Reaction of chlorine with organic polyelectrolytes in water treatment: A review

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ABSTRACT

Polyelectrolytes when used as coagulants or coagulant aids in water treatment can react with oxidants used for disinfection, the by-products formed being analogous to those obtained from the reaction of chlorine with natural organic matter. A review of currently available literature shows that, with the concentrations of the commonly used cationic polymers and chlorine normally met in water treatment, the formation of trihalomethanes is minimal, and the polymer is not the principal precursor. When unsatisfactorily high levels of by-products are formed on polymer usage, other chemicals present in the commercial product have usually been identified as the precursors. The most potent of these is residual acrylamide monomer. As long as strict checks are maintained on the amount of this monomer present, trihalomethanes are formed in insignificant amounts. However, the other by-products that can be produced may warrant further exploration, such as the total halogenated organic species obtained from polyamines ($192\,\mu g\,l^{-1}$). For poly(diallyldimethylammonium chloride) the formation is much lower ($12\,\mu g\,l^{-1}$). Nitrosodimethylamine has been reported as another serious contaminant, formed to a limited extent from normal operations with cationic polymers, but at levels of concern when other nitrogen compounds are present. More data are needed on cationic polyacrylamides, which appear to have been somewhat neglected, especially the possible contribution from the cationic acrylate monomer when it is present. Anionic and non-ionic polyacrylamides do not form significant levels of trihalomethanes on reaction with chlorine either. These polymers also have contributions equivalent to the amount produced by the residual monomer present. The choice of the most appropriate treatment polymer should hence always be on the basis of the absence of low molecular weight material as well as on process performance. Strict regulatory control on monomer and impurity content hence has to be maintained.

Key words | cationic polyacrylamide, chlorine, polyamines, poly(diallyldimethylammonium chloride)

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INTRODUCTION

Polyelectrolytes (PEs) are widely used as coagulants and coagulant aids in the water treatment industry. The possibility that, in the disinfection step with chlorine, reactions to form trihalomethanes (THMs) and other potentially harmful chlorinated organic compounds could occur, much as happens with natural organic matter, appears to have been first suggested nearly three decades ago (Symons *et al.* 1975). In a survey of 63 water treatment plants, 18 of which used PEs, it was noticed that the product waters from the latter had an average THM level that was about 50% higher than that for waters from plants that did not utilise PEs. The higher formation levels were consistent across waters with a wide organic content range of 0 to $>5\,mg\,l^{-1}$, for which the PE dose varied from 0.02 to

$7.7\,\mathrm{mg\,l^{-1}}$. The survey also showed that high pH levels encouraged THM formation. Some 17 treatment plants where precipitative softening was practised usually had finished waters with a pH of 9 or above. The average THM concentration of waters from these plants was about 70% higher than that from conventional clarification plants.

The impact of polymer degradation on process performance in coagulation and filtration can be significant. The reaction of polymers with other disinfectants such as ozone, permanganate and UV to form possible harmful reaction by-products also needs consideration, but the emphasis here is on chlorine.

The mechanism of its reaction with organic compounds has been much reviewed (Morris 1978). In water under normal treatment conditions at pH 6, chlorine is 98% hydrolysed to form HOCl:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Other species such as H_2OCl^+ and OCl^- are also present. H_2OCl^+ is the most reactive, but it is present in infinitesimal amounts, making HOCl the dominant reactant. It has strong electrophilic properties; the reaction takes place via the chlorine or oxygen atom. For reactions with organic compounds there is attack by the chlorine atom, which reacts in an electropositive manner. Reactions relevant to polyelectrolytes, such as the haloform reaction, reaction with nitrogenous compounds, addition to double bonds or reactions with aromatic moieties, are examples of this form of electrophilic attack.

In the haloform reaction the pattern of reaction is the successive replacement by Cl of the H at a C atom adjacent to a carbonyl group, which leads to the eventual formation of chloroform and a carboxylate group. In polymers the point of vulnerability will be adjacent to carbonyl groups, which can produce chloroform and result in cleavage of the polymer backbone.

In reactions with nitrogenous compounds, amide groups can dissociate to give anionic structures and their chlorination can proceed by a mechanism similar to that of the haloform reaction. The reaction of chlorine with amines proceeds by the attack of the electron deficient Cl of the HOCl on the electron pair of the nitrogen, followed by concurrent release of H^+ to form water. The rate of reaction depends on the basicity of the groups; amino groups of higher basicity are more vulnerable to attack.

The addition of HOCl to double bonds is a similar attack by the electropositive chlorine in HOCl, this time on one of the double bond C atoms, with an OH group attaching to the other carbon. Reactions of this type may be of relevance where residual double bonds occur in polymers made by free radical polymerisation. Low molecular weight (MW) compounds should not be formed.

Attack by the electron deficient Cl in HOCl on electron rich C and N centres will be the dominant type of reaction for polyelectrolytes; polymers will in all probability not be significantly subjected to addition and substitution reactions. However, unpolymerised monomer residues in the case of free radical polymerisations will have substantial unsaturation that can react in this way. Further degradation to chloroform is possible.

Many organochlorine compounds other than chloroform can be produced on chlorination of carbon compounds. These include carbon tetrachloride, mono-, di- and tri-chloroacetic acids and similarly substituted chloroacetonitriles and chloropropanones. In the reaction with chlorine, chain scission of the polymer can occur, decreasing the size of the polymer, reducing its flocculating properties and producing a variety of chlorinated organic compounds. If there are many organic compounds present, as in secondary sewage effluents, the range of products is greatly extended to include dichlorobutane, chlorocyclohexane and tetra-, penta- and hexa-chloropropanone, as well as a host of chlorinated aromatic compounds (Glaze *et al.* 1978). In drinking water situations the items of most concern are chlorinated acetic acids, nitriles and propanones (Chen and Weisel 1998).

