A STUDY OF THE EFFECT OF POLYMERS ON POTENTIAL N-NITROSODIMETHYLAMINE (NDMA) FORMATION AT WATER AND WASTEWATER TREATMENT PLANTS

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MESL-03-07 **June 2007**

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Abstract

N-Nitrosodimethylamine (NDMA) is a semi-volatile organic chemical that is soluble in water. It was used as a commercial chemical in industry for several decades and also it is naturally occurring in the environment. More recently NDMA occurrence in wastewater treatment sludge is reported in the literature. In the USA concern over the formation of NDMA during the treatment is linked to a data reported by a water reclamation plant in Southern California (DHS., 2000). Since NDMA is considered to be a carcinogen this issue has become a significant concern to US regulatory agencies. The concern is based on the observation that although NDMA does not persist in the environment for long periods of time, it may persist in enclosed systems thus becoming a source of exposure through man made environmental pathways.

Currently research programs in US as well as Canada are focused on understanding the kinetic processes that may lead to the formation of NDMA in a water treatment system. There is some data in the literature that may link the formation of NDMA to polymers that are used during water treatment process. *SNF FLOERGER* is a producer of these polymers.

During a meeting between *SNF FLOERGER* personnel and Multimedia Environmental Simulations Laboratory (*MESL*) research group several questions and concerns regarding NDMA formation in water treatment plants and potential exposure levels and pathways analysis issues were brought to the attention of the *MESL* research team. This study was conducted in an effort to address these concerns.

1 Introduction

N-Nitrosodimethylamine (NDMA) is a human carcinogen as classified by the US Environmental Protection Agency (USEPA) (Figure 1.1). It is a yellow liquid with no distinct odor. The production of NDMA is very limited in the US and this production is only for use as a research chemical. In early 1900's NDMA was used to make rocket fuel, but this use was terminated after unusually high levels of this compound were found in air, water, and soil samples that were collected near rocket fuel manufacturing plants in US. However, NDMA may unintentionally be formed during various manufacturing processes at many industrial sites and it can also be produced in air, water and soil from reactions involving other chemicals identified as alkylamines. Alkylamines are both natural and man-made compounds, which are widely distributed throughout the environment.

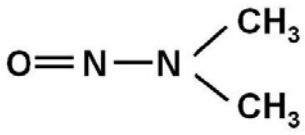


Figure 1. 1 Structure of *N*-Nitrosodimethylamine (NDMA).

Investigations on NDMA indicate that it does not persist in the open environment. When NDMA is released to the atmosphere, it breaks down in sunlight in a matter of minutes. When it is released to soil surfaces, NDMA may evaporate into air, break down upon exposure to sunlight, or sink into deeper soil. It is reported in the literature that NDMA should break down within a few months in deep soil, although conclusive evidence substantiating this claim is not available in the literature. When NDMA is released into water, it may break down upon exposure to sunlight or break down by natural biological processes. The rate of breakdown of NDMA in water is not known.

The general population may be exposed to NDMA from a wide variety of sources, including environmental, consumer, and occupational sources. USEPA records indicate that, NDMA has been found in at least 1 out of 1177 hazardous waste sites on the National Priorities List (NPL) in the US. At NPL sites NDMA has been found in groundwater samples, in amounts of 10 parts NDMA per billion parts of water (10 ppb). No information is available on contamination of soil, drinking water, irrigation water, sewers, storm drains, or the human food chain with NDMA near NPL sites.

Other than contaminated sites the primary sources of human exposure to NDMA are tobacco smoke, chewing tobacco, diet (cured meats [particularly bacon], beer, fish, cheese, and other food items), toiletry and cosmetic products (for example, shampoos and cleansers), interior air of cars, and various other household goods, such as detergents and pesticides. In addition, NDMA can form in the stomach during digestion of alkylamine-containing foods. Alkylamines are naturally occurring compounds that are found in some drugs and in a variety of foods. Infants may be exposed to NDMA from the use of rubber baby bottle nipples and pacifiers which may contain very

small amounts of NDMA, from ingestion of contaminated infant formulas, and from breast milk of some nursing mothers. Very low levels of NDMA have been found in some samples of human breast milk.

