Kinetic Studies of the Photopolymerisation of Acrylamide in Aqueous Solution: Effects of Bromoform as a Chain Transfer Agent

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ABSTRACT

The effects of adding bromoform ($CHBr_3$) as a potential chain transfer agent in the photopolymerisation of acrylamide (AM) in aqueous solution have been studied both in terms of influencing the rate of polymerisation and the molecular weight of the polyacrylamide (PAM) formed. Using 4,4′-azo-bis(4-cyanopentanoic acid) (ACPA) as photoinitiator, two different $CHBr_3$ concentrations as chain transfer agent were compared: 0.5 and 2.0 mol % (relative to AM), the higher of which was determined by the limit of $CHBr_3$ water solubility. The results showed that $CHBr_3$ was an effective chain transfer agent that could regulate the molecular weight of the PAM formed without seriously affecting the polymerisation rate. It is concluded that chain transfer to $CHBr_3$ occurs by both Br and H atom transfer although Br transfer is the more favoured due to the weaker C-Br bond. Furthermore, Br transfer leads to Br-terminated chains in which the terminal C-Br bond can re-dissociate leading to re-initiation and re-propagation of the same chain, thereby maintaining the polymerisation rate. Continuing studies into how this mechanism can be exploited in order to synthesize water-soluble block copolymers of potential biomedical importance are currently in progress.

Keywords: acrylamide, polyacrylamide, bromoform, photopolymerisation, chain transfer

1. INTRODUCTION

Polyacrylamide (PAM) is a synthetic polymer which has a wide range of industrial applications due almost entirely to its high water solubility. These applications include its use as a flocculating agent, an additive in paper manufacture, a thickening agent, and as an agent for water clarification and oil recovery [1,2]. Commercial PAM polymers

have typical number-average molecular weights $\overline{M}_n$ in the range of 10^5 - 3×10^6.

The most common method of synthesis of PAM is by free radical polymerisation of acrylamide (AM) monomer in aqueous solution [3]. Moderate temperatures in the range of 20-60°C are normally used with the polymerisation rate increasing with temperature. Above 60°C, the polymerisation rate starts to decrease due to higher rates of termination and also crosslinking by intermolecular imidization of the substituent amide groups which causes the polymer to precipitate out of solution. Radical initiation can be by a variety of means: chemical, redox, UV light or high-energy (X-ray, γ-ray) radiation.

An important reason why PAM has attracted such widespread attention stems from the fact that AM is able to polymerise to high molecular weight ($> 10^5$) quite easily in aqueous solution under mild conditions. This is due to the chain transfer constant to monomer being very low and those to polymer and water being virtually zero, findings that date back to the pioneering work of Dainton and co-workers [4,5]. Another contributing factor is the strong PAM-water interactions which produce a strongly bound hydration shell that helps to shield the propagating chain radical and hinders termination [6]. Consequently, molecular weight control in AM polymerisation has tended to be by the addition of an alcohol chain transfer agent such as ethanol, propanol and isopropanol [1, 2, 7].

In this work, the effects of a purposely-added chain transfer agent, namely bromoform ($CHBr_3$), on the kinetics of AM photopolymerisation in aqueous solution have been studied both in terms of polymerisation rate and polymer molecular weight. To the best of our knowledge, $CHBr_3$