There are also various brominated analogues, with in all some five major haloacetic acids of concern (Xie *et al.* 1998). Organo bromine compounds are formed from organic compounds under disinfection conditions if there is bromide and free chlorine present. Bromide usually occurs in saline groundwaters and where seawater intrusion has taken place. The following reaction occurs rapidly (Morris 1978):

$$Br^- + HOCl \rightarrow HOBr + Cl^-$$
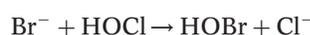
The resulting HOBr is also an electrophilic reagent that is more powerful than HOCl. After reaction bromide ion is

reformed, whereupon it is reoxidised to HOBr while there is residual chlorine left. The overall result is that the bromide ion brings about an enhanced reactivity of the aqueous chlorine.

If nitrite is present in the raw water, the possibility of nitrosation reactions occurring has been raised, if chlorination produces suitable substrates (Child *et al.* 1991). One example of a compound that may be formed is trichloronitromethane, or chloropicrin. Another of recent concern is *N*-nitrosodimethylamine.

CATIONIC POLYMERS

Poly(diallyldimethylammonium chloride)

The first detailed studies of the reaction of chlorine with ten commercial PEs showed chloroform levels of a few $\mu g l^{-1}$ (Kaiser and Lawrence 1977). The results for poly(diallyldimethylammonium chloride) or PDADMAC, which has the structure shown in Figure 1, are summarised in Table 1.

At a $10 \, mg l^{-1}$ polymer dose, presumably in distilled water although this was not mentioned, $2 \, mg l^{-1}$ of chlorine formed $1.2 \, \mu g l^{-1}$ of chloroform after a two hour reaction time in the dark at 20°C, increasing to $1.5 \, \mu g l^{-1}$ after 24 h. In the presence of UV there was photo enhancement of the reaction to double the yield to $3.1 \, \mu g l^{-1}$. At a polymer level of $1 \, mg l^{-1}$ under UV for one hour one commercial PDADMAC produced $1.5 \, \mu g l^{-1}$ of chloroform, but with a chlorine dose of $10 \, mg l^{-1}$. With a very high polymer concentration of $100 \, mg l^{-1}$ the same chlorine dose produced $29.2 \, \mu g l^{-1}$ of chloroform under UV, but only $2.4 \, \mu g l^{-1}$ in the dark.

Coloured waters of chemical oxygen demand (COD) 10–20 $mg l^{-1}$ were treated with alum with and without $0.5 \, mg l^{-1}$ of PDADMAC, followed by $6 \, mg l^{-1}$ of chlorine after polymer addition (Alekseeva and Khromchenko 1988). Chloroform amounts were determined after 2 h, immediately following
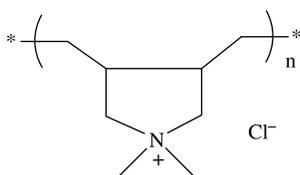

Figure 1 | Structure of poly(diallyldimethylammonium chloride) or PDADMAC.

filtration. A significant decrease in chloroform formation was observed on adding the polymer, from 109 to 37 $\mu g l^{-1}$ for one water and from 123 to 50 $\mu g l^{-1}$ for another water. Such behaviour is expected because of the removal of the coloured compounds. Here natural organic matter (NOM) must be the main source of chloroform.

Detailed work in Taiwan on water of turbidity 131 nephelometric turbidity units (NTU) and total organic carbon (TOC) $3 \, mg l^{-1}$ from the Pan-Hsing water treatment plant focused on a range of conditions, including the chlorine demand of $50 \, mg l^{-1}$ solutions of polymer and monomer (Chang *et al.* 1999). After seven days at a chlorine dose of $2.5 \, mg l^{-1}$ the monomer consumed only $0.1 \, mg l^{-1}$, versus $0.8 \, mg l^{-1}$ for the polymer, showing that the allyl groups in the monomer are not very reactive towards chlorine. With a chlorine dose of $6 \, mg l^{-1}$ the polymer consumed $3 \, mg l^{-1}$ of chlorine, which was taken to indicate a different mechanism under the more forcing conditions, with the initial fragmentation of the polymer giving further reactive species. At a chlorine dose of $2.5 \, mg l^{-1}$, $15 \, \mu g l^{-1}$ of chloroform was formed after 24 h, rising to $53 \, \mu g l^{-1}$ after a week. At the still high PDADMAC concentration of $10 \, mg l^{-1}$ the production was only $2 \, \mu g l^{-1}$ after 24 h and $5 \, \mu g l^{-1}$ after a week. The chlorine demand was reduced by 50% on adding $0.002 \, mol l^{-1}$ of sodium sulfate, and by 67% on adding sulfuric acid to pH 3. These additions also lowered chloroform production by 50% and 90%, respectively. Using $11.6 \, mg l^{-1}$ of chlorine and polymer concentrations of 0, 2, 5 and $10 \, mg l^{-1}$ and a 2 h reaction time the chloroform formation was 102, 85, 94 and $137 \, \mu g l^{-1}$ with pre-chlorination and 93, 26, 66 and $95 \, \mu g l^{-1}$ with post-chlorination. The addition of the chlorine after coagulation naturally yielded less chloroform. Adding polymer reduced by-product formation because of the enhanced removal of organics that are more potent precursors. Overdosing polymer disperses the organics again so that there is an increase in chloroform production.

