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

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In the quest for commercially relevant block copolymer additives, for which overall average molecular composition is key but molar mass distribution is of little importance, we present a straightforward, sulfur- and metal-free aqueous route to block copolymers using commercially available starting materials. Based on synthetic techniques first described in the 1950s for hydrophobic monomers in organic solvents, we have shown that bromoform ($CHBr_3$) can be used to create block copolymers. Unlike common bromine-containing chain transfer agents such as carbon tetrabromide (CBr_4), bromoform is partially water-miscible and relatively inexpensive. Herein, we demonstrate this new aqueous-based technology using N,N-dimethylacrylamide (DMA) and N-isopropylacrylamide (NIPAM) as exemplar monomers to synthesise PDMA-b-PNIPAM block copolymers of varying composition directly in water. This study demonstrates the potential for such a simple, inexpensive route to functional block copolymers where further research to decipher the detailed mechanism and true potential of this technique will be of great value.

The last three decades have marked unprecedented advances in polymer chemistry, with the advent of reversible-deactivation radical polymerisation (RDRP) techniques such as nitroxide-mediated polymerisation[1–3] (NMP), atom transfer radical polymerisation[2,4–8] (ATRP) and reversible addition–fragmentation chain transfer[1,2,9–14] (RAFT) polymerisation, enabling the production of a wide range of well-defined block copolymers. Such well-defined macromolecules are crucial for structure–property relationship studies,[15] bulk block copolymer self-assembly (where low mass dispersities are required to produce sharp nanophase boundaries[16–19]) and in the pursuit

of sequence-controlled macromolecules for biomimicry.[20–22] Despite the drive for narrow molar mass distributions, this is not always necessary to prepare materials with desired characteristics and performance.[23–30] In industrial settings, polymers with broader molar mass distributions are often easier to process[31] and the breadth and shape of the molar mass distribution[32] can impart desirable physical properties (*e.g.* processability).[33,34] Indeed, Parker *et al.*[35] reported the synthesis of block copolymers *via* RAFT dispersion polymerisation with high molar mass dispersity values (*Đ* > 3) that self-assembled into extremely well-defined spherical nanoparticles which show promise as friction reduction agents in automotive engine oil.[36]

One of the drawbacks of conventional RDRP techniques is that they often rely on toxic transition metals,[4] sulfur[37–41] or unstable compounds[42] to provide control and often produce inherently coloured polymers (*e.g.* in the case of RAFT). Indeed, recent work by Haddleton *et al.*[43] elegantly highlights one of the challenges in polymer chemistry; the need to produce block copolymers without the use of sulfur or transition metals. Their group utilised ω-unsaturated oligomers as chain transfer agents, similar to studies of Rizzardo and co-workers[44,45] who previously used this approach to prepare poly(butyl methacrylate)-b-poly(phenyl methacrylate) block copolymers with narrow molar mass distributions.[46]

Alkyl halides are useful compounds often used in RDRP techniques (such as ATRP, iodine transfer polymerisation (ITP),[47–52] reverse iodine transfer polymerisation (RITP)[53–58] and bromine-iodine transformation reversible-deactivation radical polymerisation (BIT-RDRP)[59–62]) due to the reversible homolytic scission of the carbon–halogen bond. ATRP uses alkyl halides as initiators whereas ITP employs typically unstable alkyl iodides as a chain transfer agents (CTAs). The alkyl iodides required in ITP processes are difficult to store due to their low bond dissociation enthalpies, which is why focus has shifted to explore the *in situ* generation of alkyl iodide compounds from the more stable alkyl bromides in both RITP and BIT-RDRP processes. Despite limited reports in

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water,[63,64] RITP and BIT-RDRP reactions commonly employ organic solvents, high temperatures (50–110 °C (ref. 53, 55–57 and 60)) and metal-containing reagents (e.g. sodium iodide in BIT-RDRP). Herein we explore the use of a water-miscible alkyl halide reagent, bromoform, to overcome these issues and generate colourless (white) block copolymers via a simple, inexpensive route.