has not previously been reported in this role. The rationale that $CHBr_3$ could be an effective transfer agent is based on the fact that carbon tetrabromide (CBr_4) is well-known to have a very high chain transfer constant when used in free radical polymerisations [8]. However, CBr_4 cannot be used in aqueous systems due to its insolubility in water whereas $CHBr_3$ can due to its slight solubility (3.2 g/l at 30°C [9]).
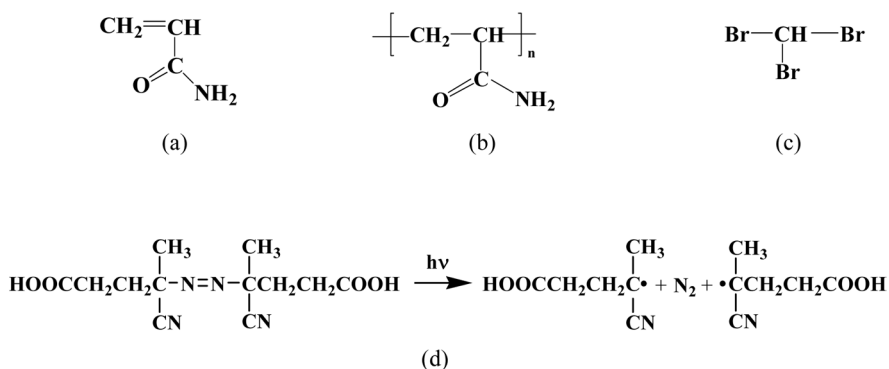
When this study is considered within its wider context, the presence of potentially photolytically reactive Br-terminated chain ends in the polymer opens up possibilities for block copolymer formation by sequential addition of a second water-soluble monomer. Water-soluble block copolymers in which the different blocks have contrasting yet complementary properties are of increasing interest in certain biomedical applications. This is currently under investigation as part of a wider study.
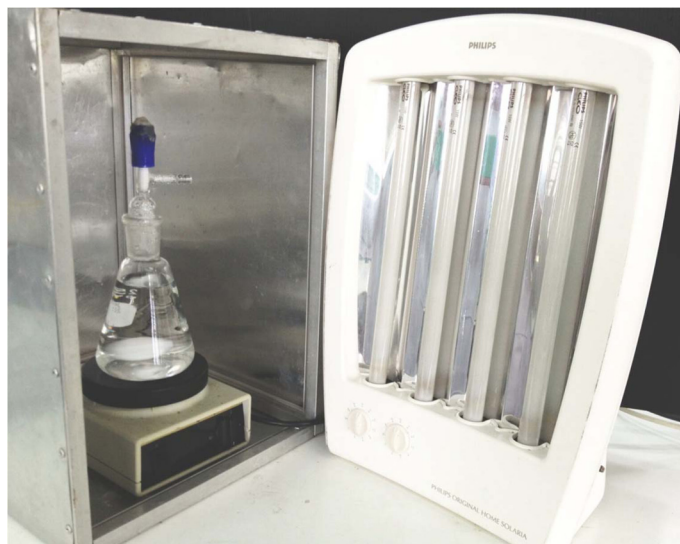
2. MATERIALS AND METHODS
2.1 Materials

Acrylamide (AM) (Merck, ≥ 99%), 4, 4′-azo-bis(4-cyanopentanoic acid) (ACPA) (Aldrich, ≥ 98.0%) and bromoform ($CHBr_3$) (Acros Organics, 96%) were all used as supplied without further purification. Their chemical structures are shown in Figure 1. The water used as the solvent in the photopolymerisations was first deionized and then deaerated (deoxygenated) by boiling.

The photopolymerisation apparatus was set up as shown in Figure 2 and consisted of the reaction flask supported on a magnetic stirrer and enclosed in an aluminium cabinet. The ultraviolet (UV) light source was a commercially available UV lamp (Philips Solarium Model MD1-15) comprising 4 parallel 15 watt fluorescent tubes which emitted UV light in the wavelength range of 100-400 nm.

Figure 1. Chemical structures of (a) acrylamide, (b) polyacrylamide, (c) bromoform and (d) 4,4′-azo-bis(4-cyanopentanoic acid) showing its photolytic dissociation into free radicals.

Figure 2. Photograph of the photopolymerisation apparatus used.

