest approach, this method is not particularly robust because of its reliance on the constant overall concentration of the mixture and failure to correct for sample-to-sample variation (e.g. slight variations in NMR tube size). (ii) The insertion of an internal standard, which will yield a peak to which all others can be normalised – again then providing a different method to the plotting of Equation 1. This means any variation associated with sample to sample concentration is negligible. (iii) The use of Equation 2 by either summing separate peaks relating to monomer or polymer or, better, the use of a pendant peak which remains constant throughout. Clearly, the use of a larger peak (i.e. one relating to a larger number of protons) will reduce any errors associated with signal to noise.

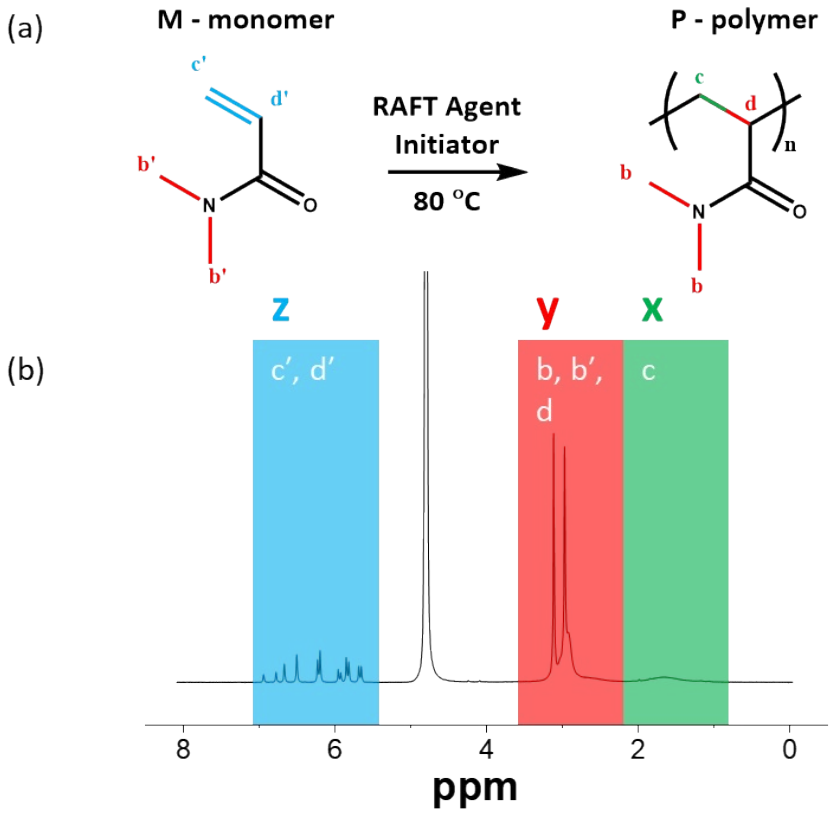

Figure SI5. (a) RAFT Polymerisation of dimethylacrylamide. (b) Assigned NMR spectrum of a partially converted polymerisation (approx. 50 % conversion).

As Figure SI5b shows, the integral of region z can be used to measure [M] (since no polymer protons are present in this region). [P] can be found using the integral of region x. This does allow for a solution of Equation 2. However, the integral of region y can be used to reduce the error in the measurement – by subtracting the appropriately proportion of the value found for [P] from region x, the integral represents [M] + [P], since protons b/b' are found in both. All values need to be normalised for the number of protons they represent.

If

$$2z = 6[M]$$

and

$$y - \frac{x}{2} = 6([M] + [P])$$

Then

$$\alpha = 1 - \frac{6[M]}{6([M] + [P])} = 1 - \frac{[M]}{[M] + [P]} = \frac{2z}{y - \frac{x}{2}}$$

Equation 3. Determination of conversion for the polymerisation of dimethylacrylamide

For the RAFT dispersion polymerisation of diacetone acrylamide (DAAm) in the preparation of (P($DMAm_{100}$-b-$DAAm_{200}$), the vinyl peak was normalised to that of a standard (3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt), before using Equation 1 to calculate conversion, where $[M]_0$ is simply the normalised integral of the first scan, and [M] the normalised integral at any time.