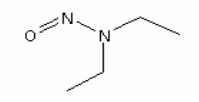
Occupational exposure may happen in a large number of places including industries such as tanneries, pesticide manufacturing plants, rubber and tire manufacturing plants, alkylamine manufacture/use industries, fish processing industries, foundries, and dye manufacturing plants. Researchers making or handling NDMA may also be exposed to this compound if it passes through the rubber gloves they wear during laboratory work. Although NDMA does not persist in the open environment over long periods, its persistence in enclosed environments such as water distribution systems or deep soil strata have not been investigated thoroughly. Both of these environments may be important exposure pathways and should be evaluated.

NDMA is a probable human carcinogen as described in EPA's Integrated Risk Information System (USEPA, 1993; USEPA, 2002). Risk assessments have estimated 10^{-6} lifetime risk level of cancer from NDMA exposures at 0.7 ng/L. Although there are no reports of NDMA causing cancer in humans, it is reasonable to expect that exposure to NDMA by eating, drinking, or breathing could cause cancer in humans (ATSDR, 1989). Mice that were fed NDMA during pregnancy had offspring that were born dead or died shortly after birth (USEPA, 1993). However, it is not known whether NDMA could cause the death of human babies whose mothers are exposed during pregnancy. The levels of NDMA in air, water, or food that result in health effects in people are unknown. It is demonstrated in literature that short-term exposure of animals to air containing levels of 16 parts per million (ppm) NDMA produces liver damage and death. Toxic effects of long-term exposure of animals to air containing NDMA are unknown. Short-term or long-term exposure of animals to water or food containing NDMA is also associated with serious effects, such as liver disease and death, at levels ranging from 5 to 50 ppm in water and 5 to 100 ppm in food (ATSDR, 1989).

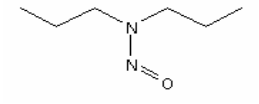
The USEPA recommends that levels in lakes and streams should be limited to 0.00069 parts of NDMA per billion parts of water (0.00069 ppb) to prevent possible health effects from drinking water or eating fish contaminated with NDMA. The USEPA requires that spills or accidental releases of 10 pounds or more of NDMA be reported to the EPA. This information is based on federal recommendations that have been updated as of July 1999.

Drinking water supplies and water processing plants are becoming more of a concern for the regulatory agencies. NDMA has been identified as a drinking water contaminant since several water utilities in Canada and the U.S. reported the occurrence of NDMA in drinking water supplies (DHS, 2000; MOE, 1998). Studies later recognized that NDMA is generated in water treatment facilities, particularly in chlorine-based disinfection processes (Choi and Valentine, 2002a; Mitch and Sedlak, 2002a; Mitch and Sedlak, 2002b). Currently, the Ontario Ministry of Environment has set an interim maximum acceptable concentration for NDMA at 9 ng/L (MOE, 1998), and the State of California has established a notification level at 10 ng/L (DHS, 2000). NDMA is now listed with five other nitrosamines (N-nitrosodiethylamine [NDEA], N-nitroso-di-n-propylamine [NDPA], N-nitoso-di-n-butylamine [NDBA], N-nitrosomethylethylamine [NMEA], and nitrosopyrrolidine [NPYR] (Figure 1.2) in the second

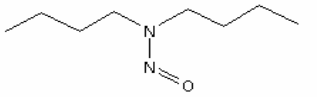
Unregulated Contaminant Monitoring Regulation [UCMR 2] for a screening survey in drinking water systems in order to determine future regulation by MCL (USEPA, 2005).



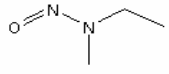
NDEA



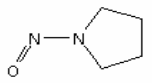
NDPA



NDBA



NMEA



NPYR

Figure 1. 2 Structures of five other nitrosamines

The recent history of NDMA findings in drinking water supplies as it relates to activities in California can be given as follows (California, 2006).

1998: In February-March, samples from a drinking water well in eastern Sacramento County confirmed the presence of N-nitrosodimethyamine (NDMA) at ~0.15 microgram per liter (µg/L). This well was taken out of service by the utility. Sampling was in response to concern about the presence of NDMA contamination at an aerospace facility.

1998: In April, DHS established an action level for NDMA of 0.002µg/L, based on a *de minimis* cancer risk level. However, analytical capabilities did not enable detection at that concentration, so any detectable quantity of NDMA was over the action level (AL). The AL was derived from regulatory risk level of 0.04 µg/day for purposes of Proposition 65 implementation (Title 22 of the California Regulations, Section 12705), which corresponds to a 10^{-5} lifetime cancer risk. Dividing 0.04µg/day by 2 liters of drinking water/day gives 0.02µg/L, and dividing by 10 yields 0.002µg/L, a *de minimis*, or 10^{-6}, cancer risk level. This is the level DHS generally uses for notification levels for carcinogenic chemicals.