The use of bromine-based chain transfer agents in polymerisation formulations has been discussed in a small number of literature reports, dating back to the 1950s.[65–67] Dunn et al.[67] described the use of bromotrichloromethane (CBrCl$_3$) and carbon tetrabromide (CBr$_4$) in the preparation of polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) copolymers under UV and thermal conditions. However, only 10% monomer conversion was achieved in these seminal studies. Miller then explored graft[65] and block[66] copolymers using acrylamide, acrylonitrile and acrylic acid monomers, where the chain transfer capabilities of monobromoethane (C$_2$H$_5$Br), dibromomethane (CH$_2$Br$_2$) and bromoform (CHBr$_3$) were investigated using photo-polymerisation. However, the UV lamp used in these studies may have heated the reaction solution up to 50 °C (over a 3 hours period, as discovered in our laboratory – data not shown), suggesting that thermal effects could also be influencing the polymerisation and thus the role of the bromine radical remains unclear. Both Dunn et al. and Millers' studies were conducted in organic solvents and were limited by the capabilities of analytical techniques of that time. Three decades later in a patent, Wu et al.[68] described the use of this bromoform-assisted copolymerisation technique in the formation of block copolymers containing 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylamide for use in oil recovery. However, the role of bromoform remains unclear. Today, there is a broader range of conventional analytical techniques that can be exploited to develop block copolymer synthesis strategies using these potentially straightforward methods.

Bromoform has been selected for use in this study as it is water-miscible (3.0 g L^{-1} at 20 °C,[69,70] 3.0 g L^{-1} at 25 °C (ref. 70 and 71) and 3.2 g L^{-1} at 30 °C (ref. 69 and 70)), readily avail-

able, inexpensive, stable (easily stored) and can be used directly at low and ambient temperatures, in contrast to other mediating agents (e.g. alkyl iodides or CTAs). Interestingly, bromoform has been reported to photodissociate under UV light (at wavelengths of 193,[72] 234,[73] 248,[74] 266,[75] 267[73] and between 266–324 nm (ref. 76)); primarily into Br$_2$HC$^•$ and Br$^•$ radicals. Herein, we explore this property of bromoform and its potential to initiate or mediate the polymerisation under UV conditions. Preliminary work by Thananukul et al.[77] reported the use of bromoform in the synthesis of polyacrylamide (PAM) homopolymer under UV conditions in water. Specifically, bromoform was suggested as a potential CTA due to the influence on the PAM molar mass. Therefore, the possibility exists to use this method in the synthesis of block copolymers owing to the potential of a photolytically reactive bromine-terminated chain end.

Whilst literature reports concerning bromoform and its chain transfer ability are limited, the foundation of this work appears promising. The work herein significantly advances this area, introducing a straightforward method to create commercially-relevant block copolymers, using free radical polymerisation without sulfur- or metal-containing compounds directly in water for the first time (Scheme 1).

