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Electronic Supporting Information

Bromoform-assisted aqueous free radical polymerisation: a simple, inexpensive route for the preparation of block copolymers

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Experimental

Materials

All materials were used as supplied without further purification. 4,4-Azobiscyanovaleric acid (ACPA, ≥98%), bromoform ($CHBr_3$, 96%, stabilised with ethanol), *N*-isopropylacrylamide (NIPAM, 97%) and *N,N*-dimethylacrylamide (DMA, 99%) were purchased from Sigma Aldrich. Deuterium oxide (D_2O, 99.9%) was purchased from Goss Scientific. Laboratory reagent grade diethyl ether, methanol (MeOH), tetrahydrofuran (THF) and HPLC grade water were purchased from Fisher Scientific.

The ultraviolet (UV) light source was a Philips Solarium Model MD 1-15 lamp comprising four parallel 15 W fluorescent tubes that emitted UV light in the 315-400 nm wavelength range. The vertical distance between the UV light source and the surface of the solution was fixed at 10 cm.

The UV irradiation is used to activate the ACPA photo-initiator in step 1. ACPA is known to photo-dissociate under UV irradiation (between 350[1] – 402[2] nm) to form two radicals capable of initiating the polymerisation described in step 1. Whilst it has been suggested in previous literature that bromoform photo-dissociates between 193 - 324 nm[3-7], we have no direct or indirect evidence of this occurring and thus suggest this process does not take place under the conditions used in this work (as the energy of the lamp is lower than the bond dissociation energy of a C-Br bond in bromoform). Instead, all of our data suggest that the role of bromoform in step 1 is only to impart the reversibly cleavable bromine chain end functionality on the PDMA chains (hence creating macro-initiator). Finally, the same UV lamp is employed in step 2 to dissociate the terminal C-Br bond of the PDMA macro-initiator to facilitate the growth of the second block. Finally, the UV lamp is employed in step 2 to dissociate the terminal C-Br bond from the PDMA macro-initiator to allow the second block to grow. A crude calculation based on the presence of a DMA monomer with a C-Br bond present[8,9] suggests that a wavelength of 442 nm would be required to cleave the C-Br bond. This shows that it is cleaved at a lower energy than the lamp (315-400 nm) and therefore the lamp is sufficient for homolytic cleavage process.

Methods

Bromoform-assisted polymerisation of *N,N*-dimethylacrylamide

N,N-dimethylacrylamide was polymerised via radical photopolymerisation in deionised water using a fixed bromoform concentration (0.0, 0.5, 1.0 and 2.0 mol %, relative to *N,N*-dimethylacrylamide monomer).

A typical experimental setup was as follows: a 50 mL round-bottomed flask was charged with 0.0565 g ACPA (2.02×10^{-4} mol; 1.0 mol % relative to *N,N*-dimethylacrylamide monomer) and HPLC water (25 mL) and stirred with heating (55 °C) for 1 hour to ensure full dissolution. After cooling to room temperature, bromoform ($CHBr_3$; 4.04×10^{-4} mol; 2.0 mol % relative to *N,N*-dimethylacrylamide monomer) and 2.00 g DMA monomer (0.0202 mol) was added to the reaction flask, which was sealed with a rubber septum and parafilm. The clear solution was degassed via vacuum and nitrogen cycles over a period of 15 minutes before being placed into an ice bath for 20 minutes. The reaction flask and ice bath was then placed in an aluminium cabinet with magnetic stirring and irradiated with UV light from above for 60 minutes. An increase in solution viscosity was observed over the course of the reaction. For kinetic studies, 0.1 mL of the reaction solution was removed periodically for analysis by gel permeation chromatography (GPC) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The resulting PDMA was isolated by removing the water via lyophilisation and redissolving in methanol before dropwise precipitation into a five-fold excess of chilled diethyl ether. The supernatant was then decanted and the PDMA was washed with the same solvent. The homopolymer precipitate was then dried in a vacuum oven to remove excess solvent (175 mbar, 40 °C) until constant weight was achieved to produce the final white solid.

This reaction was also scaled up, at 2 mol % bromoform (relative to monomer) to produce 20 g of PDMA macro-initiator for use in future block copolymer reactions (93 % yield).

Bromoform-assisted polymerisation of *N*-isopropylacrylamide

N-isopropylacrylamide was polymerised via radical photopolymerisation in deionised water using a fixed bromoform concentration (0.0, 0.5, 1.0 and 2.0 mol %, relative to *N*-isopropylacrylamide monomer).

A typical experimental setup was as follows: A 50 mL round-bottomed flask was charged with 0.0496 g ACPA (1.77×10^{-4} mol; 1.0 mol % relative to *N*-isopropylacrylamide monomer) and HPLC water (25 mL) and stirred with heating (55 °C) for 1 hour to ensure full dissolution. After cooling to room temperature, bromoform ($CHBr_3$; 3.53×10^{-4} mol; 2.0 mol % relative to *N*-isopropylacrylamide monomer) and 2.00 g NIPAM monomer (0.0177 mol) was added to the reaction flask which was sealed with a rubber septum and parafilm. The clear solution was degassed via vacuum and nitrogen cycles over a period of 15 minutes before being placed into an ice bath for 20 min. The reaction flask and ice bath was then placed in an aluminium cabinet with magnetic stirring and irradiated with UV light from above for 30 minutes. An increase in solution viscosity was observed over the course of the reaction. For kinetic studies, 0.1 mL of the reaction solution was removed periodically for analysis by GPC and

^{1}H NMR spectroscopy. The resulting PNIPAM was isolated by dropwise precipitation into a five-fold excess of warm (40 °C) HPLC water. The supernatant was then decanted and the PNIPAM was washed with the same solvent. Residual water was then removed using lyophilisation to produce the final white solid (96 % yield for the 20 g batch).

Synthesis of poly(*N,N*-dimethylacrylamide)-*block*-poly(*N*-isopropylacrylamide) [PDMA-*b*-PNIPAM]

The synthesis of PDMA-*b*-PNIPAM was conducted using a PDMA macro-initiator (PDMA-Br, synthesised using 2.0 mol % bromoform and 1.0 mol% ACPA, and purified as described above) as follows: A 50 mL round-bottomed flask was charged with PDMA-Br (1.00 g; 0.0101 mol), NIPAM monomer (at 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 molar ratios of DMA:NIPAM) and HPLC-grade water (25 mL). The clear solution was sealed using a rubber septum and parafilm and degassed via vacuum and nitrogen cycles over a period of 15 minutes before being placed into an ice bath for 20 minutes. Finally, the reaction flask and ice bath were placed in an aluminium cabinet with magnetic stirring and irradiated with UV light for 120 minutes.

All PDMA-*b*-PNIAM samples were isolated by the following process: deionised water was removed via lyophilisation, then the copolymer was dissolved in the minimum amount of tetrahydrofuran prior to dropwise precipitation into five-fold excess of chilled diethyl ether. This precipitation step was repeated a further three times before washing with the same solvent. After the final precipitation step, residual solvent was removed *in vacuo* before lyophilisation until constant weight was achieved to produce the final white solid (average yield of 88 %).

Characterisation

^{1}H nuclear magnetic resonance (NMR) spectroscopy was performed using a 300 MHz Bruker Avance Spectrometer. Samples were dissolved in D_2O. ^{1}H NMR was used to calculate monomer conversion throughout the polymerisations. Specifically, the integrals of the vinyl monomer peaks (5.7, 6.0 and 6.6 ppm) were compared to the integral for the methyl group protons in the polymer (2.9 ppm) for the polymerisation of *N,N*-dimethylacrylamide. For the kinetic studies of poly(*N*-isopropylacrylamide) the integrals of the vinyl monomer peaks (5.6 and 6.0 ppm) were compared to the integrals of the methyl group protons in the polymer (1.0 ppm). *Gel permeation chromatography (GPC)* was performed at 40 °C using an Agilent Infinity II multi-detector GPC comprising two PL gel Mixed-C columns and a guard column. The eluent solution consisted of HPLC-grade DMF containing 0.10% w/v lithium bromide (LiBr) and the flow rate was 1.0 mL min^{-1}. Calibrations were generated using near monodispersed poly(methyl methacrylate) standards (M_p range = 550 to 2,210,000 g mol^{-}

[1]) and experimental data were analysed using Agilent GPC/SEC software (Version A.02.01) supplied by Agilent Technologies. *Differential scanning calorimetry (DSC)* measurements were performed using a Metller Toledo DSC 1 system under a nitrogen atmosphere (20 mL min^{-1}) at a heating rate 10 °C min^{-1} from 0 to 200 °C, and analysis was conducted using STARe software (Version 12.0). *Thermogravimetric analysis (TGA)* was performed using a Pyris 1 thermogravimetric analyser under nitrogen atmosphere (flow rate 25 mL min^{-1}). All samples were heated between 100-600 °C at a heating rate of 10 °C min^{-1}.