2.2 Experimental Methods
2.2.1 Photopolymerisation

For photopolymerisation, 10.0 g of acrylamide monomer were dissolved in 200 ml of water (5% w/v, $[AM]_o$ = 0.703 mol l^{-1}) in a 250 ml 'Quickfit' conical flask and 0.2 g of ACPA (0.5 mol % relative to AM) added as photoinitiator. The flask was then placed in the aluminium cabinet and irradiated with UV light with magnetic stirring at a starting temperature of $33 \pm 1°C$ for 60 mins. During this time period, it was observed that the solution temperature increased gradually up to 45-50°C. This was partly due to the exothermic nature of the reaction and partly due to the warming effect of the UV light. However, for the main part of the reaction (10-70% monomer conversion), which was the focus of attention for the kinetic studies, the temperature variation was in the much narrower range of $40 \pm 2°C$. Similar experiments were carried out as follows, each in duplicate in order to verify the results.

• With no added ACPA as photoinitiator
• With 0.5 mol % of CHBr$_3$ as a possible photoinitiator instead of ACPA
• With 0.5 mol % of ACPA and 0.5-2.0 mol % of CHBr$_3$ as a chain transfer agent

In each of the 3 experiments in which CHBr$_3$ was added, it was important to observe that the initially dispersed CHBr$_3$ droplets dissolved completely on magnetic stirring in the water prior to polymerisation. This dissolution was facilitated by heating to disrupt the polar aggregation of the CHBr$_3$ molecules after which the solution could be cooled back to room temperature without precipitation. The limited solubility of CHBr$_3$ in water has been variously reported in the literature as 3.0 g/l at 20°C [9], 3.2 g/l at 30°C [9] and 3.0 g/l at 25°C [10]. In this work, the higher CHBr$_3$ concentration of 2.0 mol % corresponded to a w/v concentration of 3.5 g/l which was the projected limit of CHBr$_3$ water solubility at the temperature of these experiments.

2.2.2 Kinetic studies
At various time intervals, a 10 ml sample of the solution was pipetted from the flask and transferred into a beaker containing 50 ml of chilled methanol as a non-solvent for polyacrylamide (PAM). After allowing sufficient time for complete precipitation, the PAM formed was filtered off and dried to constant weight in a vacuum oven at 60°C. The % conversion at each sampling time was calculated from equation (1).

$$\% \text{ Conversion} = (\text{Wt. of dry polymer} / \text{Initial wt. of monomer}) \times 100\% \quad (1)$$

In addition, the molecular weight of each sample was estimated from dilute-solution viscometry flow-time measurements at a single concentration of 0.2 g/dl in water at 30°C using the Solomon-Ciuta One-Point Equation (2) to calculate the intrinsic viscosity [η]

$$[\eta] = [\, 2(\eta_{sp} - \ln\eta_{rel})\,]^{0.5} / c \quad (2)$$

where η_{sp}, η_{rel} and c are the specific viscosity, relative viscosity and solution concentration respectively. The intrinsic viscosity [η] is related to the viscosity-average molecular weight $\overline{M}_v$ through the Mark-Houwink Equation (3)

$$[\eta] = K\overline{M}_v^{\,a} \quad (3)$$

where K and a are interaction constants characteristic of a given polymer-solvent-temperature system. For PAM in water at 30°C, equation (3) has been reported as [11]:

$$[\eta] = 6.31 \times 10^{-5}\, \overline{M}_v^{\,0.80} \ \text{dl/g} \quad (4)$$

It should be noted here that this equation (4) applies only to unfractionated PAM samples such as those produced in these experiments. To a reasonable approximation, assuming a most probable molecular weight distribution, the value of $\overline{M}_v$ can be converted into the number-average and weight-average molecular weights, $\overline{M}_n$ and $\overline{M}_w$, via the ratio

$$\overline{M}_n : \overline{M}_v : \overline{M}_w = 1 : [(1+a)\Gamma(1+a)]^{1/a} : 2 \quad (5)$$

where $\Gamma(1+a)$ is the gamma function of $(1+a)$. When a = 0.80 is substituted into this equation (5), it yields a ratio of