Some 23 halogenated by-products are reported to be formed on chlorinating tap water spiked with varying amounts of the clays kaolinite, calcium montmorillonite or illite, and treated with various polymers. The polymers tested included PDADMAC in concentrations of 0.1 to $3 \, mg l^{-1}$, and the chlorine levels were 1 and $50 \, mg l^{-1}$ in pre- and post-chlorination modes (Lee *et al.* 1998). A few of the

Table 1 | Reaction of chlorine with PDADMAC at neutral pH

PE dose, mg l⁻¹	Chlorine dose, mg l⁻¹	Time, h	Pre or post chlorination	Other conditions; TOC, mg l⁻¹	THM production, μg l⁻¹	Reference
10	2	4		Dark *	1.2	Kaiser & Laurence 1977
10	2	24		Dark *	1.5	
10	2	2		UV *	3.1	
1	10	1		UV *	1.5	
100	10	4		Dark *	2.4	
100	10	1		UV *	29	
0	6	2		17.4 * *	109	Alekseeva & Khromchenko 1988
0	6	2		19.8 * *	123	
0.5	6	2		9.9 * *	50	
0.5	6	2		11.7 * *	37	
10	2.5	24		3.0	2	Chang et al. 1999
10	2.5	160		3.0	5	
50	2.5	24		3.0	15	
50	2.5	160		3.0	53	
0	11.6	2	pre	3.0	102	
2	11.6	2	pre	3.0	85	
5	11.6	2	pre	3.0	94	
10	11.6	2	pre	3.0	137	
0	11.6	2	post	3.0	93	
2	11.6	2	post	3.0	26	
5	11.6	2	post	3.0	66	
10	11.6	2	post	3.0	95	
2	25	4		Nil	1.0	Fielding et al. 1999

* TOC nil; * * COD values.

compounds, mostly aromatics, were not found in the absence of clay, which contained 0.12 to 0.15% organic carbon that could result in NOM levels of above $1 \, mg \, l^{-1}$, so some of the THMs may well have arisen from the organic material in the clays.

For a zero turbidity water at a $1 \, mg \, l^{-1}$ pre-chlorination dose the by-products amounted to $31 \, \mu g \, mg^{-1}$ polymer with PDADMAC (specific dose unclear), whereas when the turbidity was raised to 5,000 NTU by adding calcium montmorillonite (surface area $600 – 800 \, m^2 \, g \, l^{-1}$) they amounted to $654 \, \mu g \, mg^{-1}$ polymer. When kaolinite (surface area $10 – 20 \, m^2 \, g^{-1}$) was similarly used, they amounted to $400 \, \mu g \, mg^{-1}$ polymer. Higher doses of clay and clays of higher surface area produced more chlorinated compounds, suggesting that polymer attached to the clay surface had an increased vulnerability to chlorine attack. The affinity of the clays for cationic polymer would mean that there would be a high organic content on the surface of the clay. The authors proposed that the particle surface provided a medium facilitating the reaction between the adsorbed polymer and chlorine. The practical aspect is that this strongly suggests that chlorination should follow turbidity and NOM removal, thus minimising THM concerns. An increase in the turbidity of the product water with an increase in pre-chlorination dose also indicated that the polymer molecules were being reduced in size and flocculating efficiency.

Bromodichloromethane, dibromochloromethane and bromoform are also reportedly formed in unstated amounts from the chlorination of tap water and treatment with PDADMAC and anionic or neutral polyacrylamides (Lee *et al.* 1998). The origin of the bromo compounds was not explained, but they could have arisen from the clays, the polymers or the tap water used.

A comprehensive study of the by-products from the chlorination of PDADMAC in distilled water has been made, using $25 \, mg \, l^{-1}$ of chlorine and $2 \, mg \, l^{-1}$ of polymer for 4 hours (Fielding *et al.* 1999). Chloroform production was only $1.0 \, \mu g \, l^{-1}$, but $33 \, \mu g \, l^{-1}$ of formaldehyde was detected, together with dichloroacetic acid ($1.3 \, \mu g \, l^{-1}$), trichloroacetic acid ($9.1 \, \mu g \, l^{-1}$) and a total adsorbable organic halogen (AOX) content as chlorine of $12.3 \, \mu g \, l^{-1}$. Chlorinating a $10 \, mg \, l^{-1}$ solution of PDADMAC with $22.5 \, mg \, l^{-1}$ of chlorine at neutral pH has been reported to form $46 \, \mu g \, l^{-1}$ of formaldehyde (Stockham and Morran 2000).

The contaminants present in PDADMAC have been detailed (Letterman and Pero 1990). The possible extraneous organic components, which have an estimated content of <1 to >5%, include DADMAC monomer, allyl chloride, allyl alcohol, allyldimethylamine, diallyl ether, 5-hexenal, dimethylamine, initiator residues and ethylenediaminetetraacetic acid. The information relating to impurities and monomer has been reviewed, and testing carried out (Fielding *et al.* 1999). For current PDADMAC no readily detectable amounts of chlorination by-products were reported. The monomer content is limited to 5%, but concentrations of <1% are more the commercial level nowadays. The small amount of by-products formed from PDADMAC in pure water shows that there is a miniscule contribution from the polymer. The great variation in chloroform formation that has been observed for the natural waters listed in Table 1 arises from the presence of NOM. Overall, relative to the amounts formed from NOM in the raw water, THM production from the reaction of chlorine with PDADMAC is very small.