1998: In May, NDMA was detected in three drinking water wells in the San Gabriel Basin. Two wells with NDMA at concentrations of 0.07µg/L were removed from service. The third well, already out of service because of trichloroethylene and perchlorate contamination, contained NDMA at 3µg/L.

1999: Limited sampling indicated that NDMA appeared to be present at very low levels (<0.01µg/L) in treated drinking water. Preliminary analyses suggested that NDMA's presence in drinking water was related to disinfection processes, but very limited data were available, and often they appeared to be inconclusive. Coincidental with more sensitive analytical methods becoming available, DHS initiated studies with drinking water utilities to investigate the occurrence of NDMA in raw, treated and distributed water, the role water quality and treatment

processes may play in the production of NDMA, and the possible extent of NDMA production at various steps in the water treatment process.

1999: As interest in NDMA monitoring increased in the water treatment community, DHS was informed of NDMA findings in treated waste water. From the standpoint of protecting drinking water consumers and sources, DHS considered this finding to be important in the evaluation of proposed recycled water projects involving waste water discharges and ground water recharge.

1999: In November, DHS revised the action level to 0.02µg/L to accommodate studies on NDMA production in drinking water.

2000: In May, two wells in Orange County had NDMA at concentrations of approximately 0.03 to 0.04µg/L, and were taken out of service. A nearby groundwater recharge operation involving injection of treated wastewater contained NDMA in its injected water. DHS informed the wastewater treatment plant that its activities were impairing groundwater, and directed them to reduce the levels of NDMA accordingly.

2000: Also in May, a system in Los Angeles County found NDMA in its groundwater sources at 0.032 to 0.076µg/L, apparently associated with the past production of chemicals used in the aerospace industry.

2000: In June, a system in Los Angeles County found NDMA at about 0.03µg/L, apparently related to resins used in water treatment for nitrate removal.

2000: Also in June, in Los Angeles County, NDMA at 0.049 and 0.074µg/L (duplicates) and 0.091µg/L was found in treated wastewater that was blended for use as groundwater recharge.

2002: In March, DHS requested a public health goal (PHG) for NDMA from the Office of Environmental Health Hazard Assessment (OEHHA). A PHG is an early step in the regulatory process involved in developing a drinking water standard.

2002: Also in March, DHS posted on its website results of studies on NDMA's production in drinking water treatment, as well as a revised notification level, to 0.01µg/L.

2004: In July, OEHHA initiated a risk assessment for NDMA that will lead to a PHG.

2004: In September, DHS added a 0.01µg/L notification level for another nitrosamine, N-nitrosodiethyamine (NDEA).

2005: In May, DHS added a 0.01µg/L notification level for N-nitroso-n-propylamine (NDPA). NDPA and NDMA were found in some disposable resins being evaluated for drinking water treatment.

2006: In February, OEHHA released a 0.003µg/L draft PHG for NDMA.

2006: In December, OEHHA established the PHG for NDMA at 0.003µg/L.

There has been a significant amount of research in recent years on the mechanisms of NDMA formation and to identify precursors of NDMA in water sources. Among many potential NDMA precursors, water treatment polymers used as coagulants and flocculants for suspended particle removal have been identified due to the presence of amine functional groups in their structures, as well as the possible presence of dimethylamine [DMA] residues in polymer products. DMA is a well recognized NDMA precursor and frequently used as a starting reagent in amine-based monomer and polymer production. Results of several recent studies have indicated that certain treatment polymers such as aminomethylated polyacrylamide [Mannich polymer], poly(epichlorohydrin dimethylamine) [polyamine] and poly[diallyldimethylammonium chloride] [polyDADMAC] can contribute to NDMA formation in chlorine-based disinfection processes (Mitch and Sedlak, 2004b; Najm and Trussell, 2001a; Najm and Trussell, 2001b; Wilczak, Assadi-Rad *et al.*, 2003a; Wilczak, Assadi-Rad *et al.*, 2003c).