$$\overline{M}_n : \overline{M}_v : \overline{M}_w = 1 : 1.91 : 2 \quad (6)$$
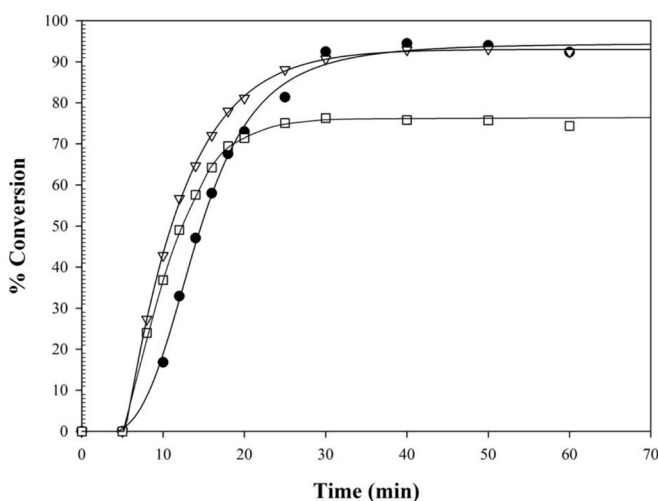
Thus, the values of $\overline{M}_n$ given in this paper were calculated from a combination of equations (4) and (6).

3. RESULTS AND DISCUSSION

3.1 Kinetics of Photopolymerisation

The kinetic plots of % conversion against time are shown in Figure 3 for the photopolymerisations of AM with ACPA alone and with ACPA + $CHBr_3$. The other two photopolymerisations without ACPA and with $CHBr_3$ alone did not produce any polymer. From these results it can be concluded that, under the particular set of conditions used in these experiments, the photodissociation of ACPA, as shown in Figure 1(d), was the only source of free radicals which were capable of initiating polymerisation. Neither the UV light alone nor in combination with $CHBr_3$ could produce radicals reactive enough for initiation. This is despite the fact that $CHBr_3$ is known to photodissociate in the UV region to give primarily (but not exclusively) $CHBr_2\bullet$ and $Br\bullet$ radicals via C-Br bond scission [12].

Figure 3. Plots of % conversion against time at different $CHBr_3$ concentrations. [$CHBr_3$] (mol %) • 0% ∇ 0.5% □ 2.0% .

The % conversion - time plots in Figure 3 show a short induction period followed by a fast polymerisation which was effectively complete within 40 mins. The short induction period was most likely due to residual dissolved oxygen in the water. At the lower 0.5 mol % concentration, the addition of $CHBr_3$ appeared to have little effect on either the rate or the final % conversion. However, at the higher 2.0 mol % concentration, there was a slight decrease in rate together with a more significant decrease in the final % conversion.

The early studies of Dainton and co-workers previously mentioned demonstrated that the kinetic dependence of the photopolymerisation of AM in aqueous solution conformed to the general prediction for free radical addition that:

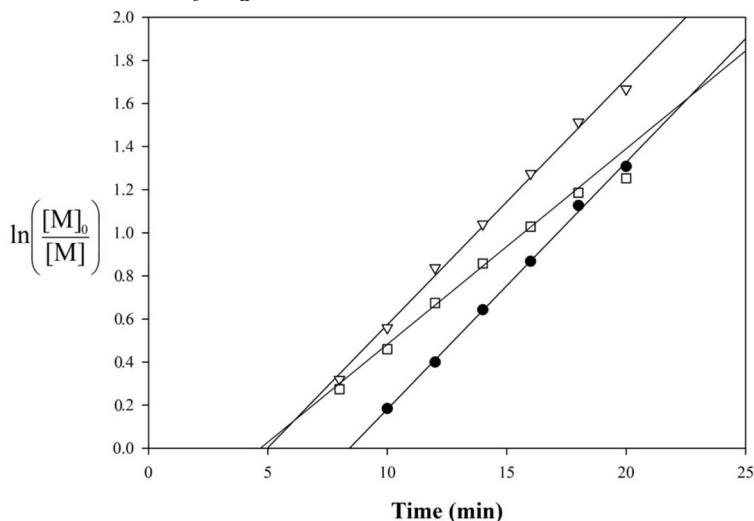$$\text{Rate of polymerisation} = R_p \propto [M][I]^{0.5} \quad (7)$$