For the solution free radical polymerisation of methyl methacrylate, the conversion was calculated in a similar method to that for the RAFT polymerisation of DMAm. Aside from the vinyl peak at 6.25 to 5.30 ppm (region z), the peak from 2.17 to 0 ppm (region y) has contributions from the chemical structure of both monomer (3H) and polymer (5H). Therefore, the contribution of monomer towards that peak is subtracted to give a measure for the relative quantity of polymer. These values can then be used in Equation 2 to calculate conversion.

If

$$10[M] = 5z$$

and

$$10[P] = 10\left(\frac{y - 3[M]}{5}\right) = 2y - 3z$$

Then

$$\alpha = 1 - \frac{5z}{5z + (2y - 3z)} = 1 - \frac{5z}{2(z + y)}$$

Equation 4. Determination of conversion for the polymerisation of diacetone acrylamide in the preparation of poly(dimethylacrylamide$_{94}$-b-diacetoneacrylamide$_{200}$) by RAFT dispersion polymerisation.

Materials

2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, Wako Speciality Chemicals), dimethylacrylamide (DMAm, 99 %, Sigma Aldrich), deuterium oxide (D_2O, 99 %, Sigma Aldrich), diacetone acrylamide (DAAm, 99 %, Alfa Aesar), and 3-((((1-Carboxyethyl)thio)- carbonothioyl)thio) propanoic acid (CTTP, 90%, Boron Molecular (Raleigh, USA)) were all used as supplied.

Gel Permeation Chromatography

Gel permeation chromatography measurements were conducted using an Agilent 1260 Infinity system fitted with two 5 µm Mixed-C columns plus a guard column, a refractive index (RI) detector and an UV/vis detector operating at 309 nm. DMF containing 1.0% w/ v lithium bromide (LiBr) was used as eluent. The pump flow rate was set to 1.0 mL min^{-1} and the temperature of the column oven and RI detector were set to 60 °C. A series of ten near-monodisperse poly(methyl methacrylate) standards (M_p ranging from 800 to 2 200 000 g mol^{-1}) were employed as calibration standards in conjunction with the RI detector for determining molecular weights and molar mass dispersities (Đ).

Preparation of poly(dimethylacrylamide) macro-CTA by RAFT polymerisation

For all experiments a standard mixing procedure was used: DMAm (19.7 g, 100 eq.), CCTP (0.51 g, 1 eq.), VA-044 (0.0128 g, 0.02 eq.) were added to a round bottom flask and dissolved in water (47 mL) with stirring, giving a 30 % w/w solution, which was sealed and sparged with nitrogen for 30 minutes, then held under a positive pressure of nitrogen using a balloon.

Batch polymerisation

For the batch experiments, the solution was immersed in a hot oil bath (at 80 °C/85 °C as applicable) with stirring. Samples were obtained either by sampling using a syringe, or for the continuous sampling method, using a peristaltic pump (Ismatec REGLO Digital MS-2/12) at 0.345 mL min^{-1}, initially through 1/16" stainless steel tubing, before 1/8" PFA tubing passed directly through the NMR spectrometer (as per Figure 1a).

Transient flow polymerisation

The sparged solution was pumped (using a Jasco PU-980 HPLC pump) through a heated 5 mL stainless steel coil at 10 mL min^{-1} for 1.5 minutes, and then reduced to 0.315 mL min^{-1} (residence time ~16 mins). The outlet of the reactor was connected to the PFA tubing passed directly through the NMR spectrometer, with a 100 psi (7 bar) back-pressure regulator used at the end of the line (as per Figure 1b).

Preparation of poly(dimethylacrylamide$_{94}$-b-diacetoneacrylamide$_{200}$) by RAFT dispersion polymerisation

DAAm (5 g, 200 eq.), $PDMAm_{94}$ macro-CTA (1.41 g, 1 eq.), VA-044 (0.0010 g, 0.02 eq.) were added to a round bottom flask and dissolved in water (47 mL) with stirring, giving a 20 % w/w solution, which was sealed and sparged with nitrogen for 30 minutes, then held under a positive pressure of nitrogen using a balloon. The sparged solution was pumped through a stainless-steel coil at 80 °C at 10 mL min^{-1} for 1.5 minutes and then reduced to 0.315 mL min^{-1} (residence time ~16 mins). The outlet of the reactor was connected to the PFA tubing passed directly through the NMR spectrometer.