Despite the above reports, knowledge regarding how water treatment polymers may form NDMA and how much they contribute to the overall NDMA formation in actual treatment plants was severely limited. The purpose of this research was to conduct a systematic investigation to determine whether the water treatment polymers manufactured by the SNF Company contribute to NDMA formation in water and wastewater treatment plants, understand the NDMA formation potential of polymers at the mechanistic level, identify factors that will enhance or reduce such a formation, and evaluate the potential exposure pathways and levels of NDMA in natural and man made environments. A major goal of this project was to provide scientific basis for strategies in minimizing NDMA formation potential and thus environmental health risk associated with SNF's water treatment polymers.

2 Literature Survey

Although NDMA is mostly considered to be an environmental contaminant, its formation in water treatment plants is also reported (Graham, Andrews *et al.*, 1996a). Given that NDMA was absent in the influent water, but was found post treatment, the authors concluded that it was formed somewhere in the treatment process.

How NDMA is formed in wastewater and natural water during treatment processes is a highly complex phenomenon and not fully understood. The recent concern of NDMA being a disinfection by-product, however have prompted many studies on the subject. Some coagulant aid polymers used in drinking water treatment have been implicated as precursors of nitrosamines. NDMA formation was also reported from the use of some strong-base anion resins. Kimoto reported NDMA formation when tap water containing residual chlorine was passed through the resin (Kimoto, Dooley *et al.*, 1980b). In that study, the quaternary ammonium groups present in the resin were believed to be the primary candidate for NDMA precursors. Other studies conducted thus far have also focused on testing various organic-N compounds for NDMA formation. Results of these studies have shown that NDMA can be produced with the right types of organic-N compounds under suitable conditions in reaction with nitrite or monochloramine. Two pathways, (i) nitrosation; and, formation by oxidation of unsymmetrical dimethylhydrazine (UDMH) intermediate, have been suggested for the formation of NDMA with nitrite and monochloramine, respectively (Choi and Valentine, 2002c; Mitch and Sedlak, 2002b).

The literature review provided below indicates that there are environmental and regulatory concerns of the natural presence and the formation of NDMA in industry or water treatment plants.

2.1 NDMA as an Emerging Disinfection by-Product [DBP]

In their study, Najm and Trussell examined various strong-base anion exchange resins and determined that the composition of the resin affected the levels of NDMA (Najm and Trussel, 2001). The dimethyl quaternary amine resin resulted in the greatest amount of NDMA when compared to the longer chain substituted resins. This indicated that the composition of the resin played an important role in the amount of NDMA formed as a DBP although the mechanism is not well understood. The authors also compared chlorine and chloramine disinfection using some natural water sources. Although NDMA did not form when chlorine was used, its formation was dependent on the chlorine dose used in chloramination but was independent of the sequence of addition of chloramines. Both natural waters and wastewaters resulted in NDMA formation when disinfected with chloramines (Najm and Trussel, 2001). The concern over the formation of NDMA in the treatment process is because the compound may persist for a long period of time in the enclosed systems such as water distribution system. An increase in NDMA is also possible when nitrites, formed from the oxidation of ammonia by Nitrosomonas bacteria present in the water distribution system, react further with chloramine residual disinfection. Thus exposure pathway through water distribution systems is important.

2.1.1. NDMA Occurrence in Drinking Water and Wastewater

NDMA is a semi-volatile, hydrophilic, and polar organic chemical. Some physicochemical properties of NDMA are given in Table 2.1. It is an oily yellow liquid of low viscosity with no distinct odor and highly soluble in water (reported solubility of 3,978 mg/L) (Wilczak, Assadi-Rad *et al.*, 2003c; Wilczak, Lai *et al.*, 2004a). NDMA is known to be sensitive to light. It undergoes rapid photolytic degradation when exposed to ultraviolet light and may decompose in aqueous acid solutions. NDMA is not likely to bioaccumulate, biodegrade, adsorb to particulate matter, or volatilize (Siddiqui and Atasi, 2001).

NDMA was used in a number of applications historically. It was used as a solvent in the fiber and plastics industry, a plasticizer for rubber and acrylonitrile polymers, an antioxidant, an additive for lubricants, a softener of copolymers, a research chemical and in inhibition, an inhibitor of nitrification in soil, in the preparation of thiocarbonyl fluoride polymers, and in other uses (MERCK, 1983). From the mid 1950's to 1976, NDMA was used as an intermediate in the electrolytic production of 1,1-dimethylhydrazine, storable liquid rocket fuel that contained approximately 0.1% NDMA as an impurity. Although current production data is not available, NDMA is no longer manufactured for commercial use in the United States.