over a wide range of conditions where [M] and [I] are the monomer and initiator concentrations respectively. When the kinetic plots in Figure 3 are converted into the first-order rate plots of $\ln([M]_o/[M])$ against time t in Figure 4 in accordance with the first-order integrated rate equation (8), good linearity is observed over the main part of the reaction from 10-70% conversion. The apparent first-order rate constants, k_1, derived from the

slopes of these plots are given in Table 1.

$$\ln([M]_o/[M]) = k_1 t \tag{8}$$

The effect of $CHBr_3$ addition is seen more clearly when $\overline{M}_n$ is plotted against time, as shown in Figure 5. As would be expected of a chain transfer agent, the final value of $\overline{M}_n$ decreases as the $CHBr_3$ concentration increases. This is because chain transfer is a type of termination reaction which results in a decrease in the length of the propagating polymer chain. It is also interesting to note in Figure 5 that, either with or without $CHBr_3$, $\overline{M}_n$ increases

rapidly up to a maximum value during the first part of the reaction ($< 50\%$ conversion) before decreasing to a constant value thereafter. This can be explained in terms of a shift in the relative rates of propagation and termination. As the monomer concentration decreases ($> 50\%$ conversion), the rate of propagation decreases proportionately more than the combined rates of termination. This results in a decrease in the kinetic chain length as the reaction progresses and the formation of lower molecular weight polymer. Consequently, the average molecular weight decreases.
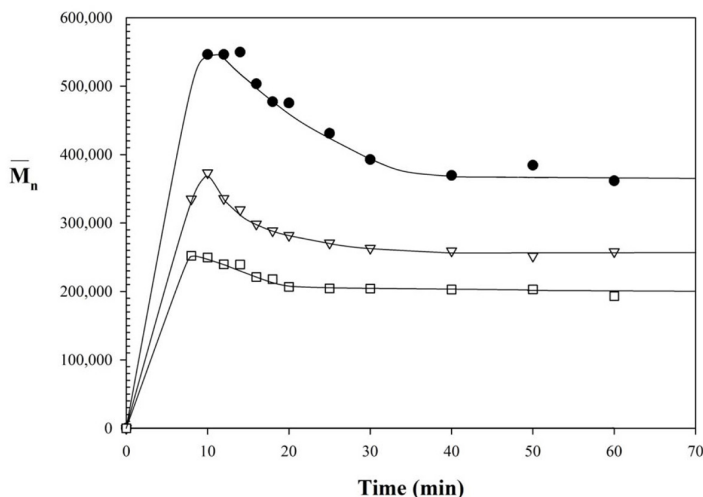

Figure 4. First-order rate plots of $\ln([M]_o/[M])$ against time at different $CHBr_3$ concentrations. $\square$
[$CHBr_3$] (mol %) • 0%   ∇ 0.5%   2.0% .

Table 1. Effect of bromoform concentration, [$CHBr_3$], on the apparent first-order rate constant, k_1, the number-average molecular weight, $\overline{M}_n$, and the final % conversion.