N-nitrosodimethylamine (NDMA), a known animal carcinogen of 1,000 times the potency of THMs, has been detected in the treated water of a small community (Child *et al.* 1991). In detailed exploratory experiments all the chemicals present were tested and most were found to be free of the chemical, but a stock solution of PDADMAC had an NDMA level of $74 \, ng \, l^{-1}$. PDADMAC is a source of dimethylamine from which the monomer is made by reaction with allyl chloride. The authors showed that the reaction of PDADMAC with hypochlorite at normal temperatures required high concentrations of polymer, a 0.6% PDADMAC solution producing NDMA at $\mu g \, l^{-1}$ levels when exposed to a 0.5% solution of sodium hypochlorite. The yield of NDMA corresponded to about 0.04 to 0.3%. It was shown that NDMA was not formed when the reagents were present at concentrations normally used in drinking water treatment, to within the existing limit of detection of $10 \, ng \, l^{-1}$. Formation was not related to polyelectrolyte use, as NDMA could be produced when polymer was absent from the system (Jobb *et al.* 1992). Later work on the formation of NDMA in the treatment process, but not related to polyelectrolyte use, identified the seed

fungicide Thiram as a precursor for NDMA (Graham *et al.* 1996). Thiram is a *bis*(dimethylamino) compound that reacts with nitrite and hydrogen ions to form NDMA, and has been detected in water sources. The decreasing level of NDMA with increasing chlorine dose was ascribed to chlorine destroying nitrite before it could react with the Thiram. NDMA formation increased with increasing levels of nitrite.

There are later reports of NDMA in surface and ground waters where no fungicide is implicated (Davis *et al.* 2000; Kruger and Gedney 2000). The surface water showed NDMA formation during the drinking water treatment process, as bench-scale tests with raw water gave amounts of 12, 10 and $6 \, ng \, l^{-1}$ being produced with the use of chlorine and PDADMAC, chlorine and alum with PDADMAC, and chlorine and alum, respectively (Davis *et al.* 2000).

NDMA is formed in the disinfection of municipal wastewater effluent with chlorine, when more than $100 \, ng \, l^{-1}$ can be produced (Njam and Trussell 2001). Other nitrogen sources are no doubt available, so this is of concern where indirect potable water reuse is practised. A suggested reaction scheme is via a nucleophilic attack of dimethylamine (or any secondary amine) on monochloramine, to form a hydrazine intermediate that is rapidly oxidised to the corresponding *N*-nitrosamine (Mitch and Sedlak 2002; Choi and Valentine 2002). Effluents from anion exchange resins also yield NDMA when the resin has been exposed to chlorinated water (Njam and Trussell 2001).

A recent article shows that NDMA is formed when water is coagulated with PDADMAC and then chloraminated, which sits well with the wastewater results (Wilczak *et al.* 2003). All PDADMAC samples tested exhibited NDMA production with chloramines, but negligible levels were produced with free chlorine at typical water treatment doses. In the presence of chloramine the cationic polymer was the only significant source of NDMA precursors, the amount formed increasing with polymer dose and longer contact times with chloramines. Recycled filter backwash supernatant can produce NDMA, the extent of which can be minimized by decreasing the polymer dose and maintaining contact with chlorinated water before chloramine formation. A reduction from $> 10 \, ng \, l^{-1}$ to $\sim 2 \, ng \, l^{-1}$ has been achieved by decreasing the dose from 0.8–1.2 to $0.3 \, mg \, l^{-1}$ and maintaining free chlorine contact before chloramine formation. Other suggested ways of reducing NDMA formation include removal of ammonia before chlorination and breakpoint chlorination in the case of effluent treatment, and complete avoidance of chloramination in drinking water disinfection (Mitch and Sedlak 2002).

Polyamines or poly(2-hydroxypropyl-1-*N*, *N*-dimethylammonium chloride)

Quaternary ammonium polymers made from epichlorohydrin and dimethylamine (EPI/DMA polymers), often referred to as polyamines, are widely used in the water industry. They have 2-hydroxypropyl-1- *N,N*-dimethylammonium chloride units in their structure (Figure 2). Their reactivity towards chlorine has been studied under various conditions, as shown in Table 2.

In quite early work, a test on a concentrated EPI/DMA polymer at $100 \, mg \, l^{-1}$ with $10 \, mg \, l^{-1}$ of chlorine under UV for one hour produced $13.8 \, \mu g \, l^{-1}$ of chloroform (Kaiser and Lawrence 1977). In a later extensive study, two commercial products were reacted at $40 \, mg \, l^{-1}$ concentrations in membrane-purified water with 20 and $50 \, mg \, l^{-1}$ doses of chlorine at neutral pH and 20°C for three days (Feige *et al.* 1980). Chloroform production from one polymer was $43 \, \mu g \, l^{-1}$ and $80 \, \mu g \, l^{-1}$ at the two dose levels, and $31 \, \mu g \, l^{-1}$ and $42 \, \mu g \, l^{-1}$ from the other polymer. Further work was done under less forcing conditions, corresponding to the maximum dose of polymer allowed by the US Environmental Protection Agency, but still far removed from actual treatment practices. One polymer was used at a $10 \, mg \, l^{-1}$ concentration and the other at $20 \, mg \, l^{-1}$, with chlorine doses of 5–$50 \, mg \, l^{-1}$. Lower amounts of chloroform resulted, in the range 3.6–$34 \, \mu g \, l^{-1}$ in the case of the first polymer and 8.5–$34 \, \mu g \, l^{-1}$ for the second, with the greatest levels at the highest chlorine doses. With a chlorine dose of $10 \, mg \, l^{-1}$ the chloroform produced was $6.3 \, \mu g \, l^{-1}$ and $9.9 \, \mu g \, l^{-1}$ for the two polymers

In research aimed at improving the methods of analysis for PEs and their impurities, ECH/DMA produced detectable levels of by-products on reaction with chlorine under realistic treatment conditions (Fielding *et al.* 1999). Chloroform formation was only $3.7 \, \mu g \, l^{-1}$, but greater amounts of dichloroacetic acid ($19.9 \, \mu g \, l^{-1}$), trichloroacetic acid
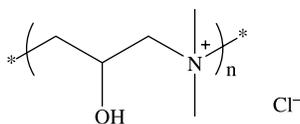
Figure 2 | Quaternary ammonium ECH/DMA polymers, made from epichlorohydrin and dimethylamine, contain 2-hydroxypropyl-1-*N,N*-dimethylammonium chloride units.