Results and discussion

Synthesis of poly(*N,N*-dimethylacrylamide)

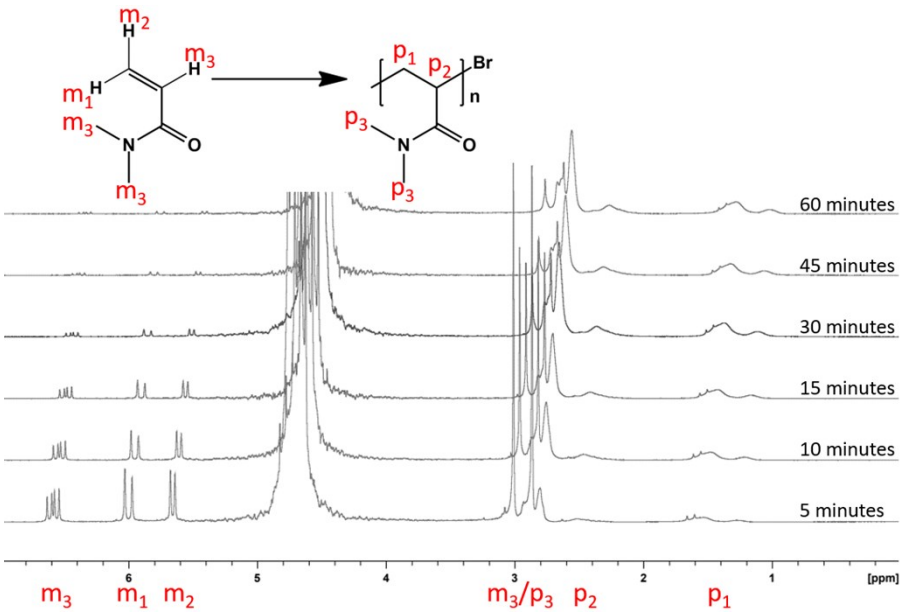

Figure S1. [1]H NMR kinetic overlay for the synthesis of PDMA at 0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

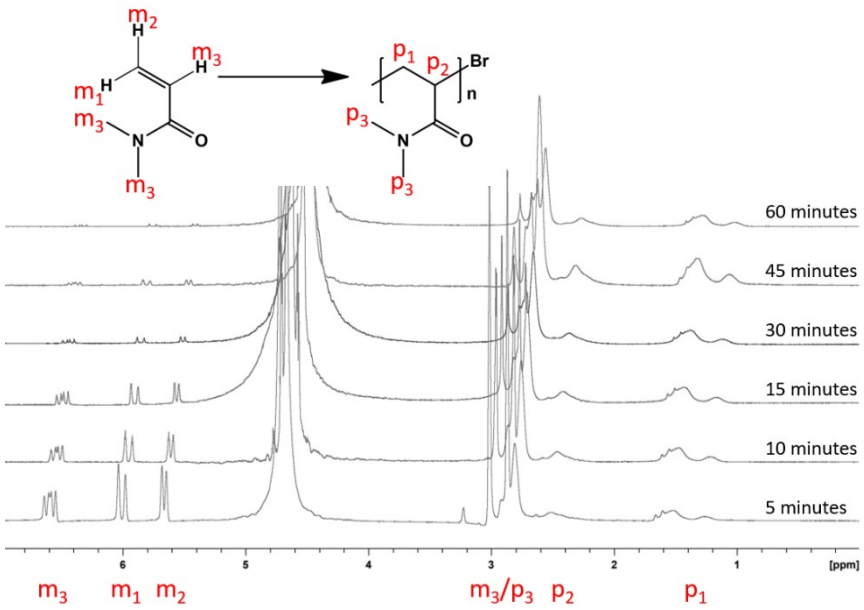

Figure S2. ^{1}H NMR kinetic overlay for the synthesis of PDMA at 0.5 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

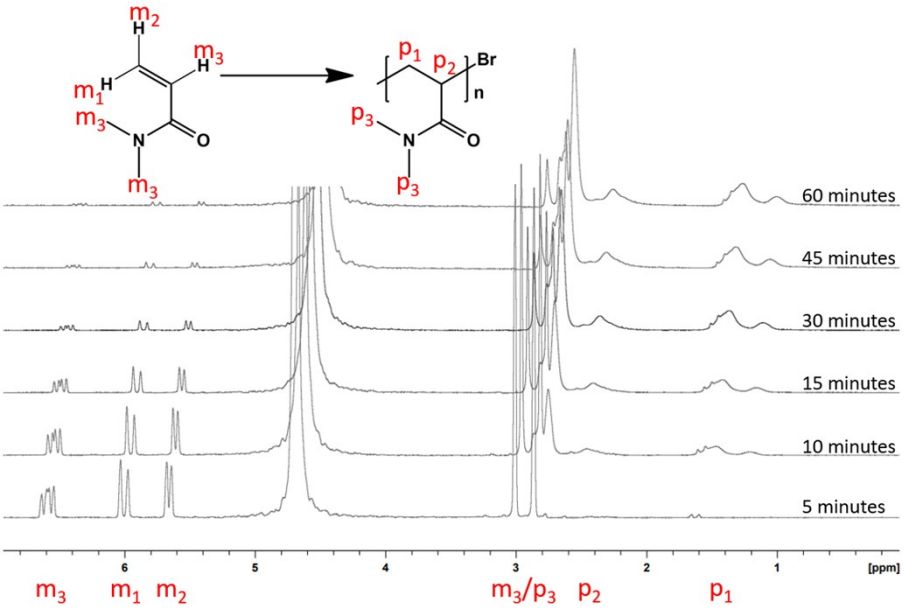

Figure S3. ^{1}H NMR kinetic overlay for the synthesis of PDMA at 1.0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

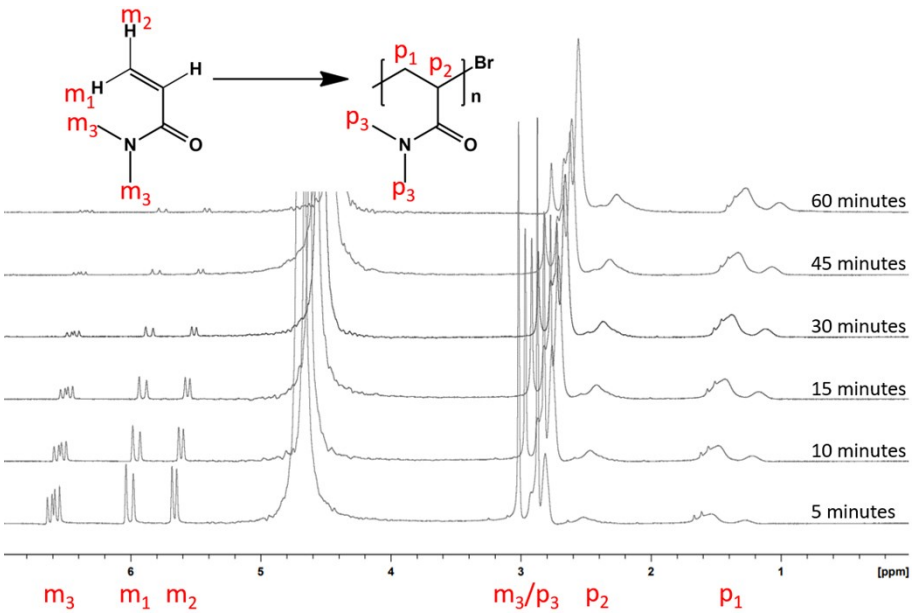

Figure S4. ^{1}H NMR kinetic overlay for the synthesis of PDMA at 2.0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