Firstly, the free radical photopolymerisation of N,N-dimethylacrylamide (DMA) at varying bromoform concentration (0.0, 0.5, 1.0 and 2.0 mol% with respect to DMA) and fixed 4,4′-azobis(4-cyanopentanoic acid) (ACPA) concentration (1.0 mol% with respect to DMA) was investigated (Scheme 1(a), see ESI† for experimental procedure) to determine the optimum route for forming bromine-terminated PDMA (referred to as PDMA-Br). The effect of bromoform on these homopolymerisations was studied by monitoring monomer conversion and molar mass evolution using ^{1}H nuclear magnetic resonance (NMR) spectroscopy (Fig. S1–S4†) and gel permeation chromatography (GPC) (Table 1 and Fig. S5†), respectively. High monomer conversions (≥93%) were achieved in each case and the final GPC traces indicated good repeatability of syntheses conducted at all bromoform concentrations (performed in triplicate, see Fig. S6†). It should be noted that the
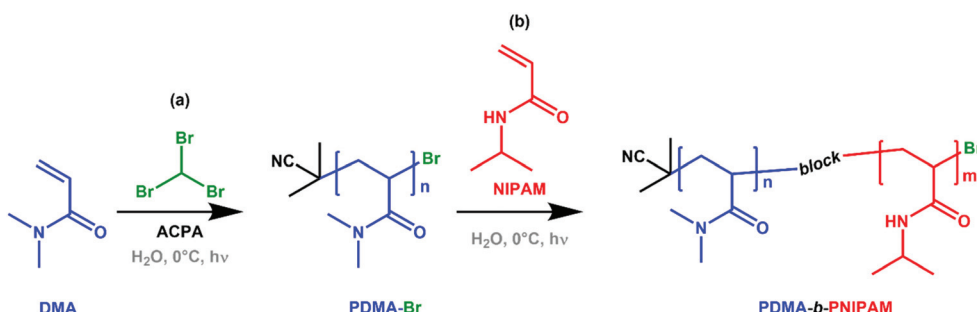
Scheme 1 (a) Step 1: bromoform-assisted polymerisation of N,N-dimethylacrylamide (DMA). The proposed structure of the poly(N,N-dimethylacrylamide) macro-initiator (PDMA-Br) is based on the 4,4′-azobis(4-cyanopentanoic acid) (ACPA) radical fragment initiating the growth of a polymer chain and the bromoform-derived bromine radical (Br$^•$) capping the chain-end. (b) Step 2: polymerisation of N-isopropylacrylamide (NIPAM) using the PDMA-Br macro-initiator synthesised in Step 1 to produce poly(N,N-dimethylacrylamide)-block-poly(N-isopropylacrylamide) [PDMA-b-PNIPAM].

Table 1 Summary of final monomer conversion, M_n and $Đ$ data for the polymerisation of *N,N*-dimethylacrylamide at varied bromoform concentrations. All experiments were performed using 1.0 mol% ACPA (relative to monomer) in 25 mL deionized water at 0 °C for 1 hour of UV irradiation

Bromoform[a] (mol %)	DMA monomer conversion[b] (%)	PDMA M_n[c] (kg mol^{-1})	PDMA $Đ$[c] (M_w/M_n)
0	97	246.7	3.4
0.5	95	294.8	2.8
1.0	93	271.2	2.8
2.0	96	242.3	3.5

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

molar mass dispersity, $Đ$, of the final polymers was high in all cases (2.8–3.5), with no suggested relationship between $Đ$ and bromoform content. As previously discussed, high $Đ$ values may not inherently have an adverse impact on the desired application.[15,23–30]

Kinetic studies shown in Fig. 1(b) suggest that the evolution of molar mass with monomer conversion is in line with conventional free radical polymerisation,[78–80] rather than RDRP,[81–85] where the relationship would be linear. The final molar mass appears to increase on addition of 0.5 mol% bromoform, however, closer inspection of the broad GPC curves

indicates that the molar mass profiles for the PDMA synthesised are near-identical in all cases (see Fig. S6†). It should be noted that the molar mass profiles exceed the upper limit of the GPC calibration range, which will affect the M_n values obtained from seemingly identical broad curves. Fig. 1(a) and (c) demonstrate little to no difference in polymerisation rate observed for all bromoform concentrations studied herein.

In parallel to our studies carried out on DMA, *N*-isopropylacrylamide (NIPAM) homopolymerisation at varying bromoform content was also explored (kinetic data are provided in the ESI: see Fig. S7–S13 and Table S1†).