$(12.8 \, \mu g \, l^{-1})$, formaldehyde $(61 \, \mu g \, l^{-1})$, glyoxal $(14.6 \, \mu g \, l^{-1})$ and methylglyoxal $(23.9 \, \mu g \, l^{-1})$ were produced. A total halogen compound level of $192 \, \mu g \, l^{-1}$ as chlorine was observed, which is of concern as it shows that many unidentified chloro compounds were being produced, indicating the need for further research.

Possible organic impurities in the polymer include the epichlorohydrin and dimethylamine starting materials, glycidol, ethylenediamine and various chlorinated aliphatic alcohols present as contaminants in the epichlorohydrin (Letterman and Pero 1990). It has been found that the production levels of by-products from the impurities was insignificant (Fielding *et al.* 1999).

For ECH/DMA there is a more variable production of THMs on chlorination than in the case of PDADMAC, but

it is still in the insignificant range, as summarised in Table 2, where all the results were obtained for reactions in distilled or membrane treated water. Of some concern is the high level of total halogen compounds produced, at $192 \, \mu g \, l^{-1}$ versus $12 \, \mu g \, l^{-1}$ for PDADMAC, indicating that there are many chlorinated compounds formed from ECH/DMA that have not been identified. The worst result is from one of the older polymers, although one of similar age parallels the more recent investigation.

Formation of NDMA has been observed in chlorination of raw surface waters where treatment has involved EPI-DMA polymers; the amount formed increases linearly with polymer dose (Kohut and Andrews 2003). However, the doses of polymer and chlorine at several $mg \, l^{-1}$ were relatively high and significant amounts of nitrogen compounds were also present.

Cationic polyacrylamides

A cationic polyacrylamide (CPAM), shown in Figure 3, of molecular weight (MW) 5 M but of undefined charge

Table 2 | The reaction of chlorine with ECH/DMA at neutral pH in pure water

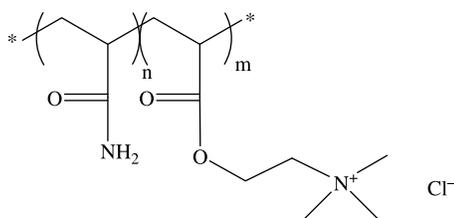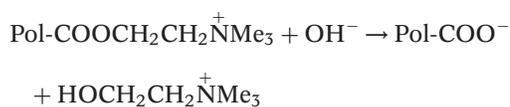| PE no.	PE dose, mg l^{-1}	Chlorine dose, mg l^{-1}	Time h	THM production, μg l^{-1}	Reference
–	100	10 plus UV	1	13.8	Kaiser & Lawrence 1977
1	10	5	72	3.6	Feige *et al.* 1980
1	10	10	72	6.3	
1	10	50	72	34	
2	20	5	72	8.5	
2	20	10	72	9.9	
2	20	50	72	34	
1	40	20	72	43	
1	40	37	72	80	
2	40	20	72	31	
2	40	37	72	42	
–	5	25	4	3.7	Fielding *et al.* 1999

Figure 3 | A cationic polyacrylamide (CPAM).

density (CD), has been treated with various disinfectants (Soponkanaporn and Gehr 1989). Chlorine was used at a $20 \, mg \, l^{-1}$ dose on 1 and $10 \, mg \, l^{-1}$ solutions of polymer at pH 3, 7 and 9. There were increases in the rate and extent of polymer degradation with increasing pH and temperature. At pH 7 with $10 \, mg \, l^{-1}$ of polymer, $28 \, \mu g \, l^{-1}$ of chloroform was produced after 20 days; at pH 9 the chloroform produced was $58 \, \mu g \, l^{-1}$. With UV irradiation at pH 3 for one hour there was a six-fold enhancement in chloroform production. The authors suggest that substandard drinking waters could be produced if there was a significant amount of residual polymer in the product water being disinfected, such as might occur with polymer overdosing, but it is difficult to see how this could happen with normal residue levels, which would reduce the amount of chloroform formed by at least an order of magnitude. The results obtained may be due to the presence of the cationic acrylate or acrylamide monomers. Acrylamide is known to be a potent precursor, $1 \, mg \, l^{-1}$ yielding $800 \, \mu g \, l^{-1}$ of chloroform (Mallevialle *et al.* 1984). However, with the limits on monomer content this would produce up to only $2 \, \mu g \, l^{-1}$ of by-product. The matter of contaminants in the polymer also needs to be addressed. These have been listed as the monomers hydroxypropionitrile and isobutyronitrile (Letterman and Pero 1990).