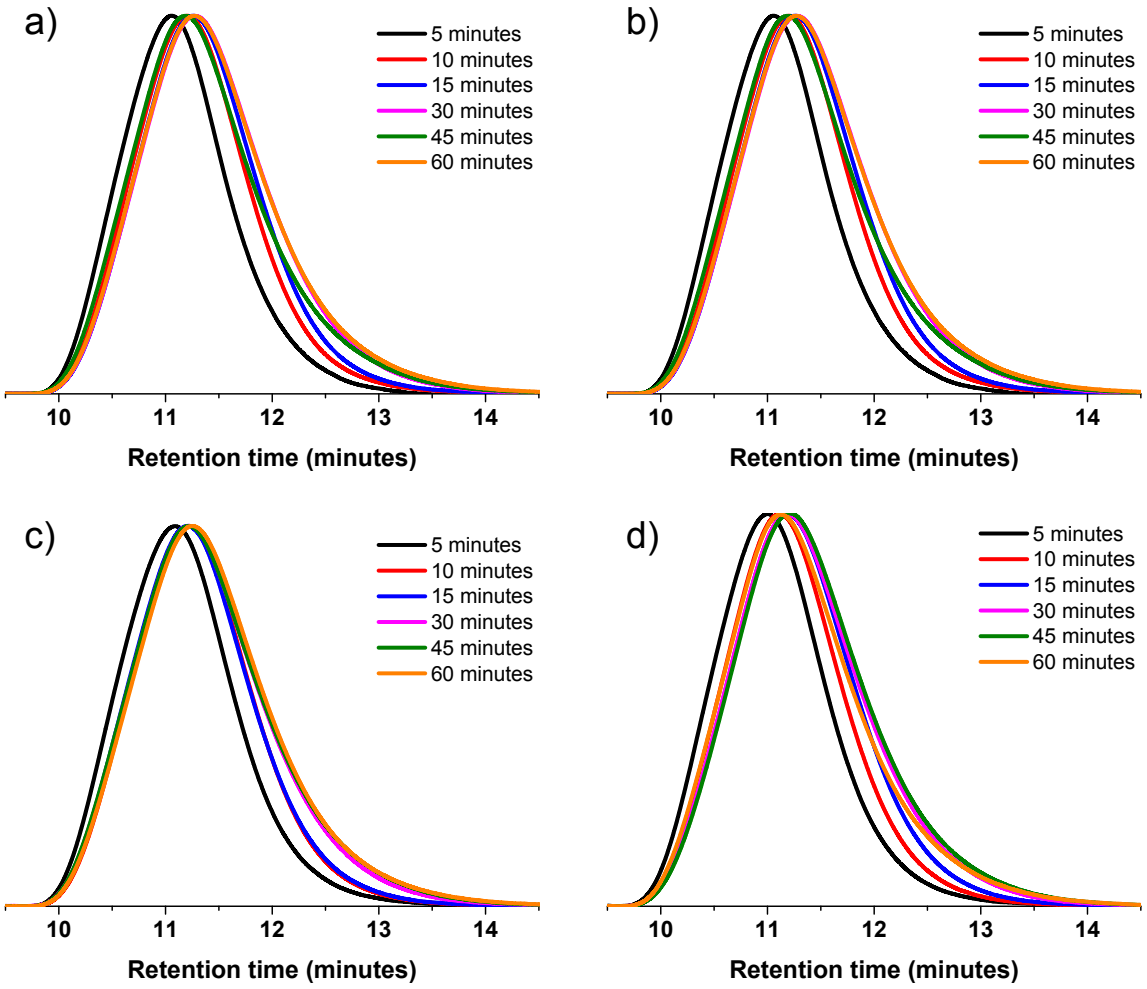

Figure S5. Kinetic GPC traces for the synthesis of PDMA in HPLC water at a) 0 mol %, b) 0.5 mol %, c) 1.0 mol % and d) 2.0 mol % bromoform (relative to monomer).

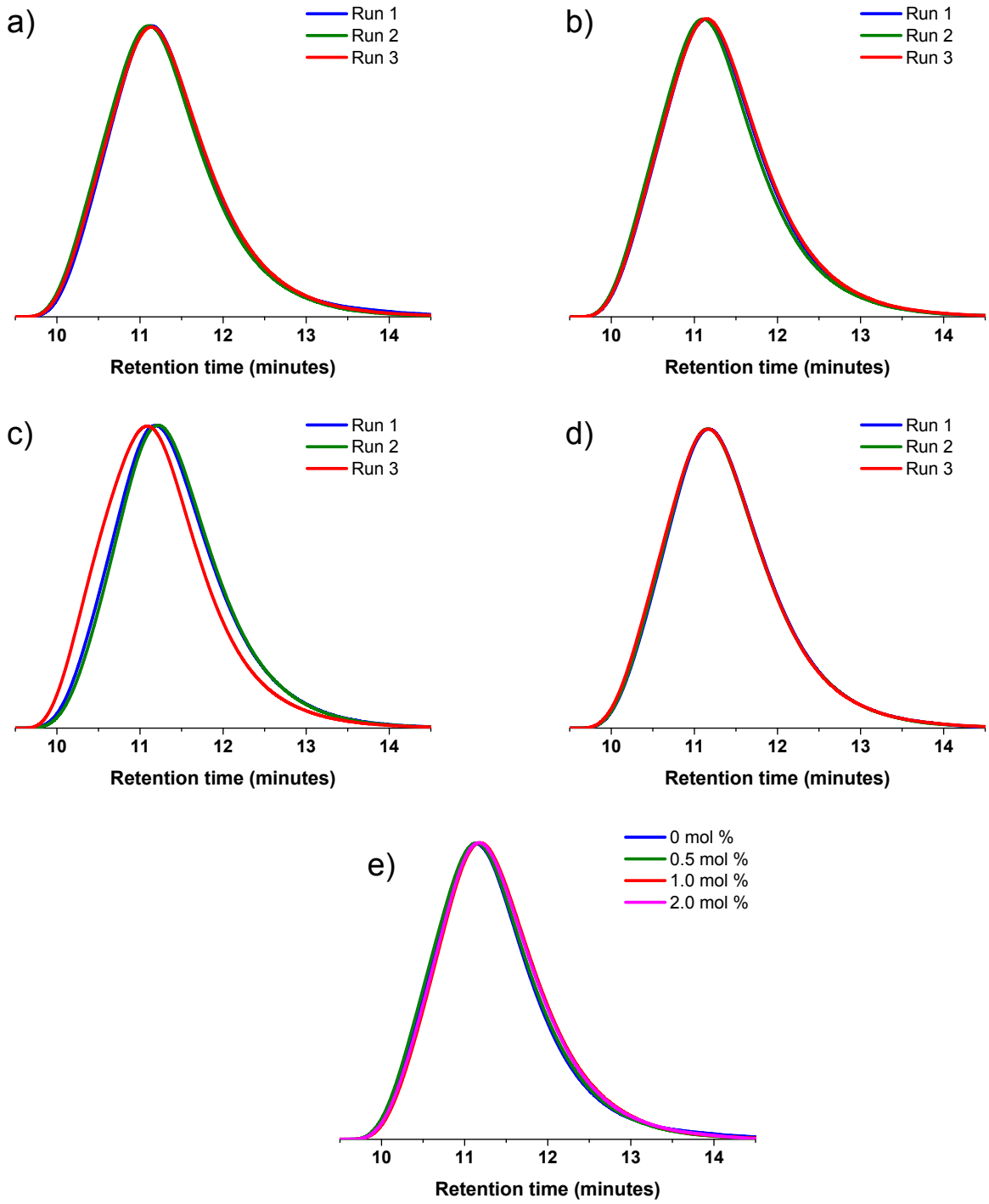

Figure S6. GPC traces of PDMA final precipitates at a) 0 mol %, b) 0.5 mol %, c) 1.0 mol % and d) 2.0 mol % bromoform (relative to monomer) demonstrating good repeatability between runs and e) near-identical GPC traces of the final precipitate at each bromoform concentration.