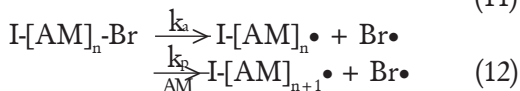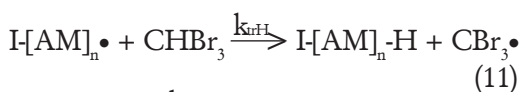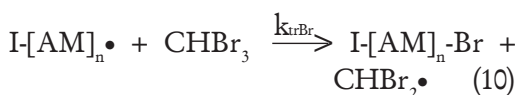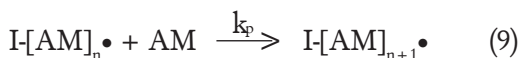| [$CHBr_3$] mol %	k_1 min^{-1}	$\overline{M}_n$ (x 10^{-5}) Maximum	Final	Conversion %
0	0.115	5.5	3.7	94
0.5	0.119	3.7	2.6	93
2.0	0.092	2.5	2.0	77

Figure 5. Plots of $\overline{M}_n$ against time at different $CHBr_3$ concentrations. $[CHBr_3]$ (mol %) ● 0% ▽ 0.5% □ 2.0% .

3.2 Mechanistic Considerations

Turning our attention now to the mechanism of the reaction and bearing in mind Dainton's findings that chain transfers to monomer, polymer and water are all very low [4,5], the main reactions can be considered to be:

$$I\text{-}[AM]_n\bullet + AM \xrightarrow{k_p} I\text{-}[AM]_{n+1}\bullet \qquad (9)$$

$$I\text{-}[AM]_n\bullet + CHBr_3 \xrightarrow{k_{trBr}} I\text{-}[AM]_n\text{-}Br + CHBr_2\bullet \qquad (10)$$

$$I\text{-}[AM]_n\bullet + CHBr_3 \xrightarrow{k_{trH}} I\text{-}[AM]_n\text{-}H + CBr_3\bullet \qquad (11)$$

$$I\text{-}[AM]_n\text{-}Br \xrightarrow{k_a} I\text{-}[AM]_n\bullet + Br\bullet$$
$$\xrightarrow[AM]{k_p} I\text{-}[AM]_{n+1}\bullet + Br\bullet \qquad (12)$$

where
I = initiator fragment from ACPA
$I\text{-}[AM]_n\bullet$ = growing PAM chain radical of
     degree of polymerisation n
$I\text{-}[AM]_n\text{-}Br$ = PAM polymer molecule capable
     of re-initiation in (12)
$I\text{-}[AM]_n\text{-}H$ = dead PAM polymer molecule
k_p = propagation rate constant
k_{trBr}, k_{trH} = chain transfer to $CHBr_3$ rate
     constants
k_a = re-initiation rate constant

When these reactions are considered together with the % conversion and $\overline{M}_n$ results in Figures 3 and 5, they provide an insight into the effects of $CHBr_3$ addition. The following conclusions can be drawn.

1. Since $CHBr_3$ addition does not appear to have a significant effect on R_p but does have a significant (but limited) lowering effect on $\overline{M}_n$, it can be concluded that $k_p >> k_{trBr} + k_{trH}$. It can also be suggested that, since the rate is not seriously affected, the results are consistent with a chain transfer model in which k_a for re-initiation is not much different from k_p for propagation ($k_a \approx k_p$) [8]. However, based on current evidence alone, this is more conjectural than conclusive since it assumes a high efficiency factor for re-initiation.

2. The main prerequisite of an effective chain transfer agent is that it contains an atom (or atoms) that can be easily abstracted and transferred to the growing polymer chain radical. In the case of $CHBr_3$, there are two possibilities: Br transfer as in reaction (10) and H transfer as in reaction (11). Which of these two possibilities is the more likely depends

