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## Review

# Organic polyelectrolytes in water treatment

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### ABSTRACT

The use of polymers in the production of drinking water is reviewed, with emphasis on the nature of the impurities to be removed, the mechanisms of coagulation and flocculation, and the types of polymers commonly available. There is a focus on polymers for primary coagulation, their use as coagulant aids, in the recycling of filter backwash waters, and in sludge thickening. Practicalities of polymer use are discussed, with particular attention to polymer toxicity, and the presence of residual polymer in the final drinking water. The questions of polymer degradation and the formation of disinfection by-products are also addressed.

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## 1. Introduction

The main applications of organic polyelectrolytes in potable water production are in coagulation and flocculation, and in the dewatering of treatment plant sludges. The water production processes are usually followed by sedimentation and filtration, although with only slightly contaminated waters the sedimentation step may be omitted. Flotation is an option instead of sedimentation, especially for algae-laden waters. The sludges obtained from the various separation processes have very high water contents and must be further concentrated to minimise transportation costs; polymers have a role in this sludge conditioning.

Polymers have been utilised in coagulation/flocculation processes for water purification for at least four decades (Kawamura, 1976). In comparison with alum, some of the advantages flowing from the use of polymers in water treatment are:

- lower coagulant dose requirements,
- a smaller volume of sludge,
- a smaller increase in the ionic load of the treated water,
- reduced level of aluminium in treated water,
- cost savings of up to 25–30% (Rout et al., 1999; Nozaic et al., 2001).

Polymers are especially beneficial in coping with the problems of slow-settling flocs in low-temperature coagulation or in treating soft coloured waters, where they improve settleability and increase the toughness of flocs (Faust and Aly, 1983). The capacity of a treatment facility may be more than doubled with the formation of larger and stronger flocs,

the rate of solid and water phase separation can be significantly increased, and the dosage of other chemicals lowered. Also, the range of waters that can be treated is wider. There are disadvantages of course, with higher costs in particular situations and environmental factors being the main concern. There is a greater sensitivity to incorrect dosage, with turbidity and natural organics removal less efficient in some instances (Nozaic et al., 2001).

With a few notable exceptions (Leu and Ghosh, 1988), there is not a great deal of published information on the relationship between polymer structure and treatment performance in drinking water production; that is, on the influence of molecular structure on coagulation/flocculation, on the rates of both precipitation and sedimentation, on product water quality and on the solids content of the final sludge. Raw water processing normally involves physicochemical procedures, based on coagulation and flocculation of suspended solids and colloids, and the adsorption of soluble material on solid substrates such as metal hydroxide flocs. The focus in this review is on the use of soluble polymers in coagulation and flocculation processes.

## 2. Natural impurities in water

The impurities present in the source water can be in the form of dissolved and colloidal natural organic matter (NOM), as dissolved salts, and as suspended material such as clays, silica, microbial cells or algae. Some of the more commonly found natural components containing organic material are, in decreasing size order, zooplankton, phytoplankton, bacteria, viruses, clay-humic acid complexes, humic acids, proteins, polysaccharides, fulvic acids, and very small species such as

fatty acids, carbohydrates, amino acids, and hydrocarbons. They are formed by the biological degradation of organic life substances (Thurman, 1985), and include highly coloured compounds. Inorganic salts of natural origin are also present to some degree.

Dissolved organic compounds, defined as those which will pass through a membrane having pores of 0.45 µm size, when measured as dissolved organic carbon (DOC), have levels in the range 0.1–115 mg/l, with 5.75 mg/l being reported as a global average for streams (Boggs et al., 1985). DOC poses a problem for the water treatment industry for a number of reasons. Apart from the aesthetic problems of colour, taste and odour, its presence poses a health hazard because of the formation of potentially carcinogenic chlorinated hydrocarbons when the water is disinfected with chlorine—the well-known problem of disinfection by-products (DBPs). Furthermore, DOC exacerbates the deterioration of the microbiological water quality in distribution systems, fouls membranes and ion-exchange resins, interferes with the oxidation of dissolved iron and manganese to insoluble easily removed forms, and can encourage corrosion, especially of copper, but not always of iron (Huang and Yeh, 1993; Broo et al., 1999). It can also block the pores of activated carbon filters, hindering adsorption of trace organic contaminants such as taste and odour compounds (Ding et al., 2006). Humic substances are troublesome materials in that they have quite variable properties, in terms of acidity ( $pK_a$  3–5), molecular weight (MW) (several hundred to tens of thousands) and molecular structure (mostly phenolic and carboxylic acid functionalities, but also alcohol, quinone, ether, ester, and ketone groups). They behave as negatively charged colloids or anionic polyelectrolytes at natural pH levels and have surface-active properties, but can interact via their hydrophobic aromatic and aliphatic regions with non-polar pollutants such as pesticides and polychlorinated biphenyls. Humic substances are often present as stable complexes with metal ions. These variable properties influence reactivity, which as mentioned changes spatially and temporally. If the smaller charged organic molecules are first removed from raw water by ion exchange, as proposed in one full-scale plant (Bourke and Slunjski, 1999), a subsequent alum clarification stage is greatly facilitated: larger flocs are formed that settle three times more rapidly, far less organics are left in the product water, and only 25% of the original alum dose is required in a conventional clarification process (Bursill et al., 1985).

Suspended particulate matter is an important component of all natural waters. Particles can range from 10 µm or more down to sub-micron colloidal size (Thurman, 1985). Such material needs to be removed from potable supplies because it supplies a surface onto which microbes can adsorb and be protected from disinfection chemicals by a coating of slime, or the particles themselves may be actual bacteria or oocysts of protozoa such as *Cryptosporidium*. Typical suspended solids levels are 2–200 mg/L, although they can be higher than 50,000 mg/L in flooding rivers. The particles have a substantial organic and biological content, typically 1–20%, but are mainly inorganic materials like silica, aluminosilicates and iron and manganese oxides. The charge on the particles is controlled by an adsorbed layer of NOM, as well as by the salinity and the concentration of divalent cations in the water (Beckett and Le,

1990). Humic substances can adsorb onto the particles via surface metal cations. The surface potential of the particles is an important parameter influencing coagulation and adsorption behaviour. It can be monitored via particle microelectrophoresis, and in natural systems is invariably negative, irrespective of the nature of the primary particle (Beckett and Le, 1990). The coating of organics has a strong impact on the amount of coagulant required and the rate of coagulation, slowing the rate markedly at low salinities, but having less of an effect as the salinity increases (Gibbs, 1983).

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### 3. Polymer types

#### 3.1. General

Polymers used in water treatment are water soluble and mainly synthetic in nature, although a few natural products may be of interest. Polymers are broadly characterised by their ionic nature: cationic, anionic and non-ionic. These will be described separately below, after a brief discussion of polymer properties and characterisation. Strictly, ionic polymers should be called polyelectrolytes, although this terminology is not always followed.

#### 3.2. Characterisation of polymers

The most important characteristics of polymeric flocculants are MW and, in the case of polyelectrolytes, charge density (CD). MW values range from a few thousand up to tens of millions. Conventionally, polymers are regarded as having, low, medium or high MW, corresponding to MW values in the ranges:  $<10^5$ ,  $10^5$ – $10^6$  and  $>10^6$ , respectively. CD will be discussed later.

All polymers used as flocculants in water treatment, must be water soluble. In aqueous solution polymers very often adopt a random coil configuration, shown schematically in Fig. 1. For very high MW polymers, the size of the coil is typically of the order of a hundred nm, with the size being proportional to the square root of the MW. A convenient measure of the “diameter” of a polymer molecule is the root mean square (rms) value of the end-to-end distance,  $r$  (see Fig. 1). For many common non-ionic polymers, this is given (in nm) roughly by  $0.06M^{1/2}$ , where  $M$  is the MW (Napper, 1983). For  $M = 1$  million this gives the rms end-to-end distance as about 60 nm. Note that if a polymer chain were fully stretched, the end-to-end distance could be up to 10 µm or more, but this is a highly unlikely arrangement. The random coil represents the most probable configuration. The extent of the random coil depends on the interaction between polymer segments. If there is appreciable repulsion between segments, then the coil expands somewhat. The most obvious examples are polyelectrolytes, where the segments are charged. In this case, the polymer coil can be significantly expanded and there are important ionic strength effects. At quite high ionic strength the repulsion between charged segments is ‘screened’ by ions in solution and so the coil expansion is not so great. As the salt concentration is reduced, repulsion becomes more significant and the polymer coil adopts a more expanded configuration. This concept is illustrated in Fig. 2. The effect can be quite important in practice.

A polymer chain in a random coil configuration effectively occupies a much larger volume than the equivalent number of isolated monomer units, simply because some of the aqueous solution is included within the coil. For this reason, polymer solutions can scatter light and show a significantly higher viscosity than water. Both of these effects can be used to estimate polymer MW. Viscosity methods are most commonly used and quoted MWs of commercial products are usually based on determinations of intrinsic viscosity. For polyelectrolytes, such measurements are normally carried out at high salt concentrations, so that repulsion between charged groups is reduced and the chains adopt an unexpanded random coil configuration. MW is a very important property, which can greatly influence the effectiveness of a flocculant.

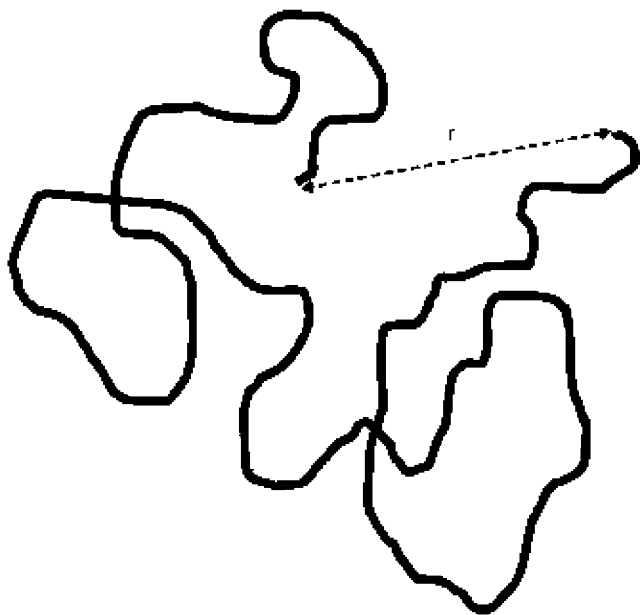


Fig. 1 – A polymer chain in a random coil configuration. The end-to-end distance,  $r$ , is shown.

When polymer solutions are subjected to high shear, the polymer chains can be considerably extended. Bonds near the middle of the chain are subjected to great strain and can rupture, leading to a reduction in MW (Abdel-Alim and Hamielec, 1973; Scott et al., 1996). This effect gives a significant reduction in viscosity and can be important for flocculation under turbulent conditions.

In the case of polyelectrolytes, the CD is also a very significant parameter, which can be experimentally determined by the technique of colloid titration (Kam and Gregory, 1999). CD can be expressed in terms of mole per cent of charged groups or as milliequivalents per gram (meq/g). As an example, for a copolymer of acrylamide and dimethylaminoethyl acrylate (DMAEA) (see below) with 30 mol% of the cationic component, we can calculate the CD from the formula weights of the monomer units (71 for acrylamide and 194 for quaternised DMAEA) and this turns out to be about 2.8 meq/g. In the case of a 100% cationic polyelectrolyte, such as poly(diallyldimethyl ammonium chloride) or PDADMAC, the CD follows directly from the formula weight of the monomer unit (162), since 1 g of polymer has 1/162 equivalents of charge. Hence the CD is 6.2 meq/g. It should be noted that these calculations of CD assume that the polymer segments are strongly ionic and hence fully charged. For weakly ionic groups, the actual CD depends on the fraction of groups that are ionised and hence on the pH of the solution.