Next, a large quantity (20 g) of PDMA was synthesised, in a single batch using 2 mol% bromoform, in an attempt to produce bromine-terminated PDMA (PDMA-Br) as a potential macro-initiator for the second step [Scheme 1(b)]. 2 mol% bromoform (relative to monomer) was selected to maximise the proportion of bromine-terminated PDMA chains within the usable bromoform miscibility range. PDMA-*b*-PNIPAM copolymers with varying block molar ratios were subsequently targeted in a polymerisation formulation containing PDMA-Br (see Fig. S14†), NIPAM monomer and water. Importantly, the PDMA-Br was purified by precipitation to remove any unreacted monomer, initiator and bromoform impurities, and no ACPA initiator was used in the second step (unlike in a RAFT polymerisation formulation). This purification step ensures that any subsequent polymerisation can only be initiated by the proposed PDMA-Br macro-initiator (and not
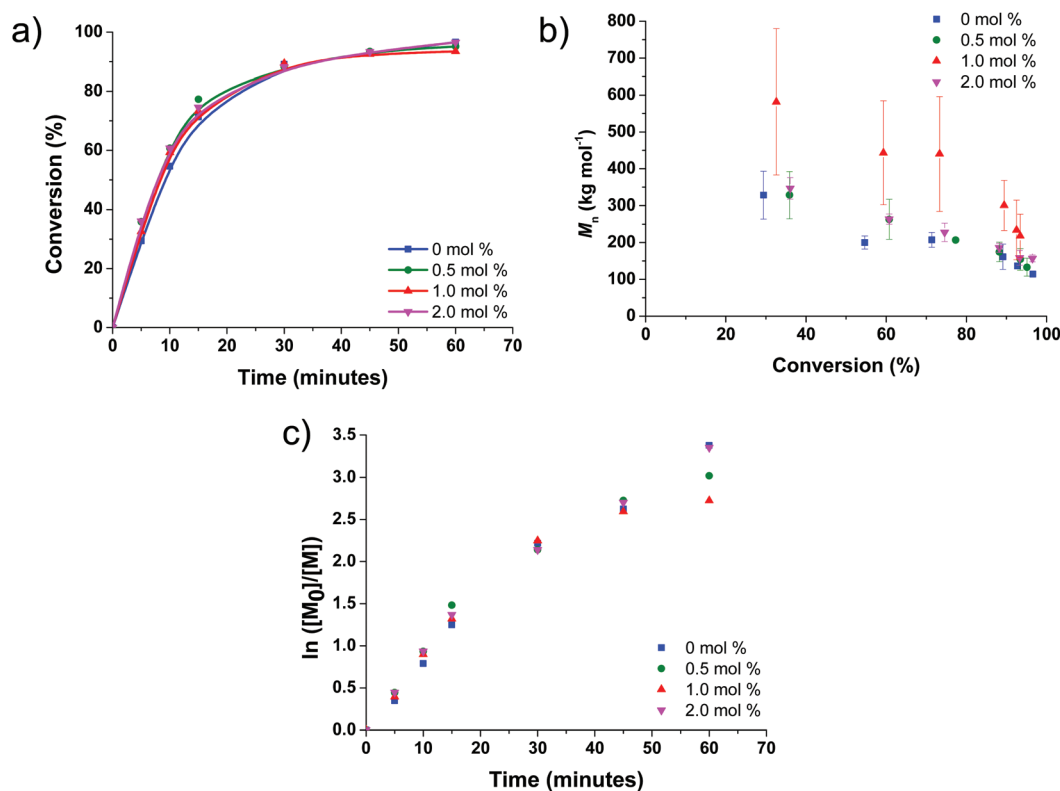

Fig. 1 Kinetic data for the polymerisation of *N,N*-dimethylacrylamide at varied bromoform content: (a) monomer conversion with time; (b) M_n *versus* monomer conversion; and (c) semi-logarithmic first-order plot.

Table 2 Summary of M_n, $Đ$ and the target and achieved PNIPAM DP in PDMA-b-PNIPAM copolymers

Target polymer[a]	NIPAM conversion[b] (%)	M_n^{c} (kg mol^{-1})	PNIPAM DP[d]	$Đ^{c}$ (M_w/M_n)
PDMA$_{1500}$[e]	—	148.4	—	3.9
PDMA$_{1500}$-b-PNIPAM$_{170}$	66	163.6	110	3.4
PDMA$_{1500}$-b-PNIPAM$_{380}$	70	165.8	270	3.4
PDMA$_{1500}$-b-PNIPAM$_{640}$	65	196.3	420	3.2
PDMA$_{1500}$-b-PNIPAM$_{1000}$	75	164.4^{f}	750	5.3^{f}
PDMA$_{1500}$-b-PNIPAM$_{1500}$	87	264.8	1310	4.1
PDMA$_{1500}$-b-PNIPAM$_{2300}$	89	392.6^{f}	2050	4.1^{f}
PDMA$_{1500}$-b-PNIPAM$_{3500}$	95	463.6	3330	3.9
PDMA$_{1500}$-b-PNIPAM$_{6000}$	85	603.7	5100	3.4