Synthesis of poly(*N*-isopropylacrylamide)

The effect of bromoform on the homopolymerisation of *N*-isopropylacrylamide was studied by monitoring monomer conversion and number-average molar mass (M_n) using ^{1}H NMR (Figure S7-Figure S10) and GPC (Figure S11), respectively. High monomer conversions (≥ 88 %) were achieved in each case, however, the M_n of the resulting PNIPAM showed no apparent trend with increasing bromoform concentration present (see data summarised in Table S1). All samples were of a similar molar mass and the final GPC traces show good repeatability at all bromoform concentrations (Figure S12). The molar mass dispersity, *Đ*, of the final PNIPAM samples was high (2.2-2.4), with no suggested relationship between *Đ* and bromoform content.

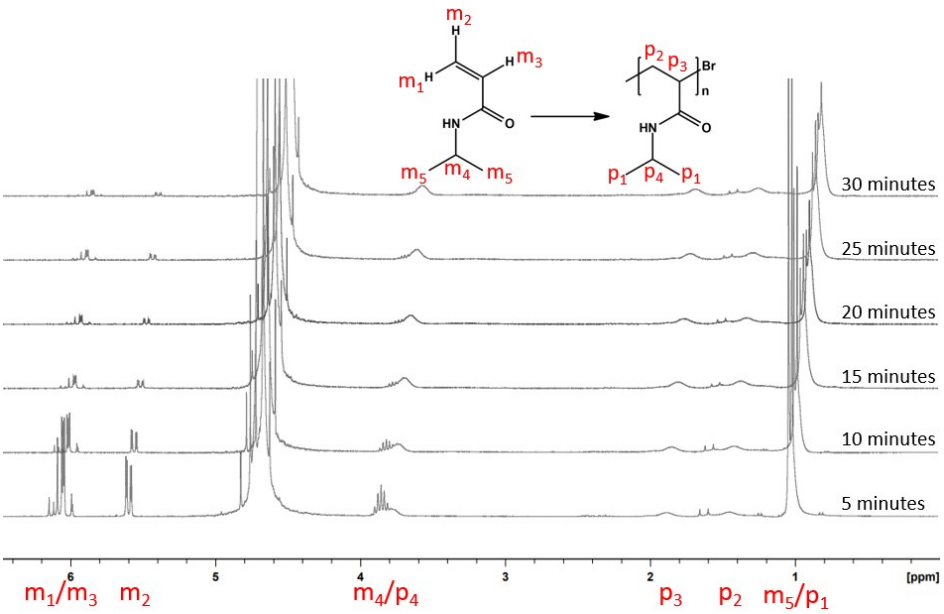

Figure S7. ^{1}H NMR kinetic overlay for the synthesis of PNIPAM at 0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

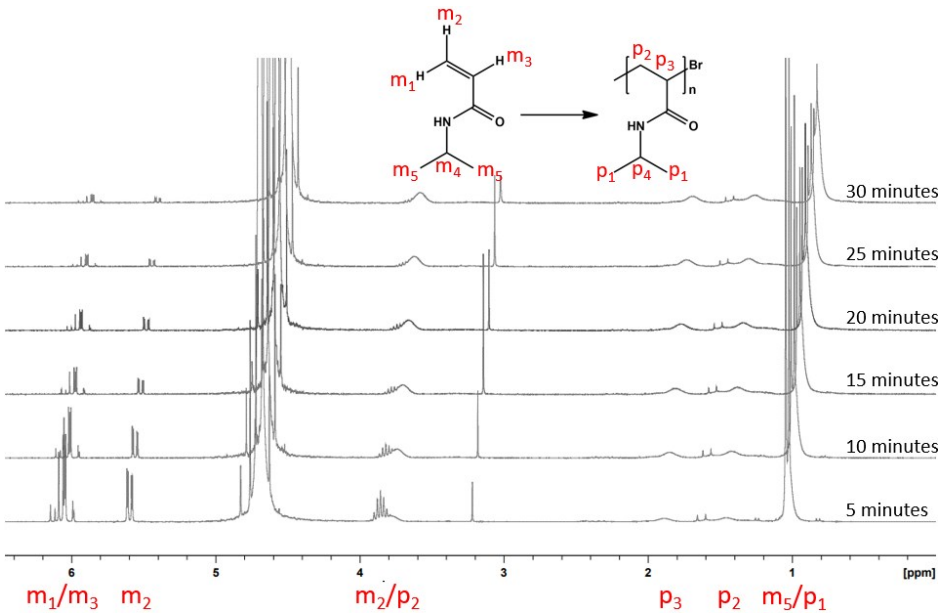

Figure S8. ^{1}H NMR kinetic overlay for the synthesis of PNIPAM at 0.5 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

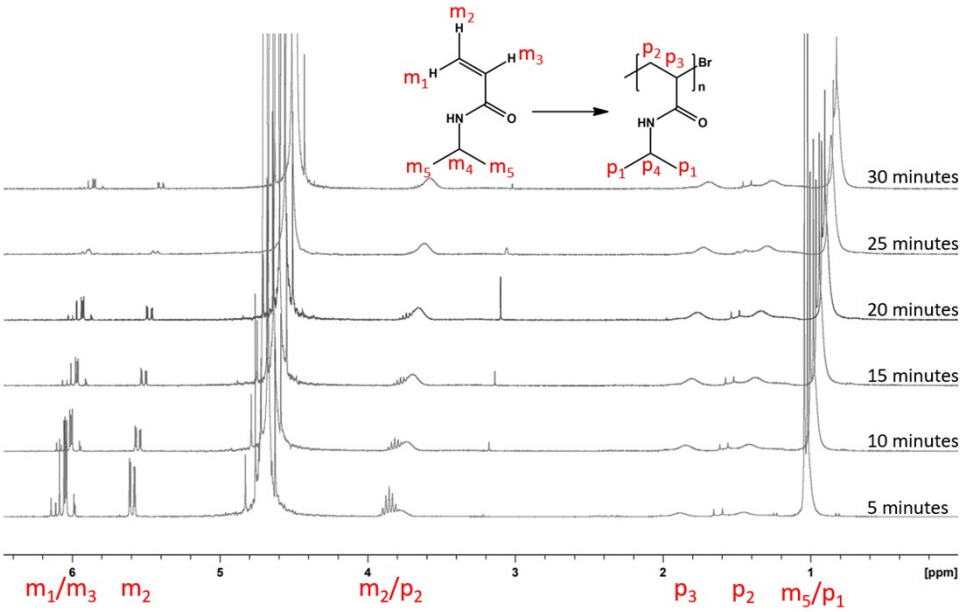

Figure S9. ^{1}H NMR kinetic overlay for the synthesis of PNIPAM at 1.0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

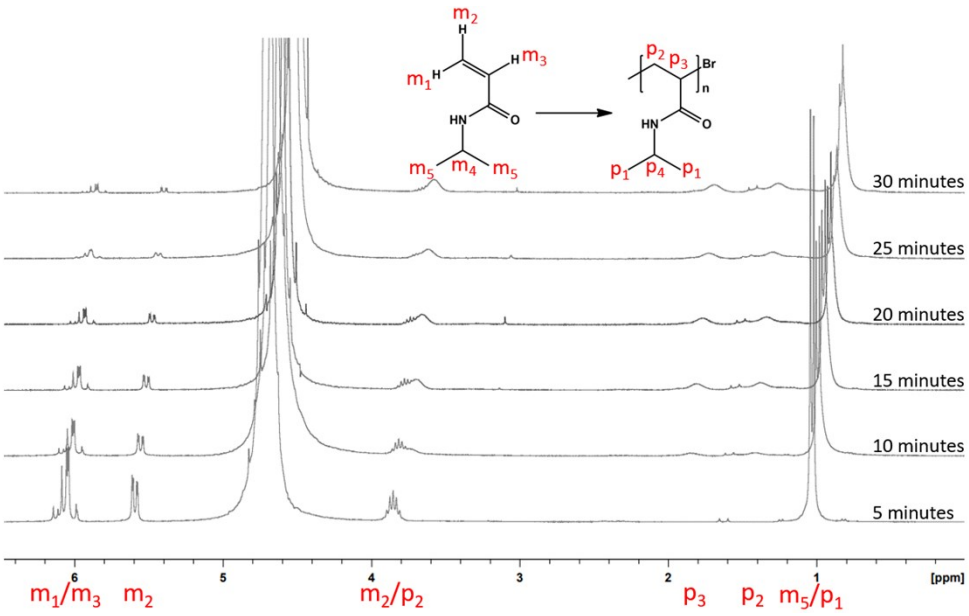

Figure S10. ^{1}H NMR kinetic overlay for the synthesis of PNIPAM at 2.0 mol % bromoform showing the disappearance of monomer and broadening of polymer peaks throughout the course of the reaction.