Broadly, polyelectrolyte CD values are regarded as low, medium or high if the mol% of ionic groups are approximately: 10%, 25%, and 50–100%, respectively

### 3.3. Cationic polyelectrolytes

There are many varieties of cationic polymers available, as has been reviewed in detail (Bolto, 1995). The structures of the polymers most commonly used are shown in Fig. 3. Usually, but not always, they possess quaternary ammonium groups that have a formal positive charge irrespective of pH, and are termed strong electrolyte polymers. Weak electrolyte polymers that acquire cationic properties in acidic media are also

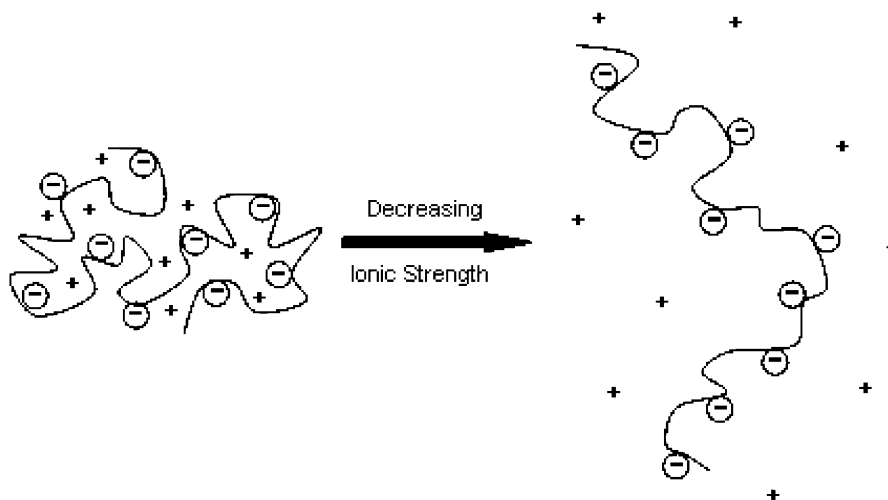
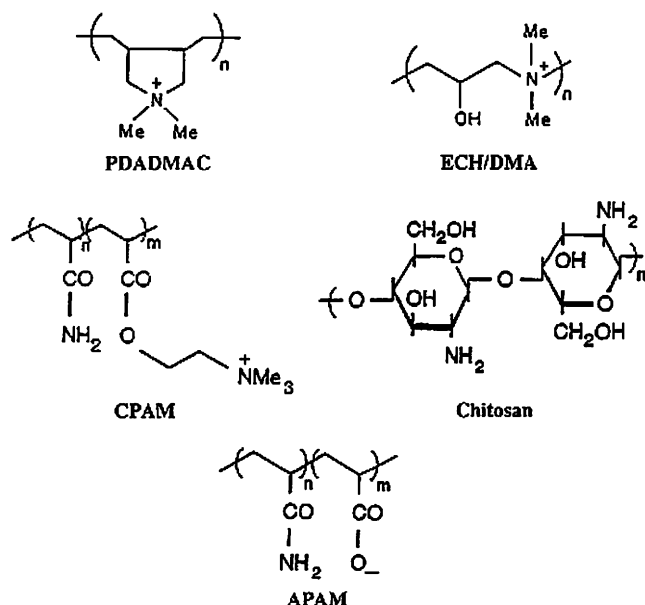


Fig. 2 – Showing the expansion of a polyelectrolyte chain with decrease of ionic strength.



**Fig. 3** – Structures of the cationic polyelectrolytes polydiallyldimethyl-ammonium chloride (PDADMAC), polymers from epichlorohydrin and dimethylamine (ECH/DMA), cationic polyacrylamide (CPAM), chitosan and anionic polyacrylamide (APAM).

available. Some natural products or their derivatives, such as chitosan, are also employed in water treatment.

### 3.3.1. Poly(diallyldimethyl ammonium chloride)

Polymerisation of diallyldimethylammonium chloride produces PDADMAC, a water-soluble polymer. The polymer is of low-to-medium MW and contains five-membered pyrrolidinium units, as shown in Fig. 3, where the counterion has been omitted. Higher MW copolymers have been made with acrylamide (Wandrey and Jaeger, 1985).

### 3.3.2. Epichlorohydrin/dimethylamine polymers

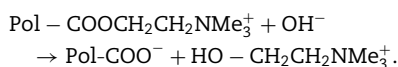
Epichlorohydrin forms polymers with ammonia and primary and secondary amines, the preparation of which has been thoroughly reviewed (Vorcheimer, 1981). The reaction of epichlorohydrin with a secondary amine such as dimethylamine produces a low MW linear polymer, denoted by ECH/DMA, in which all the active sites are quaternary ammonium groups, belying the common term of ‘polyamine’ for this polymer.

### 3.3.3. Cationic polyacrylamides (PAMs)

Random copolymers of acrylamide and the cationic ester acryloyloxyethyltrimethyl-ammonium chloride, formed by quaternisation of DMAEA with methyl chloride, are extensively used in the water industry (Hoover, 1970; Baade et al., 1989). The methacrylate analogue is also commercially available. The cationic content in the cationic PAMs or CPAMs can be in the approximate range 10–80%.

Hydrolysis of the ester groups and consequent loss of cationic charge has been found to be CD and pH dependent,

with hydrolysis encouraged by more alkaline conditions:



It has been observed that some degradation occurs even at pH 6 for polymers having a CD of 24%, with a half life of 24 h at pH 7 and 0.25 h at pH 8.5 (Aksberg and Wagberg, 1989). The polymer is stable at pH 4. There is no hydrolysis of acrylamide units up to pH 8.5. More recent work on ester hydrolysis on less ionic polymers having a CD of 6% found a half life of 22 months, but the pH level was not specified (Smith-Palmer et al., 1994). For a CD of 30% the process is also very slow, especially for pure solutions, whereas salt or pH levels above 8 causes an ease of degradation that is not observed for the polymer of 100% charge (Lafuma and Durand, 1989). As well as the loss of cationic sites, there is a change in the chain conformation on hydrolysis because of the formation of anionic carboxylate groups, which reduces the chain extension and make the polymer less efficient as a flocculant. For the homopolymers, the corresponding methacrylate is less vulnerable to hydrolysis (van de Wetering et al., 1998).

### 3.3.4. Natural cationic polymers

There are several naturally occurring polymers that have inherent cationic properties or the polymer can be modified to yield a cationic polyelectrolyte. The most prominent of these is chitosan, a partially deacetylated chitin which is as a 1:4 random copolymer of N-acetyl- $\alpha$ -D-glucosamine and  $\alpha$ -D-glucosamine (Rinaudo, 2006). The commercial product is of medium MW and has a CD that is pH dependent (Muzzarelli, 1977). It can be quite effective at NOM removal (Bolto et al., 1998, 2001; Eikebrokk and Saltnes, 2002), even though it is but slightly charged (17%) at neutral pH levels. Such a weakly basic polymer may be operating via hydrogen bonding through the free amino groups on the polymer and aliphatic and aromatic hydroxyl groups on the NOM. The use of chitosan in water purification applications generally has been extensively reviewed, with references to its use in decolourising dyehouse effluents, the treatment of food processing wastes, metal ion removal and sludge conditioning (Pariser and Lombardi, 1989). The effect of MW and degree of deacetylation on the coagulation and flocculation of bentonite suspensions has been explored (Roussy et al., 2005).

Starch, a polymer composed of  $\alpha$ -D-glucose units, can be converted to a cationic derivative by the reaction of the primary OH group in alkali treated starch with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, so that the cationic site is attached via an ether link to the polymer chain (Harrington and Engelhardt, 1979). The product has medium MW and the CD can be low or medium. A medium CD material was better in tests on clarifying clay, raw and treated sewage suspensions, and has been used as a demulsifier for oil in water emulsions. Graft copolymers of starch and 2-hydroxy-3-methacryloyloxypropyltrimethyl ammonium chloride or mixtures of dimethylaminoethyl methacrylate and acrylamide have been prepared and evaluated for flocculation performance (Jones et al., 1972; Fanta et al., 1972). Highly substituted cationic starches have been studied also (Sableviciene et al., 2005).

The modification of natural polysaccharides has been explored as a way of combining their best attributes with those of synthetic polymers (Pal et al., 2006). Polysaccharides are fairly shear stable, in contrast with long-chain PAMs, and are biodegradable. However, they have lower efficiencies so need to be used at higher concentrations. Grafting synthetic polymers onto amylopectin, guar gum and starch has yielded polymers that are claimed to be more effective because of dangling polymer chains, particularly in the case of amylopectin, which is of high MW and has a highly branched structure. A similar approach was made with glycogen, a very high MW and highly branched polysaccharide, by reacting the OH groups with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride. The product performed better in the flocculation of iron ore particles than a commercial CPAM of medium MW and low CD.

A number of flocculating agents have been reported which are lignin based, being prepared by modifying kraft lignin to give it cationic character (McKague, 1974). A Mannich reaction product and a quaternary ammonium derivative made by chloromethylation and amination were less efficient than alum for the removal of colour from pulp mill effluents.

The aqueous extract from macerated seeds of the horse-radish tree *Moringa oleifera* yields a cationic protein that can be effective in water treatment applications, and is especially appropriate for developing countries (Ndabigengesere et al., 1995). The treatment performance has been discussed (Coghlan, 1991; Folkard, 2002).

### 3.3.5. Charge densities of cationic polyelectrolytes

Table 1 outlines the CD of various cationic polymers in mol% and meq/g of polymer. The former is only an approximation as there are other components present in the polymers such as co-monomers used to increase chain length or to create chain branching, as well as initiator fragments.

## 3.4. Anionic polyelectrolytes

The most commonly used anionic polymers contain weakly acidic carboxylic acid groups, so the CD depends on pH.

### 3.4.1. Anionic PAMs

High MW carboxylic acid polymers derived from PAM are extensively employed as flocculating agents in the water and

other process industries, where a low CD is the general rule. Copolymers with the anionic structure shown in Fig. 3 can be prepared either by copolymerisation of acrylamide and acrylic acid or its salts, or by polymerisation of acrylamide followed by partial hydrolysis (Vorchheimer, 1981). The former approach gives a roughly random copolymer, whereas some clustering of anionic groups can occur when alkaline hydrolysis is employed. The CD can be determined by potentiometric titration of the copolymers or by direct polyelectrolyte titration (Wassmer et al., 1991). Anionic PAMs, or APAMs, containing varying proportions of acrylamide co-monomer are listed in Table 2 in terms of their CD, as mol% and calculated on a theoretical basis in meq/g of polymer.

### 3.4.2. Natural anionic polymers

Many sulfated polysaccharides are available as natural biopolymers or their derivatives, some examples being heparin, dextran sulphate, mannan sulphate and chondroitin sulphate, but the applications are mainly medical (Voycheck and Tan, 1993). One proposed for use in the water industry is the modified natural polymer lignin sulphonate, made by sulfonating low MW kraft pine lignin (Meister and Li, 1990). Certain of these polymers are equivalent in performance to cationic PAMs for the dewatering of sludge. Tannins have also received attention (Rice et al., 1964).