The use of high pH levels raises the polymer hydrolysis issue, relevant to CPAMs, where the cationic groups are attached to the polymer backbone by ester linkages. These links are susceptible to cleavage, especially under alkaline conditions, to produce carboxylate groups and choline:

$$\text{Pol-COOCH}_2\text{CH}_2\overset{+}{\text{N}}\text{Me}_3 + \text{OH}^- \rightarrow \text{Pol-COO}^-$$

$$+ \, \text{HOCH}_2\text{CH}_2\overset{+}{\text{N}}\text{Me}_3$$

The hydrolysis has been researched to some degree, shown to be pH and CD dependent and more facile as the

pH is increased. Earlier studies suggested that, while a polymer of CD 24% is stable at pH 4, some degradation occurs even at pH 6. At pH 7 the half-life was 24 h, but was shortened to 15 min at pH 8.5 (Aksberg and Wagberg 1989). More recent work on less ionic polymers of CD 6% gives a half-life of 22 months, presumably at neutral pH (Smith-Palmer *et al.* 1994). For the methacrylate version of Figure 3 with a CD of 30% the process is also very slow, especially for pure solutions, whereas salt or pH >8 cause an ease of degradation which is not observed for the polymer of CD 100% (Lafuma and Durand 1989). Amide groups generally are much more stable, with no evidence of their hydrolysis at pH ≤ 8.5 (Aksberg and Wagberg 1989). The amount of information openly available is small and of varying quality. A more rigorous examination of the influence of CD and MW on ease of hydrolysis is warranted, together with a clear comparison of acrylate versus methacrylate. However, disinfection at pH 9 will always involve the production of choline, which although very susceptible to biodegradation may be more reactive towards chlorine than the polymer.

Compared with the other cationic polymers there is a considerable quantity of THMs formed in the case of CPAMs after exposure of $10 \, mg \, l^{-1}$ of polymer in pure water to chlorine, when the yield is $28 \, \mu g \, l^{-1}$ at neutral pH, versus $1.5 \, \mu g \, l^{-1}$ for PDADMAC and $6.3 \, \mu g \, l^{-1}$ for an ECH/DMA polymer, although the chlorine doses and reaction times are rather different at 20, 2 and $50 \, mg \, l^{-1}$ and 20, 1 and 3 days, respectively (Feige *et al.* 1980; Soponkanaporn and Gehr 1989; Fielding *et al.* 1999). More work is warranted on CPAMs, particularly with regard to the hydrolysis of these polymers as a function of CD, and the reactivity of the hydrolysis products towards chlorine. This is especially so because of the age of the data, as polymer purity and stability have improved much in the interval. Measurement techniques are also much better.

ANIONIC POLYMERS

Anionic polyacrylamides

Chlorine under disinfection conditions in a pilot plant certainly reacts with commercial anionic polyacrylamides (APAM) to form THMs. Data on this class of polymer are

summarised in Table 3. In early work a commercial APAM was reacted at $40\,mg\,l^{-1}$ concentrations in membrane-purified water with 20 and $50\,mg\,l^{-1}$ doses of chlorine at neutral pH and 20°C for three days, as described above for a similar study with ECH/DMA polymers (Feige *et al.* 1980). Chloroform production was 70 and $94\,\mu g\,l^{-1}$ at the two dose levels. Trace amounts of bromodichloromethane, at 0.3 and $0.9\,\mu g\,l^{-1}$ respectively, were attributed to the presence of bromo compounds in the original polymer, since the reaction was carried out in purified water and three other polymers did not yield any of this by-product. When a polymer dose corresponding to the maximum allowed by the US EPA was used ($4\,mg\,l^{-1}$), and chlorine doses ranging from 5 to $50\,mg\,l^{-1}$, lower amounts of chloroform of $24–58\,\mu g\,l^{-1}$ resulted. Both sets of tests gave by-product levels up to twice those found for EPI/DMA, even at a much lower polymer concentration. The conclusion was that the polymer itself is not the principal precursor, rather the other chemicals present in the commercial product.

Further studies using GC/MS confirmed the presence of low MW ingredients in the form of alkyl hydrocarbons and cyclic and other unsaturated hydrocarbons, but in very small amounts. Choice of polymer should hence be on the basis of absence of low MW material. For a polymer of MW 10 M and CD 10–12%, by-product formation was attributed mostly to the low MW compounds present. As they were at very low levels the THMs produced were not a problem; there was $<100\,ng\,l^{-1}$ of monomer actually present in the finished water (Fiessinger *et al.* 1983).

The THM levels obtained from the same APAM in another report were given as $7–8\,\mu g\,l^{-1}$ when 1 and $5\,mg\,l^{-1}$ samples of the acrylamide/sodium acrylate copolymer were both reacted with 2 and $10\,mg\,l^{-1}$ of chlorine for 1 to 24 h (Mallevialle *et al.* 1984). Although the polymer produced little THM, the contaminants were capable of forming much larger amounts, particularly acrylamide monomer, which at $1\,mg\,l^{-1}$ yielded $800\,\mu g\,l^{-1}$. This shows the importance of adequate quality control during manufacture. An acrylamide specification limit of $500\,mg\,kg^{-1}$ of polymer would yield $0.4–2.0\,\mu g\,l^{-1}$ of THM at the polymer doses cited. Other contaminants such as acrylic acid and hydroxypropionitrile, an impurity in the acrylamide, were present at much lower specified limits of 50 and $100\,mg\,kg^{-1}$ of polymer, respectively. They also form THMs, but in smaller quantities than acrylamide.

Table 3 | Reaction of chlorine with APAMs

PE dose, mg l^{-1}	Chlorine dose, mg l^{-1}	Time, h	COD, mg l^{-1}	THM production, μg l^{-1}	Reference
40	20	72	Nil	70	Feige *et al.* 1980
40	37	72	Nil	94	
4	5	72	Nil	24	
4	50	72	Nil	58	
1–5	2–10	1–24	Nil	7–8	Mallevialle *et al.* 1984
0	6	2	17.4	109	Alekseeva & Khromchenko 1988
0	6	2	19.8	123	
0.5	6	2	12.1	97	
0.5	6	2	13.8	79	
0.5	6	2	14.4	76	
10	25	4	Nil	1.2	Fielding *et al.* 1999

Chloroform production from coloured waters (COD $12–20\,\mathrm{mg\,l^{-1}}$) treated with alum and then $6\,\mathrm{mg\,l^{-1}}$ of chlorine for 2 hours was lowered from $109–123$ to $76–97\,\mu\mathrm{g\,l^{-1}}$ when $0.5\,\mathrm{mg\,l^{-1}}$ of APAM was later added and chloroform amounts were determined after 2 hours (Alekseeva and Khromchenko 1988). This indicated that polymer after alum enhanced the removal of coloured compounds, and that NOM was the main source of chloroform.