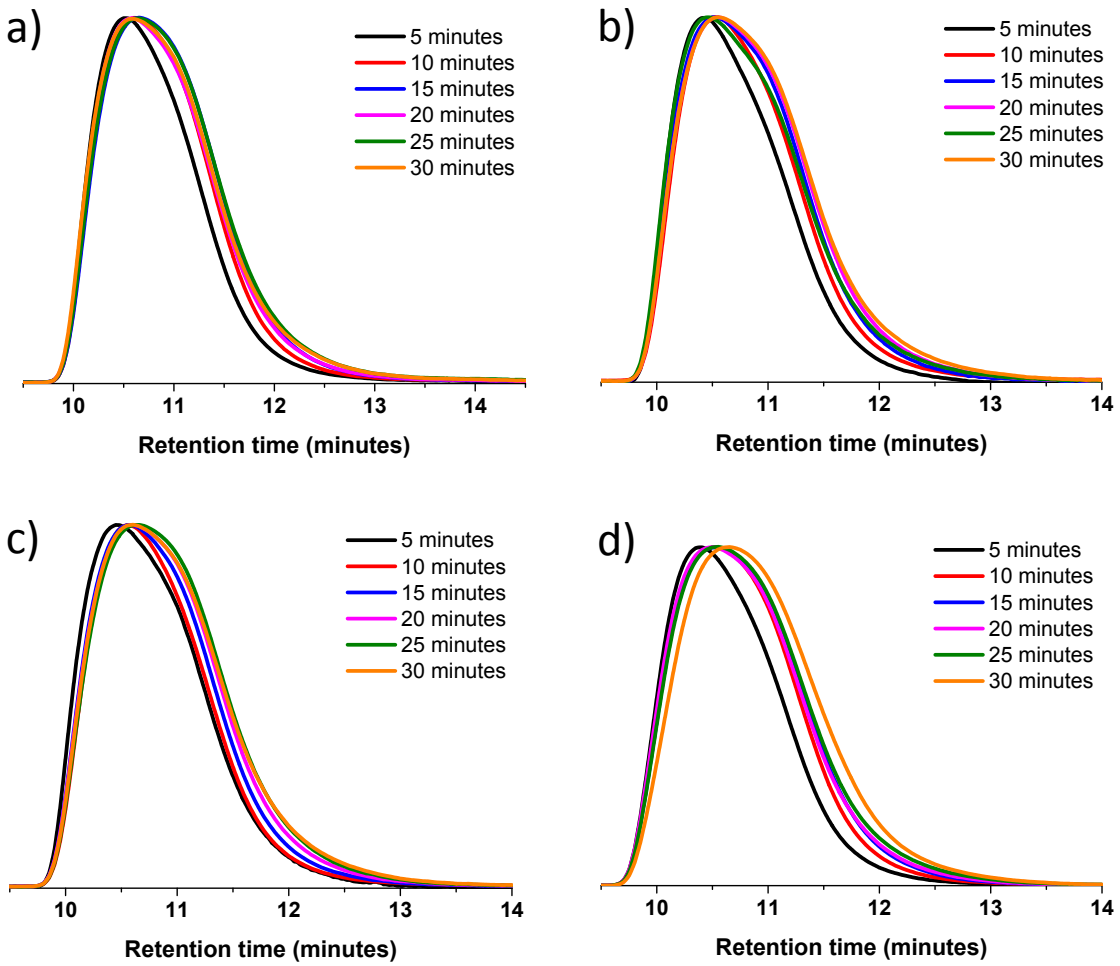

Figure S11. Kinetic GPC traces for the synthesis of PNIPAM at a) 0 mol %, b) 0.5 mol %, c) 1.0 mol % and d) 2.0 mol % bromoform (relative to monomer).

Table S1. Summary of final % conversion, M_n and $Đ$ data for the polymerisation of *N*-isopropylacrylamide at varied bromoform concentrations. All experiments were completed with 1.0 mol % ACPA (relative to monomer) in 25 mL deionized water for 1 hour of UV irradiation.

Bromoform (mol %)[a]	Final monomer conversion (%)[b]	M_n[c] (kg mol^{-1})	$Đ$[c] (M_w/M_n)
0	92	521.1	2.4
0.5	88	532.6	2.2
1.0	92	535.2	2.2
2.0	91	530.2	2.2

a) Relative to DMA monomer.
b) Calculated using ^{1}H NMR spectroscopy and Equations S1.
c) Determined by DMF GPC using poly(methyl methacrylate) standards.