[a] Target PNIPAM DP calculated using eqn (S2)† and GPC. [b] Calculated using ^{1}H NMR spectroscopy and eqn (S1).† [c] Determined by DMF GPC using poly(methyl methacrylate) standards. [d] Calculated using ^{1}H NMR spectroscopy and eqn (S3).† Values are rounded to the nearest ten. [e] PDMA macro-initiator synthesized using 2 mol% bromoform (relative to monomer), achieving a final DMA monomer conversion of 91%. [f] M_n appears smaller than expected due to broad GPC trace, suggesting a significant amount of unreacted PDMA is still present.

Fig. 2 GPC traces of PDMA-Br macro-initiator and PDMA-b-PNIPAM copolymers with target PNIPAM DPs ranging from 170 to 6000.

residual ACPA or bromoform used in Step 1), as the NIPAM does not self-polymerise under these conditions (*vide infra* and ESI, Fig. S15†).

PDMA-b-PNIPAM copolymers with a target range of DMA : NIPAM molar ratios were synthesised as summarised in Table 2. DMF GPC analysis was performed to determine the M_n values for the PDMA-Br macro-initiator and subsequent PDMA-b-PNIPAM block copolymers. The mean degree of polymerisation (DP) of the PNIPAM block was determined using NIPAM monomer conversions as judged by ^{1}H NMR spectroscopy (see eqn (S3)†). The length of the PNIPAM block increased when targeting higher DPs, as expected, and the monomer conversion was greater when longer PNIPAM blocks were targeted, which is attributed to increased NIPAM concentrations during the polymerisation.

Although the GPC traces of the first two block copolymers (PNIPAM DP ≤ 270) in Fig. 2 suggest that little or no PDMA-Br chain extension was achieved, the M_n values (Table 2) suggest that block extension has been successful and the ^{1}H NMR spectra confirm the presence of PNIPAM in all cases (Fig. S16†). The GPC traces for the purified PDMA-b-PNIPAM copolymers (PNIPAM DP > 270) suggest successful chain-extension of the PDMA-Br macro-initiator with NIPAM, but this alone is not conclusive evidence.[86] Additionally, as the NIPAM content increases (determined by ^{1}H NMR spectroscopy) the M_n (measured by GPC) increases, as expected for chain-extension.

Due to the inherent termination events of free-radical polymerisation and the observed uncontrolled nature of this bromoform-assisted reaction ($Đ$ = 3.9 for the macro-initiator), we anticipate that there will be a portion of PDMA that is incapable of chain extension. Indeed, the GPC traces in Fig. 2 suggest that there could be some residual PDMA homopolymer in the block copolymer samples, particularly for PNIPAM DP = 2050, where a significant shoulder is observed. As aforementioned, this is

attributed to competing termination events in Step 1 resulting in PDMA chains without the necessary bromine functionality. For example, the competing dissociation pathways of bromoform (between bromine and hydrogen transfer[72–76]), combination, disproportionation or unwanted chain transfer (*e.g.* to polymer, monomer or solvent) would also result in 'dead' PDMA rather than Br-terminated chains. It is important to note that the presence of homopolymer impurity is not of concern for industrially relevant additives, where blends are often employed to achieve desired properties.