on a combination of two factors: bond stability (C-Br versus C-H) and radical stability ($CHBr_2\bullet$ versus $CBr_3\bullet$). This poses an interesting question because, on the one hand, the weaker C-Br bond would favour Br transfer while, on the other hand, H transfer is favoured by the more stable $CBr_3\bullet$ radical. It is also relevant to note that these two alternatives lead to contrasting outcomes. Whereas H transfer produces a dead polymer molecule and an unreactive $CBr_3\cdot$ radical (degradative chain transfer), Br transfer produces a Br-terminated chain which can undergo re-initiation by dissociation of the terminal C-Br bond followed by re-propagation, as shown in reaction (12). In this way, I-[AM]$_n$-Br is essentially a monofunctional telechelic polymer molecule. Therefore, since Br transfer followed by re-initiation and re-propagation would not significantly decrease R_p (assuming that $k_a \approx k_p$), whereas H transfer certainly would, it is reasonable to conclude that Br transfer is the more favoured alternative. This would be consistent with the previously mentioned report that $CHBr_3$ photodissociates to give primarily $CHBr_2\bullet$ and $Br\bullet$ radicals via C-Br bond scission [12]. However, the observed decrease in $\overline{M}_n$ with increasing $CHBr_3$ concentration (Figure 5), not predicted if Br transfer is the only mechanism, is evidence that at least some H transfer leading to permanent termination also occurs.

3. Further evidence of some H transfer comes from the observed decrease in the final % conversion at the higher $CHBr_3$ concentration from > 90% down to < 80% (Figure 3). This reduced yield is a sign that the active centre concentration has prematurely decreased to zero while there is still a significant amount of monomer (i.e., more than the expected equilibrium monomer concentration) present in the system. This

in turn is an indicator of an increase in the incidence of degradative chain transfer by H transfer leading to a decline in the active centre concentration.

4. Finally, in the above discussion it is considered that, following chain transfer, the $CHBr_2\bullet$ and $CBr_3\bullet$ radicals are either inactive or have extremely low activities for re-initiation due to their resonance stabilization ($CBr_3\bullet > CHBr_2\bullet$) by delocalization of the free pairs of electrons on the Br atoms. This view is supported by the fact that polymerisation did not occur when UV light was used with $CHBr_3$ alone which produces mainly $CHBr_2\bullet$ radicals. Thus, re-initiation by $CHBr_2\bullet$ as in reaction (13), following on from reaction (10), is not considered to be competitive with reaction (12).

$$CHBr_2\bullet + AM \xrightarrow[\text{unlikely}]{} Br_2HC\text{-}AM\bullet \quad (13)$$

4. CONCLUSIONS

The results presented in this paper have demonstrated clearly that $CHBr_3$ is an effective chain transfer agent in the photopolymerisation of AM monomer in aqueous solution. This has been made possible by the fact that $CHBr_3$ has a limited solubility in water unlike the more widely reported CBr_4 which is insoluble and can only be used with organic solvents. Over the concentration range studied (0.5-2.0 mol % relative to monomer), $CHBr_3$ can regulate the molecular weight of the PAM formed without seriously affecting the polymerisation rate.

Based on the foregoing discussion, it is concluded that chain transfer to $CHBr_3$ is more likely to involve Br transfer than H transfer although it is probable that both occur. Since Br transfer leads to a Br-terminated chain with a terminal C-Br bond, the possibility exists that this C-Br

bond can dissociate under UV light resulting in re-initiation and re-propagation of the same chain. Normally, re-initiation following chain transfer refers to the initiation of a new chain by the radical of the chain transfer agent. However, in the case of $CHBr_3$, the $CHBr_2\bullet$ radical is unreactive in re-initiation due to its stabilization by electron delocalization, a view supported by the fact that polymerisation did not occur with UV light + $CHBr_3$. In other words, $CHBr_3$ is not a photoinitiator in this system. On the other hand, H transfer leads to a dead polymer molecule and, with the $CBr_3\bullet$ radical being even more stable than $CHBr_2\bullet$, results in degradative chain transfer leading to molecular weight reduction.

As mentioned at the end of the Introduction, the significance of these findings within the wider context of this work is that, by using $CHBr_3$ as a chain transfer agent leading to Br-terminated chains which can undergo re-initiation, it opens up a route to block copolymer formation by sequential addition of a second monomer. This is currently the focus of attention of ongoing work, the results of which will be described in a future paper.

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