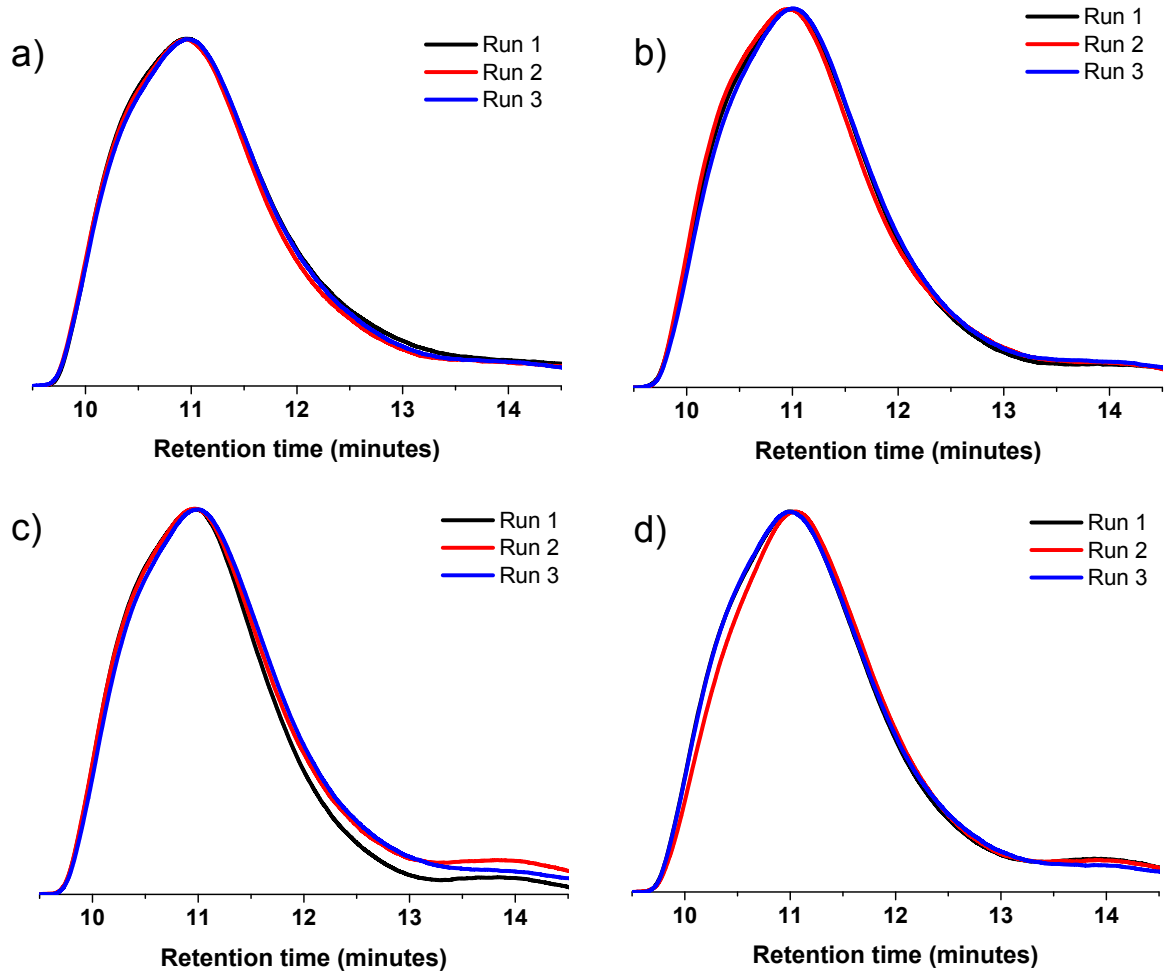

Figure S12. GPC traces of PNIPAM final precipitates (synthesised in HPLC water) at a) 0 mol %, b) 0.5 mol %, c) 1.0 mol % and 2.0 mol % bromoform (relative to monomer) demonstrating good repeatability between runs.

Kinetic studies performed during the polymerisation of *N*-isopropylacrylamide [Figure S13(a) and Figure S13(c)] show little to no difference in polymerisation rate at all bromoform concentrations. Figure S13(b) indicates that the PNIPAM M_n decreases as the polymerisation proceeds, which is typical for free radical polymerisations due to high initial rates of propagation leading to the formation of high molar mass chains, before the monomer concentration is reduced and thus shorter polymer chains are synthesised, resulting in a reduction in the M_n.[10–12]

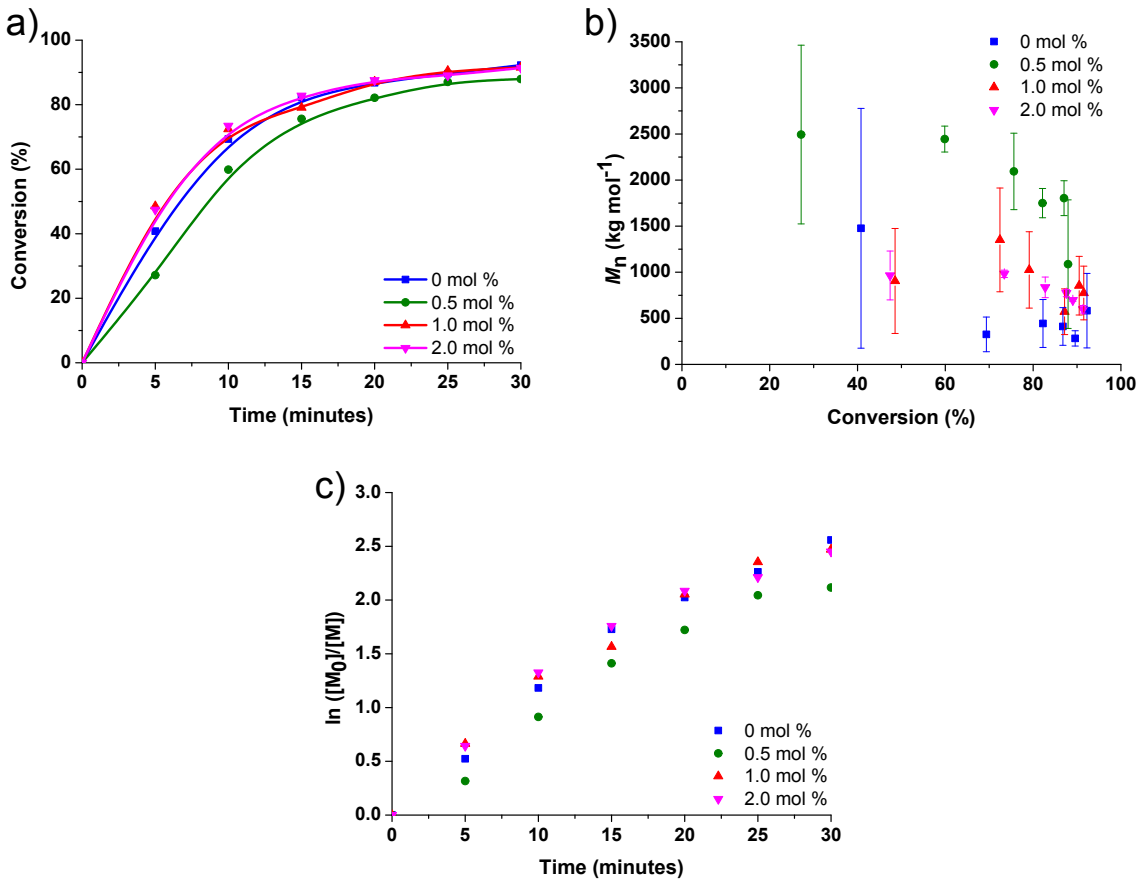

Figure S13. Summary of the kinetic data obtained for the polymerisation of *N*-isopropylacrylamide at varied bromoform content: (a) monomer conversion with time; (b) M_n versus monomer conversion; and (c) semi-logarithmic first-order plot.

Equation S1 is used to calculate % monomer conversion from ^{1}H NMR for PDMA and PNIPAM syntheses. The numerator (monomer) is the average vinylic monomer integral (present at 5.7, 6.0 and 6.6 ppm for DMA or at 5.6 and 6.0 ppm for NIPAM) and the denominator (monomer + polymer) refers to the sum of the integral for the methyl protons (present at 2.9 ppm for PDMA or 1.0 ppm for PNIPAM).

$$\frac{monomer}{monomer + polymer} = \frac{1 - x}{6(1 - x) + 6x}$$ **Equation S1.**

Control experiments for poly(*N,N*-dimethylacrylamide)-*block*-poly(*N*-isopropylacrylamide)

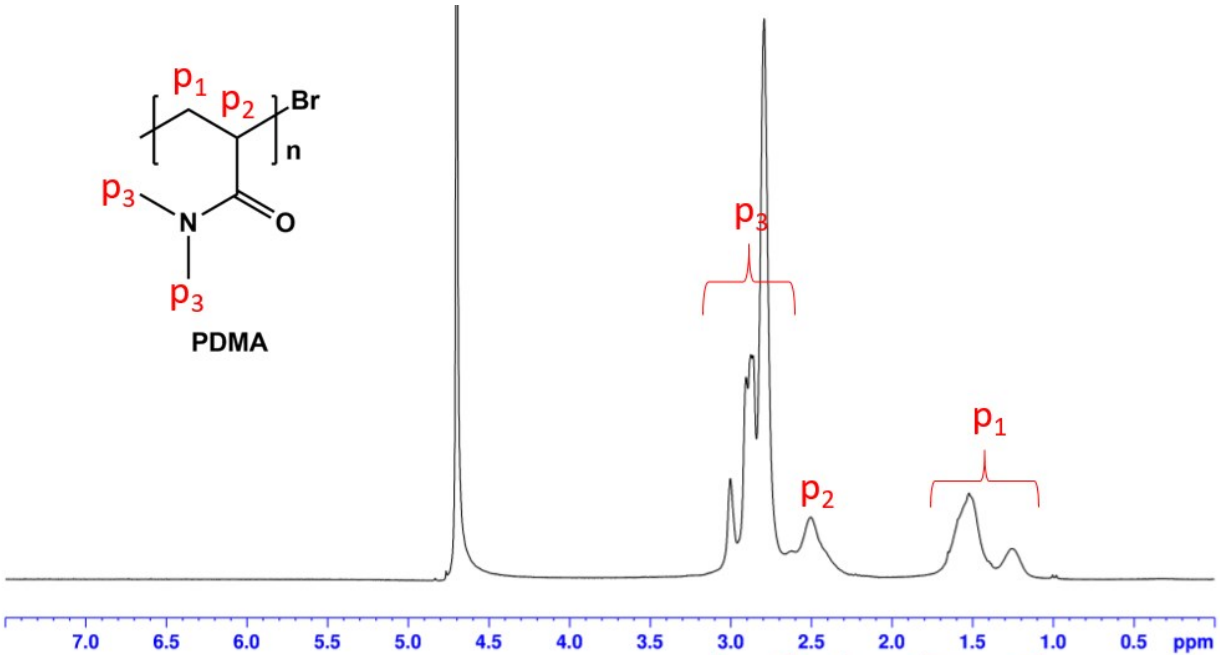

Figure S14. ^{1}H NMR of PDMA macro-initiator showing no residual monomer peaks present in the sample.