## 3.5. Non-ionic polymers

Synthetic polymers like PAM have been used in the water industry for some four decades, but some polymers of natural origin have been in use for centuries.

**Table 2 – Charge densities of anionic polyacrylamides**

Molecular formula	CD (mol%)	CD (meq/g)
$C_3H_3O_2 Na$	100	10.6
$(C_3H_3O_2 Na)_{0.75} (C_3H_5ON)_{0.25}$	75	8.5
$(C_3H_3O_2 Na)_{0.50} (C_3H_5ON)_{0.50}$	50	6.1
$(C_3H_3O_2 Na)_{0.25} (C_3H_5ON)_{0.75}$	25	3.3
$(C_3H_3O_2 Na)_{0.1} (C_3H_5ON)_{0.9}$	10	1.4

**Table 1 – Charge densities of some cationic polyelectrolytes**

Polymer	Molecular formula	CD (mol%)	CD (meq/g)
PDADMAC	$C_8H_{16}N Cl$	100	6.2
ECH/DMA	$C_5H_{12}ON Cl$	100	7.3
CPAM	$C_8H_{16}O_2N Cl$	100	5.2
CPAM	$(C_8H_{16}O_2N Cl)_{0.5} (C_3H_5ON)_{0.5}$	50	3.8
CPAM	$(C_8H_{16}O_2N Cl)_{0.25} (C_3H_5ON)_{0.75}$	25	2.5
CPAM	$(C_8H_{16}O_2N Cl)_{0.1} (C_3H_5ON)_{0.9}$	10	1.2
Chitosan	$C_6H_{11}O_4N.HCl$	100	5.2

### 3.5.1. Polyacrylamide

Synthetic polymers often described as non-ionic actually contain some 1–3% of anionic groups, as in the case of PAM where they arise from hydrolysis of the amide groups under the preparative conditions employed (Luttinger, 1981). PAM having less than 1% hydrolysis has been made by careful attention to the monomer concentration, pH, temperature and initiator, using a redox type preferably (Vorchheimer, 1981).  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy is the most reliable method of determining the degree of hydrolysis of concentrated PAM samples (Taylor and Nasr-El-Din, 1994).

### 3.5.2. Natural non-ionic polymers

Those utilised include starches, galactomannans, cellulose derivatives, microbial polysaccharides, gelatins, and glues. They are used as flocculants to aid solid–liquid separations, and vary in their structure, MW, biodegradability, and ease of dissolution (Levine, 1981). Their main advantages are ready acceptance on health grounds and ease of biodegradation. Grafting PAM onto amylopectin, guar gum and starch has yielded polymers that are claimed to be quite effective because of dangling PAM chains, particularly in the case of amylopectin (Rath and Singh, 1997). PAM-grafted amylopectin is better at flocculating a kaolin suspension than analogous grafts of PAM onto starch or amylose, as these water-soluble polysaccharides are less branched and of lower MW than amylopectin. Of the amylopectin products, that with fewer but longer grafts was the best of the series.

## 4. Mechanisms of action

Mechanisms of flocculation of particles by polymers can be described under the following headings:

- polymer bridging,
- charge neutralisation, including ‘electrostatic patch’ effects,
- depletion flocculation.

The last of these, depletion flocculation (e.g. Jang et al., 2004), which depends on the presence of free, *unadsorbed* polymer, is probably not significant in water treatment practice and will not be considered here. The other effects are crucially dependent on the adsorption of polymers on particle surfaces and the topic of polymer adsorption will be introduced first.

### 4.1. Polymer adsorption

If there is some affinity between polymer segments and a particle surface, then adsorption of polymer chains may occur. The adsorption affinity must be sufficient to outweigh the loss of entropy associated with polymer adsorption, since an adsorbed chain will have a more restricted configuration than a random coil in free solution. Actually, the affinity between a polymer segment and a surface site need not be great, since there are many attachment points. For a long polymer chain, the chance of all attached segments becoming detached simultaneously is very remote. For this reason,

polymer adsorption is often considered to be irreversible. The configuration of an adsorbed polymer chain can be very different from the random coil in solution. A widely accepted model of an adsorbed polymer chain (Napper, 1983) is shown in Fig. 4. In this model, three distinct categories of segment are assumed:

- attached to the surface in *trains*,
- projecting into the solution as *tails*,
- in the form of *loops*, between trains.

It must be stressed that this is an *equilibrium* arrangement, which may take some time to achieve after the first contact of the polymer coil with the surface. The rate at which equilibrium is attained is difficult to assess, but times of the order of several seconds for long-chain polymers may be reasonable. This is a very important factor in the kinetics of flocculation by polymers (see later).

The extent of the tails and loops and hence the effective thickness of the adsorbed polymer layer, depends greatly on the interaction of polymer segments with the solvent (water) and with the surface. Generally if the interactions with the surface are fairly weak, segments of the adsorbed chain extend further into the solution. With polyelectrolytes, there can be important ionic strength effects (Dahlgren, 1994).

There are several possible types of adsorption interaction:

**Electrostatic interaction:** Polyelectrolytes with a charge opposite to that of the surface (e.g. cationic polyelectrolytes on negative surfaces) nearly always adsorb strongly, simply because of attraction between oppositely charged ionic groups. Even for quite low MWs, polyelectrolyte adsorption can be essentially complete, at least up to the point where the charge of the surface has been neutralised. It is usually found that oppositely charged polyelectrolytes adsorb in a rather flat equilibrium configuration, without extensive loops and tails, especially for polymers of high CD. In some cases, there are important salt effects. For instance, (Pelton, 1986) found that a cationic polyelectrolyte adsorbed on cellulose fibres could be desorbed by the addition of salts, especially those with high cation charge.

**Hydrogen bonding:** Polymers such as PAM (Griot and Kitchener, 1965) and polyethylene oxide (Rubio and Kitchener, 1976) can adsorb on surfaces with suitable H-bonding sites. For instance, oxides such as silica have surface hydroxyl groups which can form H-bonds with amide groups of PAM or

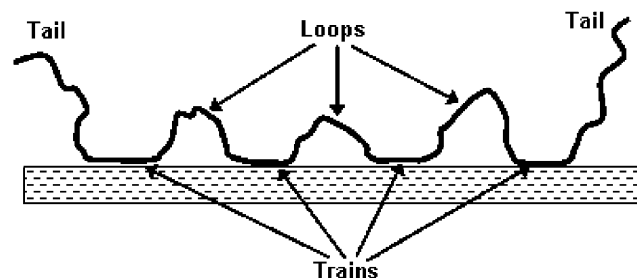


Fig. 4 – Model of an adsorbed polymer chain.

the ether oxygens of polyethylene oxide. Such interactions are important in a wide range of applications.

**Ion binding:** In many cases, anionic polyelectrolytes can adsorb on negatively-charged surfaces, despite electrostatic repulsion. However, often this may only occur if there is a sufficient concentration of divalent metal ions (O’Gorman and Kitchener, 1974; Berg et al., 1993). It is very likely that ions such as  $\text{Ca}^{2+}$  can act as ‘bridges’ between anionic groups on the polymer and negative sites on the surface. Some negatively charged particles can be readily flocculated by anionic PAM at fairly low calcium concentrations (around 1 mM or more), but in the absence of divalent cations, no flocculation occurs, even at quite high ionic strengths.

Although polymer adsorption is essentially irreversible in many cases, there are examples where desorption of polymer chains can occur. For instance, with a range of MWs, small molecules may adsorb first (because of their faster diffusion) and then be gradually displaced by higher MW material (Tanaka et al., 1990; Lipatov et al., 2005).

#### 4.2. Polymer bridging

Long-chain polymers adsorbed on particles in the manner shown in Fig. 4 can have loops and tails extending some way into solution. This gives the possibility of attachment of these ‘dangling’ polymer segments to other particles, thus ‘bridging’ particles together. Such a mechanism has been recognised since the 1950s (Ruehrwein and Ward, 1952) and is extremely important in practice. A schematic picture of particles bridged by adsorbed polymer is given in Fig. 5a.

An essential requirement for bridging flocculation is that there should be sufficient unoccupied surface on a particle for attachment of segments of polymer chains adsorbed on other particles. It follows that the adsorbed amount should not be too high, otherwise the particle surfaces will become so highly covered that there are insufficient adsorption sites available. Here the particles are said to be *restabilised* (Fig. 5b). Of course, the adsorbed amount should not be too low; otherwise not enough bridging contacts could be formed. These considerations lead to the idea of an *optimum dosage* for bridging flocculation. An early concept introduced by La Mer

(1966) was that the optimum dosage corresponds to “half surface coverage”. If the fractional surface coverage is  $\theta$ , then the uncovered fraction of surface is  $1-\theta$  and it is not difficult to show that the fraction of successful (bridging) contacts between particles (i.e. those between coated and uncoated surfaces) is proportional to the product  $\theta(1-\theta)$ . This term has a maximum value when  $\theta = 0.5$ , in line with the half surface coverage idea. However, for adsorbed polymers, it is difficult to define “surface coverage” precisely and so quantitative predictions based on this concept are of limited value. It is generally found that optimum bridging flocculation occurs at well below saturation (monolayer) coverage of the particle surfaces by adsorbed polymer. Under these conditions, practically all the polymer is adsorbed and it follows that the optimum dosage should be directly proportional to the total particle surface area and hence to the particle concentration. Typical optimum dosages in practical systems are of the order of 1 mg polymer/g of suspended solids or less.

It is well established that polymer bridging can give much stronger aggregates (flocs) than those formed in other ways (for instance by metal salts). This is clearly evident by the common observation that very large flocs can be formed by long-chain polymers even under conditions of quite high shear, as in a stirred vessel. The flocs usually grow to an equilibrium (steady state) size, which is dependent on the applied shear, or stirring speed. The stronger the flocs, the larger they can grow under given shear conditions (Mühle, 1993). Bridging contacts are also more resistant to breakage at elevated shear levels. However, floc breakage can be irreversible, so that broken flocs do not easily re-form under reduced shear conditions (Yoon and Deng, 2004). Irreversible breakage may be due to scission of polymer chains under turbulent conditions (Sikora and Stratton, 1981) or the detachment of adsorbed polymer segments followed by re-adsorption in a manner less favourable for bridging interactions.

The strength of flocs has been studied in a more fundamental manner by direct measurements of the force required to cause floc rupture. The “micromechanics” approach (Yeung and Pelton, 1996) can measure forces of the order of a few nN, whereas typical flocs may show rupture forces up to several hundred nN. The force needed to break a single carbon-carbon bond in a polymer chain is in the range 1–10 nN, but there are usually multiple bridging links between particles, so that the actual rupture force can be much higher. Part of the reason for the very strong flocs produced by polymer bridging may be the flexibility of the links, allowing for stretching before rupture occurs.