Chain scission occurs on reacting an APAM of MW 16 M and CD 10% with $69\,\mathrm{mg\,l^{-1}}$ of chlorine for 3 hours, the MW decreasing from 16 M to 30,000; longer reaction times can lower it to 8,000 and eliminate any effectiveness as a flocculant (Aizawa *et al.* 1991). Under practical conditions, such a dose of chlorine caused a residual turbidity after 1 minute of 30 NTU, versus 11 NTU when there was no chlorine added. After 30 min the turbidity levels were similar at 10 and 11 NTU, respectively, showing that chlorination significantly increased the sedimentation time.

Later work in the area shows little in the way of chloroform formation ($1.2\,\mu\mathrm{g\,l^{-1}}$) from APAM, using $10\,\mathrm{mg\,l^{-1}}$ of solid polymer and $25\,\mathrm{mg\,l^{-1}}$ of chlorine for 4 h at pH 7 (Fielding *et al.* 1999). The total halogen compounds, however, amounted to $21\,\mu\mathrm{g\,l^{-1}}$. Other compounds produced were dichloroacetic acid ($9\,\mu\mathrm{g\,l^{-1}}$), trichloroacetic acid ($13\,\mu\mathrm{g\,l^{-1}}$), formaldehyde ($34\,\mu\mathrm{g\,l^{-1}}$) and glyoxal ($1.9\,\mu\mathrm{g\,l^{-1}}$). Similar results were obtained for an emulsion form of the polymer, although the total halogen compounds level was much higher at $69\,\mu\mathrm{g\,l^{-1}}$, which suggests that the chemicals used to stabilise the emulsion may have been responsible. Contaminants in APAMs other than monomers have been listed as hydroxypropionitrile and isobutyronitrile (Letterman and Pero 1990). They have been assessed, and polymer testing carried out; for APAM no readily detectable amounts of chlorination by-products from monomer or impurities were reported (Fielding *et al.* 1999).

Thus APAMs do not form significant levels of THMs on reaction with chlorine, with THM formation at trivial levels compared with the amounts produced by NOM (Table 3). The synthetic polymers provide contributions equivalent to the amount of monomer present, with acrylamide monomer the most potent precursor. It is essential that the NOM precursor compounds be removed before chlorination. If treatment to remove NOM includes polymer use, it would be advantageous to have an effective method for analysing the level of residual polymer in the product water. A simple method of tagging polymers is required as has been proposed (Bennett *et al.* 2000). The APAM data show a definite improvement in polymer quality over the years.

NON-IONIC POLYMERS

Polyacrylamide

Similar results to the cationic and anionic polyacrylamides were obtained in tests on $10\,\mathrm{mg\,l^{-1}}$ of non-ionic polyacrylamide (PAM) with $10\,\mathrm{mg\,l^{-1}}$ of chlorine, which produced $1.8\,\mu\mathrm{g\,l^{-1}}$ of chloroform under UV irradiation (Kaiser and Lawrence 1977). None was detected when the polymer dose was $1\,\mathrm{mg\,l^{-1}}$. At $100\,\mathrm{mg\,l^{-1}}$ of polymer, the yield increased to $10.9\,\mu\mathrm{g\,l^{-1}}$ under UV conditions. The data are shown in Table 4, together with the results from other studies of PAMs. Damage to the polymer has been shown to be detrimental to treatment efficiency, in tests on a kaolinite suspension of turbidity 2 NTU (Bolto and Levine 2002). Data on the final turbidity of the product water and the rate of filtration when PAM was added are shown in Table 5. A range of polymer doses was explored, from 0 to $1\,\mathrm{mg\,l^{-1}}$, which determined the optimum dose. UV treatment resulted in the need for a higher dose of polymer, and chlorine lowered the product water quality, which was worst when chlorination followed UV. Filtration times were shortened on progressive degradation of the polymer. Filterability was slower with undegraded polymer as the longer, intact polymer chains actually lowered permeability, and in the process resulted in a higher quality product water.

Two commercial PAMs were reacted at $40\,\mathrm{mg\,l^{-1}}$ concentrations in membrane-purified water with 20 and $50\,\mathrm{mg\,l^{-1}}$ doses of chlorine at neutral pH and 20°C for three days, as mentioned already for APAM (Feige *et al.* 1980). Chloroform production was 140 and $110\,\mu\mathrm{g\,l^{-1}}$ at the two dose levels for one polymer, and 30 and $50\,\mu\mathrm{g\,l^{-1}}$ for the other. When a much less concentrated polymer solution was used, corresponding to the maximum allowed by the US EPA ($1\,\mathrm{mg\,l^{-1}}$), plus chlorine doses of 5 to $50\,\mathrm{mg\,l^{-1}}$,