Figure S15 shows the ^{1}H NMR spectra obtained for the reactions without ACPA (after 7 hours of UV exposure), and highlights that, even with extended UV exposure, NIPAM will not polymerise under these conditions since only the NIPAM monomer peaks are present. Additionally, the reaction without ACPA or bromoform (0% bromoform in Figure S15) also indicates that NIPAM will not self-polymerise under the described conditions.

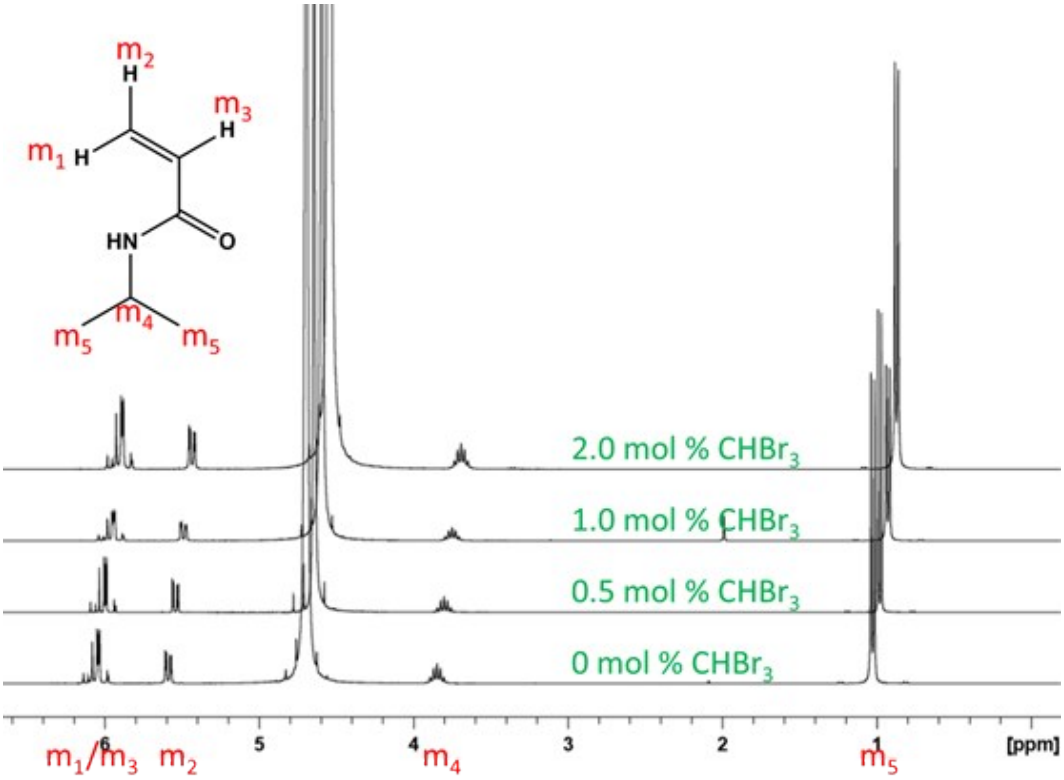

Figure S15. ^{1}H NMR spectra showing only monomer peaks present for the attempted synthesis of PNIAPM in the absence of photoinitiator (namely ACPA) at varied bromoform (0, 0.5, 1.0 and 2.0 mol % relative to monomer) concentrations. All experiments were completed in 25 mL deionized water for 7 hours of UV irradiation (starting temperature 0 °C, ice bath replenished every 1 hour to maintain temperature control).

Equation S2 was used to calculate the target degree of polymerisation of the NIPAM block in PDMA-*b*-PNIPAM copolymers:

$$\frac{DP\ of\ PDMA\ starting\ block}{DMA\ ratio\ in\ block\ copolymer} \times NIPAM\ target\ ratio\ in\ block\ copolymer \qquad \textbf{Equation S2.}$$

Equation S3 was used to calculate the average experimental degree of polymerisation of the NIPAM block in PDMA-*b*-PNIPAM copolymers:

$$\frac{Conversion\ of\ NIPAM\ block}{100} \times target\ DP \qquad \textbf{Equation S3.}$$

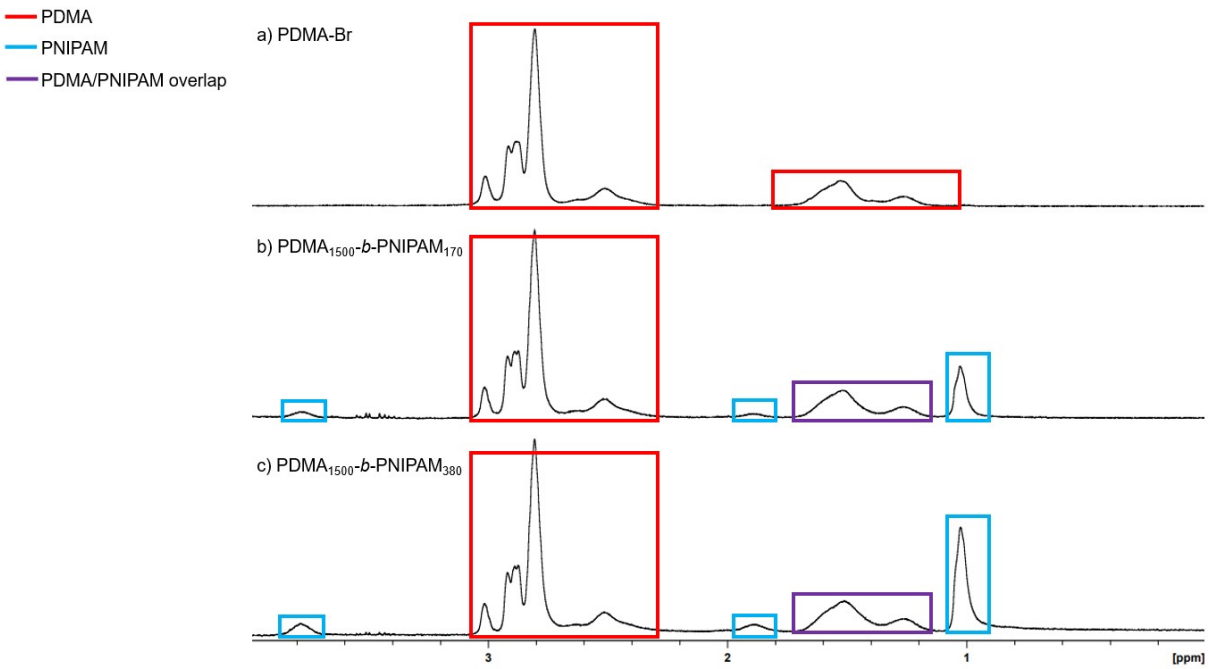

Figure S16. ^{1}H NMR spectra showing (a) PDMA-Br, (b) $PDMA_{1500}$-*b*-$PNIPAM_{170}$ and (c) $PDMA_{1500}$-*b*-$PNIPAM_{380}$ after precipitation, indicating the presence of PNIPAM in the block copolymers.

Figure 3(c) [main manuscript] and Figure S17(c) show the ^{1}H NMR spectra obtained after the reaction in which no bromoform was used to synthesise the PDMA during step 1, and are directly compared to the ^{1}H NMR spectra of the PDMA-Br macro-initiator [Figure 3(a) main manuscript and Figure S17(a)] and a successful PDMA$_{1500}$-*b*-PNIPAM$_{3330}$ block copolymer [Figure 3(b) main manuscript after precipitation and Figure S17(b) before precipitation].