It is generally found (e.g. Caskey and Primus, 1986) that the most effective polymers for bridging are linear chains of high MW (up to several million). In the case of polyelectrolytes, the CD can have a large influence on bridging effectiveness. If the CD is high, there would be difficulty in adsorbing to particles of the same sign of charge (as in the case of anionic PAM and negative particles). Also, the adsorbed polymer configuration may not favour bridging when the CD is high. However, some degree of charge is beneficial since repulsion between charged segments gives expansion of the chain, as explained earlier, and this should enhance the bridging effect. For these reasons, there is often an optimum CD for bridging flocculation. Early work of Michaels (1954) with anionic PAMs

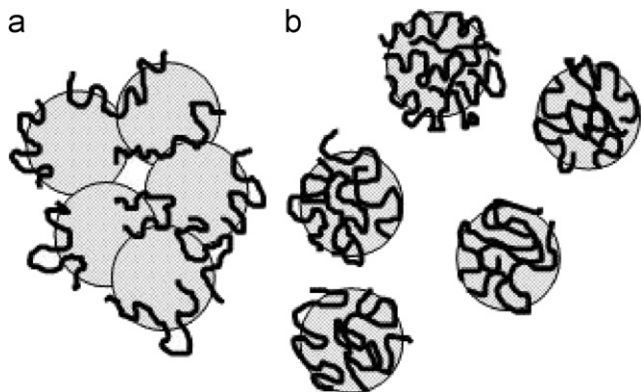


Fig. 5 – Schematic picture of (a) bridging flocculation and (b) restabilisation by adsorbed polymer chains.



suggested that about 30% anionic groups gave optimum flocculation, but for other systems the optimum CD can be lower—around 15% or less.

Repulsion between charged particles depends greatly on ionic strength and it has been found that bridging by non-ionic polymers only occurs when the adsorbed layer thickness is greater than about twice the electrical double layer thickness, which determines the range of repulsion (Dewitt and van de Ven, 1992). This is another reason why ionic strength effects are important in bridging flocculation.

There is some evidence that higher CD polymers are more resistant to shear degradation (Henderson and Wheatley, 1987). The same authors showed that flocculation by anionic PAM was adversely affected in the presence of multivalent metal ions such as  $\text{Fe}^{3+}$ . This was attributed to complexation of the metal with carboxylate groups on the polymer chain and thus an effective reduction in CD. However, as mentioned above, adsorption of anionic polyelectrolytes on negative surfaces may require a certain concentration of divalent metal ions. It may be that there is an optimum salt concentration for bridging flocculation, but there is little systematic information on this point.

Ageing of polymer solutions can have important effects on their flocculation performance. For instance Owen et al. (2002) showed that PAM stock solutions, aged between 1 and 6 days, gave optimal flocculation after 72 h. This is likely due to a slow ‘disentangling’ of polymer chains from aggregates present immediately after dissolution of the solid polymer. Long-term ageing (weeks) generally gives a significant reduction in viscosity of polymer solutions (Shyluk and Stow, 1969; Henderson and Wheatley, 1987), suggesting a reduction in MW. In some cases, this may lead to a slow deterioration in flocculation performance (Shyluk and Stow, 1969). However, Henderson and Wheatley (1987) showed that polymer degradation could be greatly reduced by low concentrations of alcohol in the stock solution, possibly by preventing free radical attack.

In summary, the following statements can be made about bridging flocculation:

- high MW, linear polymers are most effective;
- only a limited adsorbed amount of polymer is needed and excess levels can give restabilisation;
- in the case of polyelectrolytes, there is an optimum CD;
- ionic strength may play a part, and the presence of certain metal ions can be very important;
- very strong flocs are formed by bridging, but broken flocs may not easily re-grow.

#### 4.3. Charge neutralisation

In very many practical cases, impurity particles are negatively charged and it is found that cationic polyelectrolytes are the most effective flocculants. It is well known that electrostatic interaction gives strong adsorption in these systems and that neutralisation of the particle surface and even charge reversal can occur. There is thus the possibility that flocculation could

occur simply as a result of the reduced surface charge of the particles and hence a decreased electrical repulsion between them.

In many studies it has been found that optimum flocculation occurs at polyelectrolyte dosages around that needed to just neutralise the particle charge, or to give a zeta potential close to zero (Kleimann et al., 2005). It has also been found that polyelectrolytes of high CD are more effective, simply because, for a given dosage, they deliver more charge to the particle surface. Since high CD polymers tend to adsorb in a rather flat configuration, there is little opportunity for bridging interactions. In fact, it is often found that quite low MW, high CD polyelectrolytes, such as poly-DADMAC, are quite effective flocculants. These additives are sometimes known as “coagulants” to distinguish them from polymeric “flocculants” which act by a bridging mechanism. However, the distinction becomes rather blurred in many instances and this terminology is not adopted here.

When high CD polyelectrolytes adsorb on negative surfaces with a fairly low density of charged sites, another possibility arises, which has become known as the “electrostatic patch” mechanism. This model was suggested independently by Kasper (1971) and Gregory (1973). The basic idea is that, when a highly charged cationic polymer adsorbs on a weakly charged negative surface, to give overall neutrality, it is not physically possible for each surface charged site to be neutralised by a cationic polymer segment. The reason is simply that the average distance between surface sites is greater than that between charged segments along the polymer chain. It follows that, although the surface may have an overall charge close to neutrality, there are “patches” or “islands” of positive charge between regions of uncoated, negatively charged surface, as shown schematically in Fig. 6. (The same argument applies to high CD anionic polymers on positive surfaces, but this situation is rather rare in practice).

An important consequence of “patchwise” adsorption is that, as particles approach closely, there is an electrostatic attraction between positive patches and negative areas, which can give particle attachment and hence flocculation. Flocs produced in this way are not as strong as those formed by bridging, but stronger than flocs formed in the presence of metal salts or by simple charge neutralisation. Re-flocculation after floc breakage occurs more readily in the case of electrostatic patch than bridging (Yoon and Deng, 2004).

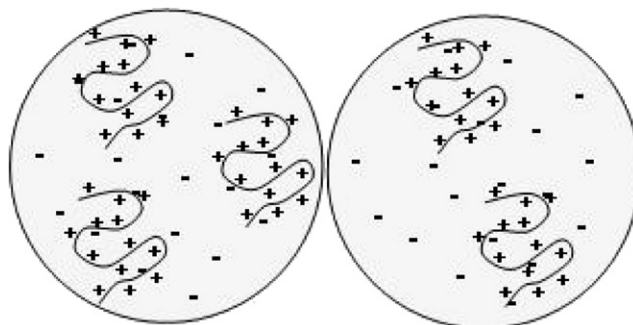


Fig. 6 – “Electrostatic patch” model for flocculation of negative particles by cationic polyelectrolytes.

At low ionic strengths, the electrostatic patch effect can give a significant increase in flocculation rate, although under these conditions, the optimum dosage range can be rather narrow. With increasing salt concentration, the effective dosage range becomes broader and the flocculation rate becomes less (Gregory, 1973). These effects are in line with standard colloid stability theory. Polyelectrolyte CD needs to be quite high for significant electrostatic patch flocculation. As the CD is reduced, bridging flocculation becomes more likely (Eriksson et al., 1993).

It is possible to model the electrostatic patch effect in a semi-quantitative manner (Mabire et al., 1984), but this has only limited application in practice. Recent direct observation of deposition of silica particles on a planar surface with “patchy” adsorption of cationic polyelectrolytes (Kozlova and Santore, 2006) gives some useful insight. The polyelectrolyte used was polyDMAEMA of low MW (around 31,000) and from the known coil dimensions in solution the effective diameter of the positive patches was calculated as 11 nm. The silica particles were spherical, with a diameter of about 0.5 μm and it was found that these could attach to a surface which had only about 10% coverage of positive patches. Under these conditions, the surface still had an appreciable negative charge and the average patch spacing was around 20 nm, so that only a few patches were involved in the attachment of individual particles.

An important practical consequence of positive patches on particle surfaces is that they can act as ‘anchor points’ for the adsorption of high mw anionic polyelectrolytes. This is the basis of one type of *dual polymer system*, where a combination of a low MW, high CD cationic polyelectrolyte and a high MW anionic material can give very effective flocculation (Petzold et al., 2003). Since there are only a limited number of positive patches, an anionic polymer chain cannot form multiple attachments to the surface, as in Fig. 4, but tends to adopt a rather extended configuration from the surface, giving greater bridging opportunity. The concept is illustrated schematically in Fig. 7.

#### 4.4. Kinetic aspects

When a polymeric flocculant is dosed into a suspension of particles, several processes are initiated, which proceed at different rates. These processes, illustrated schematically in Fig. 8, are discussed briefly below:

(a) *Mixing*: This is an essential process, in which the polymer (usually added as a fairly concentrated solution) becomes distributed evenly throughout the suspension. It is important that this is achieved rapidly; otherwise local excess concentrations will give non-uniform adsorption and some particles may become restabilised as a result of adsorbing excess polymer. Poor mixing is thought to be responsible for residual haze in water after polymer-flocculation and sedimentation. In a stirred 1-L vessel (as used in many laboratory studies) mixing times of the order of a few seconds are typical. In full-scale treatment plants mixing times depend very much on the hydrodynamic conditions at the dosing point. Generally, a high

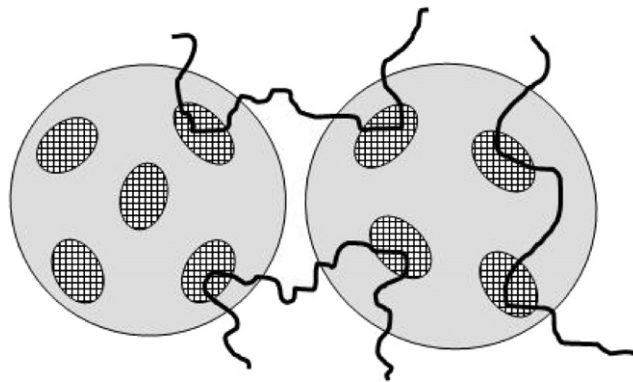


Fig. 7 – Possible mode of adsorption and flocculation by anionic polymers on particles with cationic “patches”. This is an example of a dual-polymer system.

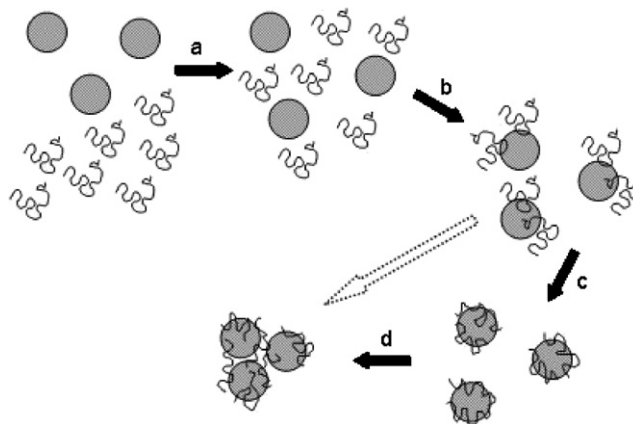


Fig. 8 – Steps involved in the flocculation of particles by adsorbing polymer (see text).

degree of turbulence is considered desirable, although some scission of polymer chains may occur under these conditions. In practice, it is likely that the rapid mixing (or “flash mixing”) conditions can have major effects on the flocculation process. Since concentrated polymer solutions can be quite viscous, mixing usually becomes easier, and flocculation more effective, with more dilute dosing solutions (Gregory and Li, 1991). Mixing effects are generally more important for more concentrated suspensions.