Table 4 | Reaction of chlorine with PAMs

PE dose, mg l^{-1}	Chlorine dose, mg l^{-1}	Time, h	COD, mg l^{-1}	Other conditions	THM production, μg l^{-1}	Reference
1	10	1	Nil	UV	0	Kaiser & Lawrence 1977
10	10	1	Nil	UV	1.8	
100	10	1	Nil	UV	10.9	
1	5	72	Nil	poly 1	7.7	Feige et al. 1980
1	10	72	Nil	poly 1	9.2	
1	5	72	Nil	poly 2	1.2	
1	50	72	Nil	poly 2	3.3	
40	20	72	Nil	poly 1	140	
40	50	72	Nil	poly 1	110	
40	20	72	Nil	poly 2	30	
40	50	72	Nil	poly 2	50	
0	6	2	17.4	NOM	109	Alekseeva & Khromchenko 1988
0	6	2	19.8	NOM	123	
0.5	6	2	11.6	NOM	94	
0.5	6	2	15.2	NOM	160	
0.5	6	2	15.4	NOM	154	

lower amounts of chloroform resulted, ranging from 7.7 to 9.2 μg l^{-1} for one polymer and 1.2 to 3.3 μg l^{-1} for the other. For the first polymer, the highest chloroform production was not from the highest chlorine dose, but from the 10 mg l^{-1} experiment. The levels obtained are relatively low,

showing that these commercial PAMs contain little in the way of precursors. The conclusion was that the polymer itself is not the principal precursor, but rather other chemicals present in the commercial product. Further studies using GC/MS confirmed the presence of low MW

Table 5 | Performance of PAM treated water after various disinfection regimes (Bolto and Levine 2002)

Optimum PAM dose, mg l^{-1}	Chlorine dose, mg l^{-1}	UV, 1 h	Final turbidity, NTU	Time to filter 100 ml, min
0.04	None	No	0.16	670
0.04	5	No	0.22	490
0.10	None	Yes	0.47	450
0.10	5	Yes	0.64	400

ingredients in the form of alkyl hydrocarbons and cyclic and other unsaturated hydrocarbons, but in very small amounts. The choice of polymer should hence be on the basis of absence of low MW material as well as on performance as a flocculant.

Chloroform production from coloured waters (COD $12-20\,mg\,l^{-1}$) treated with alum and then $6\,mg\,l^{-1}$ of chlorine for 2 hours was about the same when $0.5\,mg\,l^{-1}$ of PAM was subsequently added, but the NOM concentration was not the same for each (Alekseeva and Khromchenko 1988). Assuming a value of $117\,\mu g\,l^{-1}$ for water of COD 15, adding the polymer raised this to a mean level of $157\,\mu g\,l^{-1}$, showing a significant contribution from the PAM, or more likely its contaminants.

The potency of acrylamide monomer in by-product formation is indicated by the production of $800\,\mu g\,l^{-1}$ of by-products from 1 mg of monomer (Mallevialle *et al.* 1984). However, with the maximum monomer limit of $500\,mg\,kg^{-1}$ of polymer this would form only $2\,\mu g\,l^{-1}$ of THMs at the doses used. Hence non-ionic polyacrylamides of high purity should not form significant levels of THMs on reaction with chlorine. As with APAMs, formation is negligible compared with the amounts produced by NOM, and is dependent on the amount of monomer present.

CONCLUSIONS

With the concentrations of the commonly used cationic polymers and chlorine normally met in water treatment, the formation of disinfection by-products can be seen to be minimal. For two of the cationic polymers most commonly used in water treatment, PDADMAC and ECH/DMA, the polymer is not the main precursor. Further checking is necessary regarding CPAMs, but the normally low residual polymer levels when chlorination takes place after treatment should result in insignificant THM levels.

When unsatisfactorily high levels of by-products have been produced, other chemicals present in the commercial product have been identified as the precursors, either directly or indirectly. The most potent of these is acrylamide monomer. As long as strict checks are kept on the amount of this monomer in commercially available CPAMs, it would appear that THM formation is minor. However, the

other by-products that can be produced may warrant further exploration. The total organic halogen compounds level of $192\,\mu g\,l^{-1}$ obtained for ECH/DMA, versus $12\,\mu g\,l^{-1}$ for PDADMAC, is the most notable item requiring attention. The detection of formaldehyde at $33-46\,\mu g\,l^{-1}$ levels for PDADMAC and $61\,\mu g\,l^{-1}$ for ECH/DMA should be less of a worry as such aliphatic compounds are biodegradable, and should be removable by the microbes that accumulate in biological activated carbon treatment. The carbon will remove any residual chlorine that would otherwise annihilate the supported microbes (Degrémont 1991), but a separate column dedicated to this step may be necessary if there is a high residual chlorine level. Nitrosodimethylamine, however, is a quite serious contaminant, formed in very small amounts in normal operations with cationic polymers, but at levels of concern when other nitrogen compounds are present, as in water reuse applications.

More data are needed on CPAMs, which appear to have been somewhat neglected, especially the possible contribution from the cationic acrylate monomer. The hydrolysis of these polymers as a function of the charge density, and the reactivity of the hydrolysis products as well as the polymer towards chlorine, also require attention.

APAMs and PAMs do not form significant levels of THMs on reaction with chlorine either, relative to the amounts produced by NOM, the synthetic polymers again producing by-products in quantities dependent on the amount of monomer present. All the results with NOM present show how necessary it is that such precursor compounds be removed before chlorination. If treatment to remove NOM includes polymer use, it would be advantageous to have a more efficient method than those currently available for analysing the level of residual polymer in the product water.

The choice of the most appropriate polymer should thus be on the basis of the absence of low MW material as well as on process performance. Other contaminants in the polymers apart from acrylamide monomer are capable of forming THMs. In APAMs, acrylic acid, hydroxypropionitrile and isobutyronitrile have been observed in the past in small amounts. Provided there is continued strict quality control during polymer manufacture the amounts of THMs produced will be insignificant. Extreme conditions can cleave the polymer chain and reduce the flocculating

powers of the polymer, which can be of serious practical significance as both chain cleavage and a reduction in polymer charge are detrimental to plant performance. More research under conditions close to those met with in practice is essential on this topic.

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