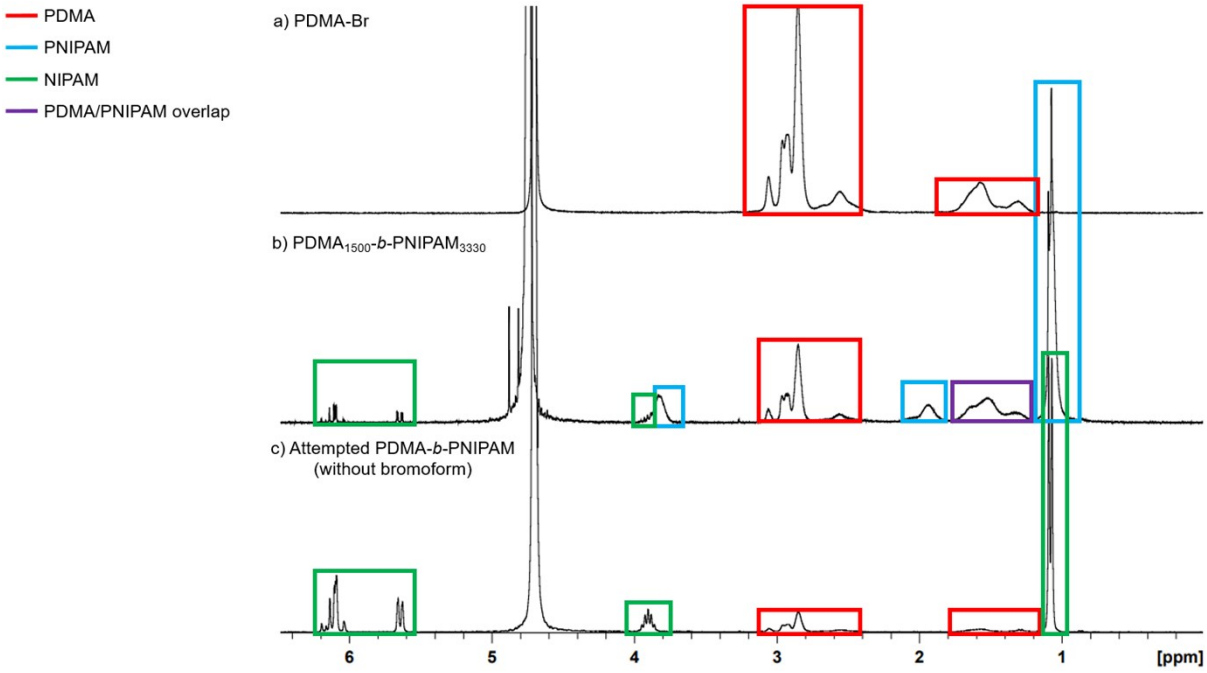

Figure S17. ^{1}H NMR spectra showing (a) PDMA-Br after precipitation, (b) PDMA$_{1500}$-*b*-PNIPAM$_{3330}$ before precipitation and (c) the attempted synthesis of PDMA$_{1500}$-*b*-PNIPAM$_{3500}$ from PDMA (0 mol % bromoform), where no PNIPAM peaks are present.

It is common for diblock copolymers to display individual glass transition temperatures (T_g values) corresponding to each constituent polymer block. Importantly, DSC analysis, as summarised in Table S2 and Figure S18, indicates the presence of two distinct T_g features for all PDMA-*b*-PNIPAM copolymers. In all cases, the first T_g (T_{g1}) is observed between 65 - 97 ^{o}C, which is closest to the experimentally determined T_g value of the PDMA-Br macro-initiator (121 °C). All T_{g1} values were either within or lower (≤ 25 ^{o}C) than the reported literature range for PDMA homopolymer (89 - 130 °C)[13–18]. The second T_g (T_{g2}) was observed between 125 and 143 °C for all copolymers. Again, all T_{g2} values were either within or slightly lower (≤ 10 ^{o}C) than the available literature values for the T_g of PNIPAM homopolymer (135-142 °C)[19–21].

Table S2. T_g values for PDMA macro-initiator, PNIPAM homopolymer (2 mol % bromoform relative to monomer) and subsequent block copolymers.

Sample	T_{g1} (°C)	T_{g2} (°C)
$PDMA_{1500}$	121	-
PNIPAM (2 mol %)	-	143
$PDMA_{1500}$-*b*-$PNIPAM_{170}$	78	125
$PDMA_{1500}$-*b*-$PNIPAM_{380}$	73	126
$PDMA_{1500}$-*b*-$PNIPAM_{640}$	76	131
$PDMA_{1500}$-*b*-$PNIPAM_{1000}$	70	132
$PDMA_{1500}$-*b*-$PNIPAM_{1500}$	69	125
$PDMA_{1500}$-*b*-$PNIPAM_{2300}$	65	138
$PDMA_{1500}$-*b*-$PNIPAM_{3500}$	71	138
$PDMA_{1500}$-*b*-$PNIPAM_{6000}$	74	133

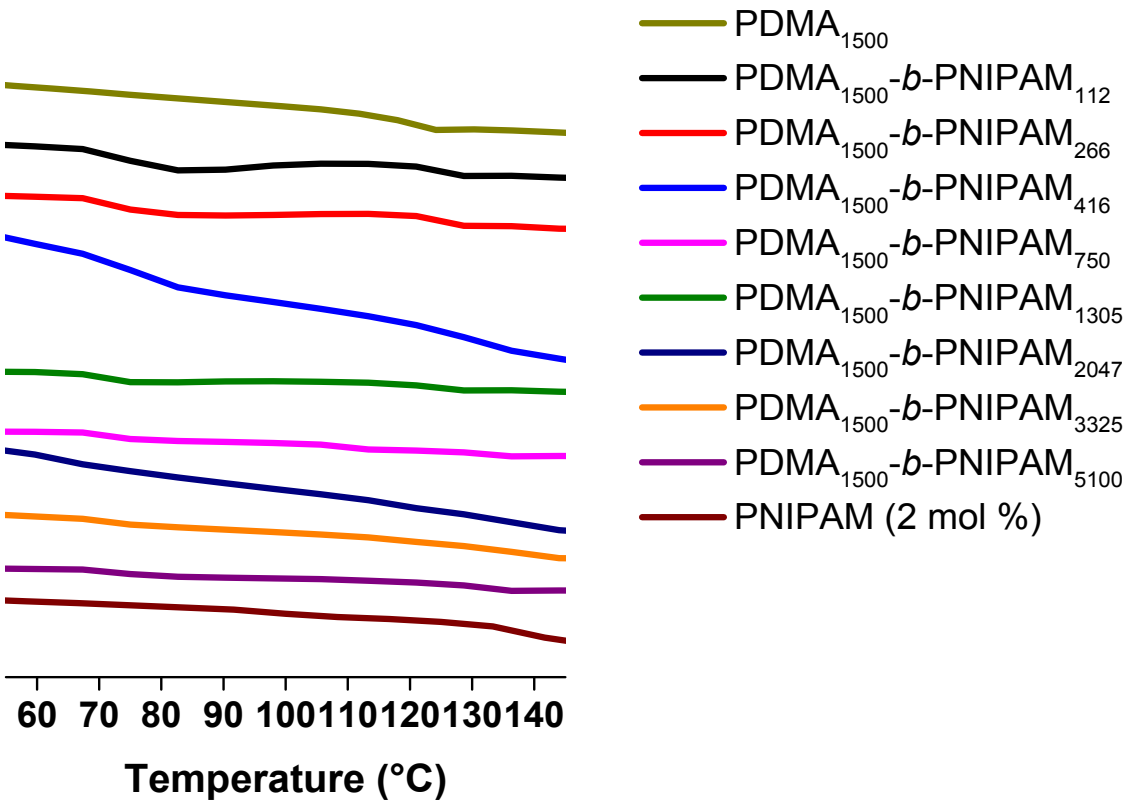

Figure S18. DSC traces showing T_g transitions of the PDMA macro-initiator, subsequent PDMA-*b*-PNIPAM block copolymers and a PNIPAM homopolymer (2.0 mol % bromoform).

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