To further confirm that PDMA-b-PNIPAM block copolymers were successfully synthesised (and not simply a mixture of PDMA and PNIPAM homopolymers that could arise from trace amounts of free-radical initiator that remained following purification in Step 1), important control experiments were conducted. Firstly, NIPAM homopolymerisations were attempted in the absence of ACPA photoinitiator (*i.e.* only NIPAM, bromoform and water present). Importantly, no polymerisation occurred after irradiation with UV light (Fig. S15†), which indicates that bromoform itself does not act as a photoinitiator under these conditions. This is contrary to previous reports by Miller[66] and Wu *et al.*,[68] who described the use of bromoform as a photoinitiator during the polymerisation of acrylamide, acrylonitrile, acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). However, as previously discussed, these studies lack thermal control and the temperatures of up to 50 °C (reached during the UV irradiation) could be causing bromoform to behave as a thermal initiator. Secondly, polymerisations without APCA and bromoform (*i.e.* only NIPAM and water present) were attempted in order to determine whether NIPAM would self-polymerise. Using the previously described conditions and even extended UV exposure times, homopolymerisation of NIPAM did not take place (Fig. S15†). Thirdly, a control reaction using PDMA synthesised without using bromoform in Step 1 was conducted. When targeting

Fig. 3 ^{1}H NMR spectrum showing (a) PDMA-Br after precipitation, (b) PDMA$_{1500}$-b-PNIPAM$_{3330}$ (using 2 mol% bromoform in step 1) after precipitation and (c) only NIPAM monomer peaks present for the attempted synthesis of PDMA-b-PNIPAM from PDMA (0 mol% bromoform in step 1).

Scheme 2 (a) Attempted synthesis of PNIPAM homopolymer in the absence of bromoform and ACPA photoinitiator. (b) Attempted synthesis of PDMA homopolymer in the absence of ACPA photoinitiator. (c) Attempted synthesis of PDMA-b-PNIPAM copolymers without bromoform in Step 1. (d) Successful two step synthesis of PDMA-b-PNIPAM copolymers using PDMA prepared using bromoform in Step 1.

$PDMA_{1500}$-b-$PNIPAM_{3500}$ under these conditions, no NIPAM polymerisation was observed (neither homopolymerisation nor PDMA chain-extension), indicating that bromoform is needed in Step 1 for the formation of the desired diblock copolymer (Fig. 3 and Fig. S17†). These control studies (summarised in Scheme 2) provide evidence that bromoform imparts bromine functionality onto PDMA chains in Step 1 to enable block copolymer synthesis in Step 2.

Based on the observations from the control experiments we speculate the following mechanism for this bromoform-assisted technique. Step one, used to produce the PDMA macro-initiator, is more akin to free radical polymerisation favouring the formation of the DMA homopolymer (in line with a decrease in M_n with monomer conversion shown in Fig. 1b). In the latter stages of this reaction, at high monomer conversion, the chains are reversibly capped with a bromine functionality from the bromoform. In the second stage, in which no photoinitiator (ACPA) is present, the bromine chain end functionality is cleaved and subsequent polymerisation of the second block (NIPAM) occurs. Overall, resulting in the observed increase in molar mass.

In summary, we describe the synthesis of block copolymers *via* metal-free, sulfur-free, bromoform-assisted aqueous free-radical polymerisation. Specifically, a PDMA precursor was first synthesised in the presence of bromoform before being chain-extended with NIPAM to produce PDMA-b-PNIPAM copolymers with varying block molar ratios in a straightforward, wholly aqueous two step procedure. This study suggests that using bromoform generates bromine-terminated PDMA chains that are capable of chain-extension with NIPAM. When bromoform is not used in Step 1, no PDMA-b-PNIPAM block copolymers were produced under otherwise identical conditions. The competition between bromine and hydrogen transfer from bromoform to the PDMA precursor block, in addition to the inherent termination and chain transfer events of free-radical polymerisation, results in block copolymers of very high molar mass dispersity. Nevertheless, this straightforward, sulfur- and metal-free route to block copolymers is useful for the preparation of materials with desired characteristics for applications that do not require exquisite control over the molar mass distribution. Further investigations are required to elucidate detailed mechanistic information and identify the scope and limitations for this promising synthetic technique.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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