(b) *Adsorption*: Attachment of polymer chains to particles occurs at a rate that depends primarily on their concentrations, broadly according to Smoluchowski kinetics (Gregory, 1988). As particle concentration is increased, the optimum polymer dosage will generally increase proportionally and, because adsorption is a second-order rate process, adsorption rate will increase markedly. For low mw polymers adsorption depends mainly on diffusion, but with higher mw flocculants shear-induced collisions between polymer molecules and particles become more important. This means that the rate of polymer adsorption can depend on mixing conditions. With low (ppm) particle concentrations, as in low-turbidity waters the time required for adsorption of

sufficient polymer can be of the order of minutes, whereas for high solids concentrations (a few %) adsorption times can be less than 1 s. When the adsorption time is of the same order as the mixing time, mixing conditions can greatly affect the flocculation performance.

- (c) *Rearrangement of adsorbed chains*: At the moment a polymer chain adsorbs on a particle, attachment is by only a few segments of the chain (in principle only one segment needs to be attached for polymer to be regarded as 'adsorbed'). After a time, the polymer chain reaches its equilibrium adsorbed configuration with a characteristic distribution of loops, trains and tails (Fig. 4). The time required for rearrangement (or *reconformation*) of adsorbed chains depends on a number of factors, which are not well understood. Nevertheless, for high mw polymers, times of several seconds may be needed (Pelssers et al., 1990), during which time the adsorbed polymer has a more extended configuration than in the final, equilibrium arrangement and so more readily forms bridging contacts. Pelssers et al. (1990) developed a kinetic model in terms of 'active' and 'inactive' adsorbed polymer chains, the former being in an extended configuration and the latter being 'flattened' on the surface. An important point to note is that the reconformation rate should be independent of the particle concentration. This has important implications for 'non-equilibrium flocculation' (see below).

Reconformation can be significantly hindered if the particle surface is already partly covered by adsorbed polymer. A good example of this is the use of 'site-blocking' polymers in a dual polymer system (Wagberg and Eriksson, 2000). If a low MW polymer is pre-adsorbed on particles to give around 50% coverage, then flocculation by a high MW polymer, added subsequently, is much improved. The reason is probably that the second polymer adopts a more extended adsorbed configuration, since the pre-adsorbed polymer makes many surface sites unavailable to the second polymer. The effect is similar to another dual polymer effect, mentioned above, in which a high MW anionic polyelectrolyte adopts a more extended configuration on a negative surface with 'patch-wise' adsorbed cationic polymer (Fig. 7). In that case adsorption sites for the high MW polymer are restricted for electrostatic reasons.

- (d) *Flocculation*: When particles have acquired enough adsorbed polymer to become destabilised, then collisions result in attachment, either by bridging or for electrostatic reasons. Flocculation is a second order rate process, so that the rate depends on the square of the particle concentration. Thus, at high solids concentrations, flocculation rates become very high. All practical flocculation processes are carried out under some form of applied shear, as in a stirred tank or in a flow-through reactor. In this case it can be shown (Gregory, 1988) that, for high MW polymers adsorption times may be considerably longer than particle collision times, so that adsorption may be the rate-determining step.

The particle collision time relative to the reconformation time also needs to be considered. If the former is quite short

(as in a fairly concentrated suspension), then particles are likely to collide before the adsorbed polymer has achieved its equilibrium configuration and so is more extended from the particle surface. Bridging interactions then become more likely, giving the possibility of *non-equilibrium flocculation*, indicated by the broken arrow in Fig. 8. It is likely that most practical applications of bridging flocculation involve this effect to some extent. So, theories of bridging flocculation assuming equilibrium conditions (e.g. Runkana et al., 2006) are probably of limited use in practice. In the case of cationic polyelectrolytes and negative particles bridging may occur during the non-equilibrium phase, but electrostatic patch flocculation would be more likely when the adsorbed chains are in a flatter configuration. The important conclusion from this discussion is that bridging flocculation is more likely in rather concentrated suspensions.

#### 4.5. Interaction with dissolved organic matter

All of the above discussion of the action of polymeric flocculants has been in terms of particle removal processes. Another very important potential application is the removal of NOM from water, which can be achieved by cationic polyelectrolytes.

In natural waters, most organic matter is in the form of humic substances, which are essentially natural anionic polyelectrolytes covering a range of MW and of rather complex structure. Although apparent MW values up to 50,000 or more are typically quoted (e.g. Kawahigashi et al., 2005), some doubt has been cast on the 'polymeric' nature of humic substances (Sutton and Sposito, 2005). Instead they may consist of relatively low MW components bound together by hydrogen bonds and hydrophobic interactions. Nevertheless, humic substances are definitely anionic in character at natural water pH values, which is responsible for their solubility in water. If the charge is reduced by lowering pH, then humic materials can be precipitated from water.

In water treatment, charge neutralisation of dissolved humic substances is thought to be the predominant mechanism of coagulation, especially with cationic polyelectrolytes. There is a lot of evidence (Kvinnesland and Odegaard, 2004) that the optimum dosage corresponds closely with charge neutralisation and there is a stoichiometric relationship between the anionic charge carried by the humics and the cationic charge of the added polyelectrolyte. Thus, it is found that high CD polyelectrolytes are more effective in removing humic substances (Bolto et al., 1999; Kam and Gregory, 2001).

A simple charge-neutralisation/precipitation picture seems to fit many experimental observations of the removal of humic substances by cationic polyelectrolytes. In many cases (Glaser and Edzwald, 1979; Kam and Gregory, 2001; Kvinnesland and Odegaard, 2004) it has been shown that mw has little or no effect, indicating that polymer bridging is not a significant mechanism. However, Bolto et al. (1999) found that higher MW polymers were more effective for removing NOM from water. They also showed that the more hydrophobic NOM fractions were more easily removed.

## 5. Applications in potable water treatment

### 5.1. Primary coagulation in drinking water treatment

#### 5.1.1. Conventional sedimentation and filtration

In the production of drinking water, a cationic polyelectrolyte of high CD and a low to medium MW such as PDADMAC can be used instead of a metal salt as the primary coagulant. ECH/DMA polymers are also effective. The CD rather than the MW is important in selecting the optimal conditions, and the initial periods of both rapid and slow mixing are critical in the formation of flocs (Leu and Ghosh, 1988). There are fewer examples of polymer-only coagulation in conventional coagulation/sedimentation/ filtration plants, compared to polymer use in conjunction with a metal salt, because of the high polymer dose that would be required. Thus a combination of 7 mg/L of alum, 0.26 mg/L of the high CD cationic polymer ECH/DMA and 0.01 mg/L of neutral PAM as filter aid successfully treated water of turbidity 21–28 NTU (Logsdon et al., 1993a). A number of workers have discussed the turbidity limits when alum is the coagulant, and this has been reviewed recently in a consideration of highly turbid waters, covering a range of 5–200 NTU (Logsdon et al., 1993b). It was noted that the alum dose required for effective coagulation and filtration could be the limiting factor, with 12–15 mg/L as Al suggested as the upper limit. Another example of the use of ECH/DMA polymers of low MW (10,000 and 50,000 Da) as primary coagulants showed that the longer chained polymer was more effective for raw waters of higher turbidity (Lee et al., 2001). Pilot work indicated a 50–80% saving of poly(aluminium chloride) using 0.4–1 mg/L of polymer for waters of average and high turbidity. The removal efficiency for organics was also enhanced.

The capacity of a filter plant that has been operated with inorganic coagulant may be increased by polyelectrolyte addition. Thus, an increased flow of 25% was achieved by adding 0.3 mg/L of cationic polymer after ferric chloride dosing, the level of which was lowered by more than a third (Reuter and Landscheidt, 1988). This was accompanied by a filter cycle time increase of 67%, and an improvement in the product water quality. A similar result was obtained on another water using alum and an anionic polymer, the filter runs presumably being determined by breakthrough. The cost of the polymer was completely recovered by the decreased outlay on inorganic coagulant.

On the debit side, inadequate backwashing, prolonged or overdosing of coagulant chemicals including polymer, may gum up a filter with mudballs. Analysis of mudballs formed in a filter where the water was dosed with ferric sulphate and a cationic polymer have shown that they are composed of a combination of inorganic precipitants, organic polymer and bio debris, with at least half of the organic matter being exopolymer, polysaccharides from bacteria in the biofilm attached to the filter medium (Arnold and Schneiders, 1999). A 3% phosphoric acid solution containing 1% dispersant was the best cleaner for rejuvenating the filter medium.

The most effective removal of humic substances prior to reverse osmosis treatment is achieved by a combination of inorganic coagulant and a cationic polymer such as PDAD-

MAC (Yu et al., 2003). Coagulation/flocculation occurred over a wider concentration range, and reduced the dosages of the reagents.

In laboratory studies, it has been demonstrated that when particles are present, as would normally occur in natural waters, the performance of quaternary ammonium polymers of high CD and MW is improved (Bolto et al., 2001). By adding kaolinite when PDADMAC was used there was a small gain, with 16% better removal of colour in one case, but there was little change in the removal of NOM, as measured by UV absorbance. The commonly used mixes of alum and polymer are a convenient way to have suitably reactive particles present; for one of the waters studied a 67% reduction in the alum dose was possible by adding 1 mg/L of PDADMAC, to give even better performance than alum alone at the optimum dose.

In similar studies of cationic polymer as the sole coagulant for the removal of NOM, a highly charged PDADMAC of the highest possible MW was found to be the most effective of commercially available polymers, with the effectiveness diminishing for PDADMACs of lower MW (Bolto et al., 1998). A CPAM of high charge also performed well, taking out double the amount of NOM compared to a low CD polymer of the same MW. Chitosan gave reasonable results, despite its low CD and MW, suggesting that a different mechanism prevails for this type of polymer. Generally, organic polymers did nearly as well as alum for the waters investigated, taking out 86–100% of the colour that alum does. The uptake of NOM after fractionation into four fractions based on hydrophobic and hydrophilic properties was also determined (Bolto et al., 1999). Alum was best for removal of humic and fulvic acids as measured by UV absorbance, although a cationic polymethacrylate or PDADMAC could perform well. Of the high CD polymers, those with the least polar structure were the most effective in removing the hydrophobic fractions. Neutral organic compounds were a very minor component and there was little effect (where data could be obtained). For proteins and other charged hydrophilic compounds, alum then PDADMAC were the best performers for one source.

#### 5.1.2. Direct filtration

The settling stage normally employed in conventional treatment plants is kinetically inefficient. In direct filtration, where some time is allowed for floc growth to achieve optimum size, there is no such sedimentation step, which makes for lower capital costs. Cationic polyelectrolytes have a distinct advantage over the metal salts that are commonly used in this procedure, because they effect charge neutralisation without the formation of additional solids in the form of a metal hydroxide precipitate. The flocs from inorganic coagulants take up much of the space in the filter media, rapidly causing a pressure drop (Coccagna, 1989). Polymers give the advantages of a deformable floc, extended filter runs, and decreased sludge volume from filter backwashing. Polymer MW does not seem to be a major variable. The initial mixing intensity and the mixing time are the most important parameters in determining the particle size of the floc formed prior to filtration (Jackson, 1981).