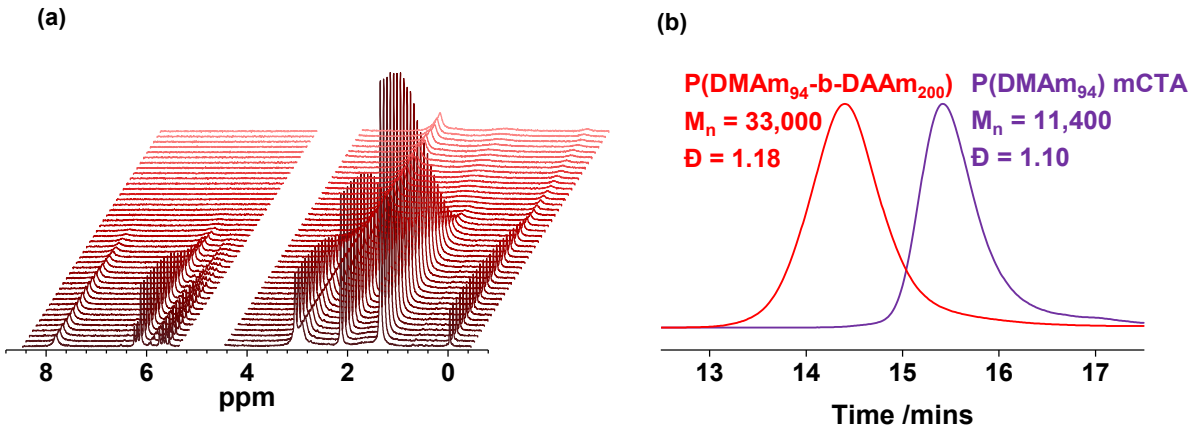

Figure SI6. (a) Waterfall plot of the polymerisation of diacetone acrylamide in the preparation of P(DMAm$_{94}$-b-DAAm$_{200}$) and (b) GPC chromatograms of PDMAm$_{94}$ macro CTA prepared by RAFT solution polymerisation and P(DMAm$_{94}$-b-DAAm$_{200}$) as prepared by RAFT dispersion polymerisation.

Preparation of poly(methyl methacrylate) by solution free radical polymerisation

Methyl methacrylate (15.00 g, 0.15 mol) and azobisisobutyronitrile (0.3050 g, 1.86 mmol) were dissolved in 1,4-dioxane (36 mL) to give a 30 % w/w solution, which was sparged with nitrogen for 30 minutes, then held under a positive pressure of nitrogen using a balloon. The sparged solution was heated to 85 °C. For offline measurements, samples were obtained using a purged syringe. For online measurements, 1/16'' stainless steel tubing was inserted through a septum and sampled using a peristaltic pump at 1 mL min^{-1}. Prior to entering the NMR spectrometer, the sample entered 1/8" PFA tubing connected to the stainless-steel tubing via an appropriate connector. This PFA tubing then passed directly through the NMR spectrometer (as per Figure 1a).

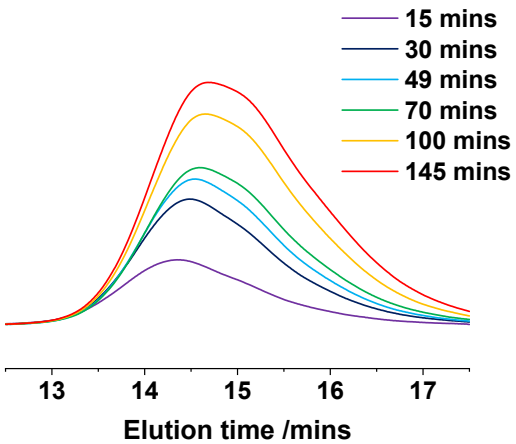

Figure SI7. GPC chromatograms for kinetic samples from the polymerisation of methyl methacrylate. The increase in signal is due to increased conversion, with a slight decrease in molecular weight also observed as the reaction progresses.