For waters high in organics, a substantial polymer dose is needed, but compared to alum usage the filter run can be

more than double in length (Edzwald, 1986). If it is found that direct filtration of waters containing large amounts of humic substances with cationic polymers as the sole flocculant is not economic because of the high dose required, conventional metal ion coagulants can be used with a lower dose than is normal, to minimise the amount of precipitate. This is followed by a high CD cationic polymer such as PDADMAC, used in charge neutralisation mode rather than causing particle bridging to give large flocs, although the floc size is still increased (Rebhun et al., 1984). Such a mode of operation is in extensive use.

Cationic polymers can coagulate freshwater algae at doses of 1–10 mg/L (Bilanovic et al., 1988). However, the high salinity of marine systems inhibits the process. Direct filtration experiments have demonstrated that the dose of cationic polymer must be more than that necessary to overcome the effects of exocellular matter released by the algae, when good cell removal is possible (Haarhoff and Cleasby, 1989). A high CD polymer is preferred. Employing an inorganic coagulant for this purpose can disrupt the cell membrane and release compounds that give rise to taste and odour in the product water (Kenefick et al., 1993). With blue-green algae, toxins are produced that can be a health hazard. They can be removed by oxidation or by adsorption onto activated carbon.

Contact or in-line flocculation and filtration is a variant of direct filtration in which the flocculation time is minimal, so the process is confined to the treatment of low turbidity waters, using deep-bed gravity filters in the most common practice. In one study, a comparison of contact and direct filtration showed no significant effect on NOM and turbidity removal, but there was a much greater head loss in the contact filtration mode (Edzwald et al., 1987).

### 5.1.3. Dissolved air flotation

In dissolved air flotation, a proportion of the treated water is recycled through a pressurised air saturation system, and the air-saturated water then released into the water to be treated (Hall and Hyde, 1992). Suitable polymers can redress any floc shearing brought about by overly vigorous contact of air bubbles with the particles (Walzer, 1981).

## 5.2. Polymers as coagulant aids

A major use of organic polymers in water treatment is as a coagulant aid to bridge the coagulated particles formed when an aluminium or iron salt has been used as the primary coagulant. An appropriate polyelectrolyte can increase floc size; a strong dense floc of regular shape is preferred. The large aggregates that form then settle more rapidly. The particles produced by the inorganic salt generally have a slightly positive or slightly negative surface charge, depending on coagulation conditions and the dose of metal salt. With flocs of slightly positive character an APAM of low or medium CD and high MW is appropriate. The use of polymers in this way results in a substantial lowering of the alum dose required, a 40–60% reduction being possible (Hall and Hyde, 1992). Thus for a water containing 5 mg/L of humic acid, a dose of 75 mg/L of alum will remove only 20% of the humics, but adding an anionic polymer in conjunction with 10 mg/L of alum will give a 95% reduction (Edzwald et al., 1977). However,

it should be noted that with alum alone higher removal of NOM (>50%) is achievable under enhanced coagulation conditions (Edzwald and Tobiason, 1999).

An excess of polymer can cause re-dispersion of the impurities. When the coagulated solids have a slightly negative charge, a cationic polymer of low CD and high MW, such as a cationic PAM, is effective in forming larger flocs (Edzwald, 1986).

Processes have been optimised for organics removal in enhanced coagulation systems so that the production of harmful disinfection by products is minimised (Tryby et al., 1993). These systems are also used for the elimination of particles to the greatest possible extent to ensure the absence of pathogenic organisms like *Giardia* and *Cryptosporidium* in the product water (Bernhardt and Clasen, 1996). This requires the best combination of inorganic salts as coagulant and polymer as flocculant, the best type of polymer, the optimum concentration ratio, and optimum process conditions (Narkis et al., 1991).

## 5.3. Recycling of filter backwash waters

In arid areas, conservation of water resources can be achieved by recycling spent filter backwash waters, and this is an economic necessity in other locations also. There is a concern that such recycling can compromise product water quality because contaminants can be concentrated to a level beyond the plant's multi-barrier treatment capability, with *Cryptosporidium* being a particular worry. A major survey of the situation and a pilot plant study of treatment options prior to recycling have been completed recently (Arora et al., 2001; Cornwall et al., 2001). *Cryptosporidium* has been detected in backwash waters at a range of levels, one result being as high as 9–33 M cells/100 L (Rose et al., 1986). In a survey of 34 water treatment plants it was found that *Cryptosporidium* levels were up to 61 times and *Giardia* levels 16 times higher in the backwash water than in the original raw water (LeChevallier et al., 1991). In the UK, it has been recorded that a backwash water contained *Cryptosporidium* at 1M/100L and supernatant water decanted from a settling tank 100,000 cells/100L (Colbourne, 1989). The most recent study puts the significantly higher levels of protozoa in backwash water than in raw water at 21 times for *Cryptosporidium* and 16 times for *Giardia* (Cornwall et al., 2001). Similar trends have been observed for NOM and other contaminants.

In a survey of the 335 water treatment plants in the US that recycle spent filter backwash water, the average generation of spent waters was found to be 2.5% (Arora et al., 2001). Most of the plants (88%) use surface water as their source, with 83% of these recycling to the head of the plant and only 2% to just before the filters. Further treatment is provided by 65% of the plants before reuse of the backwash water, the type of treatment varying from site to site. Options include sedimentation with or without added coagulants, dissolved air flotation with and without polymer, oxidation, conventional filtration and membrane filtration. Pilot studies of various methods to establish appropriate strategies showed that 0.5 mg/L of a CPAM of very high MW and medium CD removed 99.6% of the turbidity after filtration, and a similar dose of an APAM removed 99.4% (Arora et al., 2001; Cornwall et al., 2001).

The polymers were selected as the best options after jar tests on two cationic, three anionic and three non-ionic polymers. Similar performance was obtained with 15–20 mg/L of ferric chloride, but treatment effectiveness was lost soon after a steady state was achieved. Ferric chloride and a CPAM in combination, however, gave stable long-term treatment with the same turbidity result as for CPAM alone. Ferric chloride was superior for NOM removal. Generally, treatment was much better when polymer was added in both sedimentation and dissolved air flotation, which gave equivalent performances. In other work on dissolved air flotation, treatment of a high degree in a very cost effective manner was achieved, a treated water turbidity of 1 NTU being easily obtainable when the original backwash water turbidity was in excess of 50 NTU (Eades et al., 2001). Chemical requirements were low, with no primary coagulants being added and only a single low dose (0.1–0.5 mg/L) of polymer being required to bind the floc particles and form agglomerates that were suitable for flotation. The optimum polymer type was site specific.

In a full-scale test there was a dramatic effect of adding polymer to a side-stream sedimentation plant. Polymer addition lowered the settled turbidity by 50%, with the addition of only 0.1 mg/L of polymer (Cornwall et al., 2001). Capital costs for a range of processes have been estimated; sedimentation plus polymer was US\$133,000–161,000/ML/day, but to return the oocyst level to less than the raw water concentration, dissolved air flotation plus polymer would be necessary. This would require capital of US\$164,000–194,000/ML/day.

The recycled water may have some influence on the treatment process. Polymer residues at the  $\mu\text{g/L}$  level will see the raw water before addition of any coagulants of either the metal salt or organic polymer variety. In turbid water, some floc building will result, and this may affect the nature of the final flocs, making them lighter and more feather-like, so that settling rates may become slower and the final water content of the settled sludge may be increased.

#### 5.4. Sludge thickening

Sludge properties are very dependent on the additives utilised, especially the amount of inorganic coagulant. The emerging technology of coagulant recovery will do much to reduce the volume of sludge for disposal (Anderson et al., 1993a; Petruzzelli et al., 2000).

A degree of concentration is normally required to reduce sludge transport costs. The various methods available are summarised in Table 3 for water treatment plant sludge (Hall and Hyde, 1992). This application consumes more polyelectrolytes than any other in the water treatment area. Polymers are used to give large dense flocs that result in a more rapid settling of sludges and also clearer supernatants, which are recycled. In static settling the resulting strengthened flocs settle to a slightly larger volume, but in raked continuous thickeners they can be compressed without being broken, thus producing a much thicker material. Polymers can also improve dewatering characteristics during centrifugation and filtration. Typically, in centrifugation 1.5–3 kg of polymer is used per tonne of dry solids (Alt, 1989). The high shear forces

present during centrifugation make the use of polymers essential.

For sludge treatment generally, polymers of low or medium CD and high MW such as cationic or anionic PAMs give best performance, with the charge type depending on the origin of the sludge. Thus for a water treatment plant sludge where a high dose of alum and/or cationic polymer is employed, the sludge particles should generally have a positive surface charge, so an anionic polymer will be appropriate, although neutral polymers such as PAM are also employed. Such an alum sludge in a typical gravity filter operation at a solids loading of 25 kg/m<sup>2</sup>/day would have 1.5–2% solids in the underflow without polymer use, and 3–4% solids when an APAM is present (Schlauch, 1981). The effect of alum dose on the consolidation behaviour of clay dispersions has been explored recently (Dixon et al., 2004). By way of contrast, in sewage treatment sludge from an activated sludge plant will have a negative surface charge, so that there a cationic polymer should be the better performer. The topic has received much attention (Dentel, 2001).

The mixing or pumping of sludges can result in an increased difficulty of dewatering because of their sensitivity to shear. When a medium CD, high MW APAM is employed on alum sludge, the dewatering response is dependent on both the shear and the mixing time (Novak and Bandak, 1994). The polymer requirements increase with longer mixing times and at higher shear because of the disaggregation of the sludge. A higher polymer dose is then needed to re-agglomerate the particles created by excessive mixing conditions.

A recent development has been the synthesis of high MW CPAMs that have been crosslinked (Mohammed et al., 2000). Since such a polymer is much less deformable it cannot spread over the surface of the particle, so that its charge cannot be neutralised by that particle. Some charge remains for flocculation or re-flocculation, to give the polymer unique dewatering characteristics. In sludge conditioning, massive agglomeration takes place that is initially capable of some breakdown with subsequent shear. Ultimately equilibrium is reached and the floc structure assumes a stable state. The floc size can be 30% larger with a crosslinked polymer than that obtained with the corresponding linear polymer, and the

**Table 3 – Concentration of sludges from water treatment plants (Hall and Hyde, 1992)**

Conditioning method	Concentration in (% solids)	Concentration out (% solids)
Batch settlement	0.03–0.2	1–3
Continuous thickening		
Without polymer dosing	0.03–0.2	2–3
With polymer dosing	0.03–0.2	5–10
Centrifuging	1–5	12–17
Filter pressing	1–10	20–25

reduction in size on applying shear about 10% instead of more than 90%. Re-flocculation can take place, the overall effect being the production of a very stable floc. Crosslinked polymers have been most successful in dewatering sludges via centrifugation, when a cake of higher solids content offers significant cost savings. Other applications include dewatering via belt presses and the sedimentation of slurries subject to high shear. Another advantage of these materials is that overdosing does not cause the restabilisation of the slurry, since adsorption of the polymer onto the surface of a particle cannot result in it occupying all of the active sites. The outcome is that there are increased throughput rates, a higher solids content of centrifuge cakes, and cleaner centrates.

Practical difficulties can arise in operating a polymer-coagulated system that has been designed for alum treatment (Nozaic et al., 2001). The clarifier hoppers have a side wall angled at 40–50°, inadequate for the use of polymer, which gives a more viscous sludge that tends to stick to the walls. Cavitation or ‘rat-holing’, arising from the failure of thick sludge to flow or the more rapid draining of thinner sludge can also be a problem.

## 6. Practical aspects

There are a number of practical issues that need particular attention when using polyelectrolytes for water treatment. Equipment designed for storing, mixing and feeding polymers takes into account the unique physical characteristics of polymers, and has been much discussed elsewhere (Hall and Hyde, 1992; Chamberlain, 1981; Lockyear et al., 1983). Mixing is of paramount importance (Amirtharajah and Jones, 1996), beginning with initial high energy mixing during the polymer wetting stage in the case of a solid polymer, especially for a polymer of very high MW, to a high rate of polymer dispersion in the reaction stage, but not of such intensity as to cause polymer fracturing (Scott et al., 1996).

Items considered here are selection of polymer type and methods of controlling and monitoring the dosage. The major concerns with polyelectrolytes, apart from costs, are the environmental impact and toxicity to aquatic life. This has given rise to investigations into polymer toxicity, the analysis of residual polymer in the product water, and in wastes from water treatment processes and polymer degradation. A recent concern has been over the production of DBPs from the reaction of residual polymers with disinfectants.

### 6.1. Polymer selection

There is a complex interrelationship involving polymer structure, MW, CD, dose, mixing conditions, amount and type of impurity particles and organic matter (Ghosh et al., 1985; Bolto et al., 1998; Lurie and Rebhun, 1997). The CD and MW of cationic polymers affect the rate of adsorption, with the CD being important in determining the optimum dosage when a charge neutralisation mechanism prevails, as the amount of positive charge adsorbed by impurities is about the same irrespective of CD (Gregory and Lee, 1990). High MWs are essential when the reactions are via a bridging mechanism.

Confirmation of the optimum type and dose of polymer is best determined by jar tests, by the same method employed for inorganic coagulants such as alum or iron salts (Schlauch, 1981; Hall and Hyde, 1992). For drinking water, typical doses are 1–10 mg/L for polymers used as primary coagulants, but only 0.1–0.2 mg/L for polymers used as coagulant aids. The maximum amount is determined by the health limit or cost, if it is lower than the optimum dose. Practical issues, such as the risk of long-term effects such as mudball formation, the development of excessive head loss and inadequate particle detachment on backwashing, also need to be taken into account.

### 6.2. Monitoring systems

Under or overdosing can have very significant detrimental effects. Underdosing causes high turbidity and colour levels in the final water; overdosing can result in the re-dispersion of impurities and carryover of polymer from a clarifier into the filtration stage, blinding the filter so that an increase in backwash frequency occurs, accompanied by a lower water yield (Veal, 1990). Avoiding overdosing helps minimise the amount of sludge formed, consequently reducing land disposal costs. Hence, a considerable effort has gone into ways of monitoring polymer feed during operation of a water treatment process.

The most successful method of controlling polymer use is by means of a streaming current detector (SCD). The movement of counter ions beyond the shear plane of surfaces within the detector gives rise to the streaming current (Dentel et al., 1994). The fluid motion carrying the ions results from piston reciprocation within a closed cylinder that is in contact with a sampled flow. The output from the SCD is related to the zeta potential or electrophoretic mobility of the solid particles. It is therefore possible to directly follow the reduction of the negative surface charge on the particles in the water, and to select the optimum dose, which occurs when the charge is neutralised. Automated control for drinking water production is then achievable when polymers are used as primary coagulants (Barron et al., 1994). The technique has also been successfully applied to sludge conditioning, optimal sludge flocculation being obtained at near neutral streaming current (Dentel et al., 1994). Rheological characteristics have been applied as well, especially on solid residuals in the mineral industry (Dentel et al., 2000). Dewatering of such sludges has received considerable attention (Hogg, 2000; Farrow et al., 2000).

Another promising method is based on measurements of fluctuations in the intensity of light transmitted through a flowing suspension (Gregory and Nelson 1986). In some cases quantitative information on floc size can be derived, but the main use of the technique is for sensitive monitoring of the state of aggregation. A fibre optic flocculation sensor has also been devised (Bartelt et al., 1994), and optimising flocculant demand by a laser light diffraction method that follows the floc size distribution has been advocated (Lartiges et al., 1995).

A charge titration unit has been designed that automatically titrates the negative charge carriers in raw waters with a cationic polymer (Bernhardt and Schell, 1996). It is capable of computing the required coagulant dose faster and more

accurately than manual titration. The dose is automatically determined and transmitted on-line from the unit to the dosing pumps.

### 6.3. Polymer toxicity

The normally used anionic and non-ionic polymers are of low toxicity generally, but cationic types are more toxic, especially to aquatic organisms. Concerns about contaminants have led Japan and Switzerland not to permit the use of polyelectrolytes in drinking water treatment, while Germany and France have set stringent limits. The health significance of possible contaminants has been reviewed in detail (Letterman and Pero, 1990). The monomers are more toxic than the polymers (Criddle, 1990). Limits on the level of monomer are strictly controlled, especially with acrylamide products, where as a general rule the maximum allowable content of free acrylamide is 0.025%, and the residue in drinking water is limited to 0.5 µg/L. For PDADMAC the monomer content limit is 0.5% in Europe and 2% in the USA (BSI, 1998); (NSF International, 2001). For drinking water production, the National Sanitation Foundation has recommended maximum doses for frequently used commercial polymers in the USA. The limits are generally <50 mg/L for PDADMAC, <20 mg/L for ECH/DMA polymers and <1 mg/L for PAMs, irrespective of the PAM charge type. The PDADMAC figure is based on a maximum carryover of polymer into the product water of 50 µg/L.

In determining the toxicity of polymers to aquatic species there are different parameters compared to non-polymeric additives (Vitvitskaya et al., 1988). Synthetic polymers tend not to be readily absorbed by organisms, and their toxicity may be substantially altered by key aquatic components (Hamilton et al., 1994). Cationic polymers are rated at moderate to high toxicity, and are markedly more toxic to aquatic organisms than anionic or non-ionic polymers (Hamilton et al., 1994). The cationic types are detrimental to fish because of mechanical gill blockage that causes suffocation (Biesinger and Stokes, 1986; Cary et al., 1987). This is greatly reduced by the addition of solids such as clays that are normally present in various forms in receiving waters and sediments, where they can strongly adsorb the cationic polyelectrolyte. Humic acids also affect the toxicity, reducing it by an order of magnitude at humic acid levels of 5 mg/L (Goodrich et al., 1991).

A study of the toxicity of CPAMs of various MW and CD towards daphnia and minnows has shown that the toxicity is greatest for polymers of high CD, almost irrespective of chain length (Timofeeva et al., 1994). At lower CD the higher MW polymers are more toxic in the case of daphnia, but the actual toxic level of 0.2 mg/L is well above the likely polymer concentration in the final product water. The toxic level for minnows is 10 times greater. For APAMs, the most toxic are those of longer chain length, but they are at least 100 times less toxic than the cationic versions. Cationic polymers drastically disrupt yeast cells at a polymer dose of ca. 70 mg/L, while anionic or non-ionic ones do not (Narita et al., 2001). The higher the hydrophobicity of the polycation the greater the disruption.

A summary of the toxicity of polymers to freshwater organisms indicates that fish are more sensitive to cationic polymers, but algae are sensitive to anionic polymers because of the chelation of nutrient metal cations (WRC, 1998). This effect can be offset by the addition of Ca<sup>++</sup>. The presence of humic substances or clays can markedly reduce the bioavailability and hence toxicity of the polymers, and this must be taken into account in any risk assessment of environmental damage resulting from the presence of polymer in surface waters.

### 6.4. Residual polymer

It is essential to determine the ultimate fate of polymers used in the treatment process, plus that of any impurities present in the original polymer, to see what quantities are present not only in the product water, but in recycled backwash water and sludge. The problem was reviewed long ago (Goppers and Straub, 1976), when by the use of thin layer chromatography it was found that as well as polymer and monomer, other contaminants appeared to be present in the product water obtained by using a CPAM of the day. In the analysis of an APAM of low CD and high MW (Fig. 1), separation by size exclusion chromatography and fragmentation by flash pyrolysis followed by gas chromatography/mass spectra have been employed (Fiessinger et al., 1983). Size exclusion chromatography was also used in a study of residual non-ionic PAM in an alum sludge (Keenan et al., 1998). A number of impurities were present at very low levels in water treated with the commercial product, including the monomers acrylamide and sodium acrylate, and also hydroxypropionitrile and traces of isobutyronitrile from the initiator. The sensitivity was 10–20 µg/L.

A number of approaches of following residual polymer have been studied. To confirm that all added polymer remains attached to particles that are removed prior to water use, it is necessary to analyse for polymer residues in solution. This can be done by colloid titration against a polyelectrolyte of opposite charge, using dyes or fluorescent compounds as indicators (Wang and Shuster, 1975; Parazak et al., 1987; Tanaka and Sakamoto, 1993). The method is not especially sensitive, 0.5–1 mg/L being the lower limit. A variation on this theme for cationic flocculants is to follow turbidity when tannic acid is used to precipitate the polymer (Attia and Rubio, 1975). A similar method measures the light absorbance at 680 nm following progressive additions of a standard solution of an *o,o'*-dihydroxyazo compound that participates in an association reaction with the polymer (Kirie et al., 1986).

In a review of methods available to determine CPAMs, fluorescence spectroscopy was selected as the most promising analytical method (Howes and Harper, 1998). Further method development is needed to achieve the desired detection limit of 50 µg/L, and it was felt that there should be more effort by polymer manufacturers to develop suitable methods. Size exclusion chromatography was also considered, but adsorption of polymer to the stationary phase made for uncertainties. Another approach is based on a standard clay test developed long ago (Burkert, 1970), where a calibration curve of polymer versus turbidity can be used to measure the content of residual polymer when its sample is tested on



the suspension. However, the sensitivity is not high (Becker et al., 2000). A review of 17 groups of methods for determining PAMs used in the petroleum industry has been published (Taylor and Nasr-El-Din, 1994). The lowest detection limits for the polymers were 10 and 20 µg/L, for SEC and fluorescence spectrometry, respectively.

A number of workers have followed the course of flocculation with specially synthesised <sup>14</sup>C tagged polymer (Black et al., 1966). It has been used to show that dissolved organic matter reacts with the polymer before the turbidity particles (Narkis and Rebhun, 1983), and that hydrolytic degradation of PAM is negligible under normal operating conditions (Hollander et al., 1981). The final destination of a polymer used in a particular treatment process has been shown to be on solid particles (Anderson et al., 1993b). A fluorescently-labelled CPAM has been made by including choline in a Hofmann reaction on PAM (Tanaka and Odberg, 1989).

More recently, PDADMACs have been made that contain 1–2% of an amine-functional monomer. These copolymers were reacted with a fluorophore so that a fluorescent tag was formed within the polymer structure (Becker et al., 2004). Residual PDADMAC could be detected fluorometrically at concentrations below 100 µg/L. Measurable amounts of residual polymer were always present in the treated water, especially at doses above or below the optimum. Turbidity particles or alum flocs lowered these levels.

### 6.5. Polymer degradation

The hydrolysis of the ester links in CPAMs is known to be pH and CD dependent, as already mentioned, and is more facile as the pH is increased. The formation of trimethylamine when these polymers are used in wastewater sludge treatment has been shown to require biodegradation as well as later alkaline conditions (Chang et al., 2005). Amide groups generally are much more hydrolytically stable. Oxidative degradation of polymers under disinfection conditions is discussed below.

Most synthetic polymer structures are resistant to biodegradation, which is usually extremely slow. Amide groups are weak points (Satyanarayana and Chatterji, 1993), as are the ester links in CPAMs (Soponkanaporn and Gehr, 1989). Partial cleavage of the latter under both aerobic and anaerobic conditions has been confirmed (Chang et al., 2001). The poly(acrylic acid) formed can be degraded in the natural

environment, but only material of very low MW (below 4000) seems to be affected (Lenz, 1993).

Natural polymers based on polysaccharides and proteins are readily degraded at the ether and amide sites respectively (Satyanarayana and Chatterji, 1993). Synthetic modifications of natural polymers that are easily degraded, such as poly(aspartic acid) and acrylic acid grafts on polysaccharides, have a future as biodegradable reagents in scale control (Low and Koskan, 1993; Dezingen et al., 1990).

Damage to polymers from oxidants used in pretreatments can be detrimental to the operational efficiency of polymers (Levine et al., 2004). It can be of serious practical significance, as chain cleavage or reduction in the CD is detrimental to plant performance. More research under conditions close to those met with in practice is essential on this topic. Disinfection procedures, including UV exposure of a kaolinite dispersion of turbidity 2 NTU, altered the final turbidity of the product water and the rate of filtration when PAM was employed, measured as the time to filter a set volume of water, as shown in Table 4. UV exposure resulted in the need for a higher dose of polymer, and any oxidant lowered the filtered water quality, which was much worse with UV and worst when chlorination followed UV. Filter runs were lengthened on progressive degradation of the polymer. Filterability was worse with undegraded polymer as the longer, intact polymer chains actually lower permeability, and in the process result in higher quality product water.

### 6.6. Disinfection by-products

Cationic polymers in common use in the water industry, such as PDADMAC and ECH/DMA, generally produce trivial amounts of DBPs from chlorine when the normal levels of polymer utilised in water treatment are exposed to conventional amounts of chlorine in prechlorination (Bolto, 2005). Such an approach is less used these days, but is still carried out for example in preoxidation of manganese-containing waters. However, there is a considerable quantity of trihalo-methanes (THMs) formed in the case of CPAMs, albeit after 20 days' exposure to an initial 20 mg/L of chlorine. 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. For ECH/DMA there is a more variable production of THMs on chlorination, but still in the insignificant range. Of some concern is the high

**Table 4 – Performance parameters after various disinfection procedures (Levine et al., 2004)**

Further treatment	Optimum polymer dose (mg/L)	Final turbidity at optimum (NTU)	Time to filter 100 mL (min)
None	0.04	0.16	670
Cl <sub>2</sub>	0.04	0.22	490
KMnO <sub>4</sub>	0.04	0.39	530
UV	0.10	0.47	450
UV+Cl <sub>2</sub>	0.10	0.64	400

level of other chlorinated organic compounds produced, at 192 µg/L versus 12 µg/L for PDADMAC, indicating that there are many chlorinated compounds formed from ECH/DMA that have not been identified.

Other PAMs of the anionic and non-ionic type present less of a problem, with DBP formation at trivial levels compared to the amounts produced by NOM (Fielding et al., 1999; Alekseeva and Khromchenko, 1988; Feige et al., 1980; Mallevialle et al., 1984). These polymers have contributions equivalent to the amount produced by the monomer present. Acrylamide monomer is a very potent precursor. Strict regulatory control on monomer and impurity content hence has to be maintained.

A serious concern is the reported formation of *N*-nitrosodimethylamine (NDMA), initially detected in the treated water of a small community where PDADMAC and chlorine were employed (Child et al., 1991). NDMA is a known animal carcinogen of 1000 times the potency of THMs. In detailed exploratory experiments, the authors showed that it was not formed when the reagents were present at concentrations normally used in drinking water treatment, to within the limit of detection of 10 ng/L. The topic has been reviewed (Nicholson, 2006). Extensive mechanistic studies in tests with no filtration step (Valentine et al., 2005) have shown that polymers containing a dimethylamino or  $-N(CH_3)_2$  group were likely precursors for NDMA formation, some of them possibly containing residual dimethylamine from manufacture. Polyethyleneimine, which contains  $-NH-$  or  $>N-$  groups but no  $-N(CH_3)_2$ , does not produce significant amounts of NDMA in the presence of chlorine. Similar results were obtained with PAM and polyethylene polyamine, which again have no  $-N(CH_3)_2$  groups. Increases in PDADMAC or chlorine concentrations increased NDMA production, as happened with EPI/DMA polymers, confirming that the polymers were the source of the NDMA. EPI/DMA-co-ethylene diamine polymers (EPI/DMA-co-ED) gave even higher yields. Only three polymers, PDADMAC, EPI/DMA and EPI/DMA-co-ED were found to produce NDMA in standard tests, with the detection of 6.2, 10.1, and 29.8 ng/L of NDMA respectively when the concentration of the polymer and chlorine was each 0.1 mM.

The use of varying doses of chloramine did not have a significant influence on NDMA production in the case of PDADMAC, but similar increasing yields with higher disinfectant dose were obtained for EPI/DMA polymers, with the yield increasing with the increasing age of stock solutions of the polymer (Valentine et al., 2005). Production of NDMA is greatest at acidic pH levels. Hence, treated water should be kept at as close to neutral pH as is possible.

Although ozone is very destructive in its reaction with polymers at high doses, it produces mainly formaldehyde when used at levels met with in water treatment. At polymer levels of 10 mg/L, the amount detected for PDADMAC is 36 µg/L, and for ECH/DMA 62 µg/L (Fielding et al., 1999). Formic acid and lesser amounts of other aldehydes are produced. For APAMs the complete destruction of polymer can be achieved under forcing conditions. Normal doses result in the production of 49 µg/L of formaldehyde as well as other compounds. More work needs to be done on identifying the compounds formed. Mutagenicity tests on an ozonated APAM have proved negative.

Chlorination when there has been no removal of low MW material after ozone treatment can result in copious quantities of chlorinated by-products. Thus for PDADMAC the extremely high level of 435 µg/L of chlorinated organic compounds was obtained, admittedly following excessive doses of both reagents (Stockham and Morran, 2000). A major product was chloropicrin (197 µg/L), but chloroform, dichloroacetic acid and formaldehyde were each produced at levels above 50 µg/L, as well as smaller amounts of many other chlorinated species and ketoacids. A biodegradation step such as that provided by biological activated carbon may be necessary prior to final chlorination.

Permanganate has a profound effect on polymer degradation, judging from results for PDADMAC, where there is a clear indication of chain shortening and loss of CD (Levine et al., 1998). The reaction between permanganate and polymer may contribute to the formation of DBPs. Here formation of haloacetic acids (HAAs) and haloacetonitriles from the reaction of chlorine alone was more significant than THM formation. Similar results were obtained with permanganate present as well. Tests on a wider range of commonly used polymers are needed.

Exposure to sunlight can have a significant effect, as an investigation of the reaction of polymers with chlorine or permanganate, or both, with and without prior irradiation with sunlight for an hour or with UV at 254 nm for 30 min has shown (Levine et al., 2004). The effects on the formation of chlorinated compounds and polymer performance were determined. Following pretreatment of 0.5 mg/L of neutral or anionic PAMs with chlorine (5 mg/L) or permanganate (0.8 mg/L), with or without exposure to one hour of sunlight, DBPs were measured after a further treatment with 10 mg/L of chlorine in the dark for 7 days. Sunlight combined with permanganate or chlorine caused an increase in the total THM and HAAs formation potentials for APAM (Table 5). For PAM exposure to a single oxidant or to sunlight combined with an oxidant increased the DBP formation potential.

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## 7. Costs of using polyelectrolytes

One evaluation of the performance and economics of 23 different organic polymers in treating a Texan turbid water source for drinking water production was aimed at identifying the polymer that reduced filter loading (Tarquin et al., 1998). Increased turbidity removal by a polymer would cause such a reduction, increasing filter run times. Filter backwash savings greater than the cost of polymer were sought. A 5.4 h increase in filter run time equated to an 18% reduction in the volume of backwash water required, and a saving of US\$0.12/kL of product water. Depending on the cost of polymer and its performance at a dosage of 0.5 mg/L, the net savings varied from US\$0.07 to \$0.09/kL. The two most cost-effective polymers were not those of lowest cost, ranking 6 and 7 in that regard.

A South African experience on changing from alum to a polymeric coagulant showed a 30% decrease in the unit cost over a three-year period despite an inflation rate of about 10% per annum (Nozaic et al., 2001). Chemical costs in US\$/kL changed from 0.19 for alum and sodium hydroxide in 1987/88

**Table 5 – DBP formation with and without sunlight exposure (Levine et al., 2004)**

Polyelectrolyte (DBP)	Disinfection by-product formation potential ( $\mu\text{g DBP/mg polymer}$ )				
	No pretreatment	Sunlight, 1 h exposure	Permanganate (0.8 mg/L)	Sunlight and permanganate (0.8 mg/L)	Sunlight and chlorine (5 mg/L)
APAM					
Total THMs	16	15	13	19	21
HAAs	11	11	10	13	16
PAM					
Total THMs	14	44	45	40	47
HAAs	36	46	39	39	45

to 0.15 for polymer in 1989/90. There was also a small reduction in power cost as the polymer dose was 10–20% of that for alum, allowing the use of smaller dosing pumps that required less power. As a further bonus the organic polymer was less aggressive than inorganic coagulant, resulting in reduced maintenance costs.

## 8. Conclusions

The role of polymers in water treatment is very well established, with myriad examples of the benefits of polymer use in conventional sedimentation and filtration, and in direct filtration, mostly arising from the lower solids production. The influence of variations in the details of the chemical structure of the polymer on performance has as yet only been investigated superficially. To illustrate the potential in this regard, it has been found recently that of high CD polymers, those with the least polar structure are the most effective in removing hydrophobic organic matter.

Issues of current relevance include:

- polymer use in cleaning up filter backwash waters, especially with regard to the recycling of *Cryptosporidium* oocysts;
- better methods for analysis of residual polymer in product water;
- reactions of polymers with oxidants used as disinfectants, to form DBPs.

Polymer toxicity does not seem to be a problem, as the normally used anionic and non-ionic polymers are of low hazard generally, although cationic types are more toxic, especially to aquatic organisms. Strict limits on the amounts that can be used for drinking water treatment are used to prevent environmental damage resulting from the presence of polymer in surface waters, as applies also to the maximum permissible carryover of polymer into product water. The monomers used in polymer manufacture are more toxic than the polymers, but rigorous limits on the level of monomer are maintained, especially with regard to acrylamide.

In reactions with chlorine, there is minimal DBP formation from polymers if normal levels of polymer and chlorine are used in a post-chlorination mode. The commonly used

polymers are not the principal precursors, except for cationic PAMs, on which more work is needed. Acrylamide monomer is a potent source, but is not of concern as a source of DBPs when its presence in the polymer is strictly controlled. With ozone, harmful by-products are formed mostly from monomers and polymer impurities. Profound shortening of the polymer chain occurs, which has an impact on water treatment performance, a point that requires further investigation. Destructive reactions are accelerated in the presence of UV, whatever the chemical oxidant present. Work so far has revealed that because of chain shortening, which can be accompanied by a loss of polymer charge, the damaged polymer results in fast filter times but a reduction in the efficiency of turbidity removal. More quantitative research is necessary on this aspect.

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