Table 2. 1 Physical and chemical properties of *N*-Nitrosodimethylamine (NDMA)

Molecular Weight:	74.08
Density/Specific Gravity:	1.0048 at 20 ºC (water = 1)
Boiling Point:	151 – 153 ºC
Vapor Density:	2.56 (air = 1)
Vapor Pressure:	2.7 mm Hg at 20 ºC
Log Octanol/Water Partition Coefficient:	-0.57
Synonyms: dimethylnitrosamine; *N*-methyl-*N*-nitrosomethanamine; DMN; DMNA	

Source references: (HSDB, 1993; MERCK, 1983; USEPA, 1997; USEPA, 2005)

NDMA was first observed in municipal drinking water in Ontario, Canada in 1989 (Taguchi, Jenkins *et al.*, 1994a) which prompted a survey of NDMA concentrations in 145 drinking water treatment plants (DWTPs) (Jobb, Hunsinger *et al.*, 1994; Jobb, Hunsinger *et al.*, 1993b; MOE, 1998). The results showed that NDMA levels in the treated water from most of the plants were less than 5 ng/L. In 2001, CDHS conducted a NDMA survey in effluents of 20 DWTPs (CDHS, 2002). The results showed that the treated water from 3 of the 20 plants surveyed contained NDMA concentrations greater than 10 ng/L. All eight DWTPs that used only free chlorine in water disinfection showed NDMA levels less than 5 ng/L. However, one of the four DWTPs that involved anion exchange in the treatment showed NDMA concentrations exceeding 10 ng/L. During 2001, a North American survey of NDMA in 21 water systems indicated the median NDMA concentration in treated effluents was less than 1 ng/L. The median NDMA concentration from distribution systems was less than 2 ng/L for chloraminated water and less than 1 ng/L for chlorinated water. High NDMA levels were found in groundwater treated with anion exchange resins and chlorination, and in groundwater treated with lime softening and chloramination. More samples with NDMA concentrations between 2.5 and 10 ng/L were found in chloraminated systems than in chlorinated systems (Barrett, Hwang *et al.*, 2003).

In contrast to the results from drinking water treatment plants, effluents from conventional wastewater treatment plants may contain relatively high NDMA concentrations. Large increases in NDMA concentrations were attributed to upstream industrial sources. Typical NDMA levels found in unchlorinated secondary effluents are less than 20 ng/L, but industrial inputs can elevate NDMA concentrations in raw sewages over 1000 ng/L. For example, effluents from printed circuit board manufacturing process using NDMA-contaminated dimethyldithiocarbamate have been reported to contain NDMA concentrations up to 105,000 ng/L (OCSD, 2002).

Schreiber and Mitch reported the detection of NDMA as well as *N*-nitrosomorpholine (NMOR) along Quinnipiac River, CT, which was impacted by wastewater effluent (Schreiber and Mitch, 2006a). Most of sampling site showed concentrations less than 10 ng/L of NDMA, but concentrations greater than 15 ng/L were measured from two sampling sites located downstream or upstream of wastewater treatment plants. Even higher concentrations of NMOR were detected in range of 20 – 200 ng/L. Although Quinnipiac River is not used as drinking water source, the results indicate nitrosamine persistence within surface water can be a major concern for consumers using wastewater-impacted surface water as drinking water sources.

Recently, USEPA proposed the second Unregulated Contaminant Monitoring Regulation [UCMR 2] for monitoring 26 chemicals using nine different analytical methods during 2007 – 2011, (USEPA, 2005). NDMA is included in UCMR, List 2 with five other nitrosamines: [*N*-nitrosodiethylamine [NDEA], *N*-nitrosodi-n-butylamine [NDBA], *N*-nitrosodi-n-propylamine [NDPA], *N*-nitrosomethylethylamine [NMEA], *N*-nitrosopyrrolidine [NPYR] for screening survey. The screening survey will be conducted during a continuous 12-month period between July 2007 and June 2009, quarterly for surface water systems, and twice at 6-month interval for ground water systems.

2.1.2. NDMA Formation Mechanisms in Drinking Water and Wastewater

High concentrations of NDMA have been observed in industrial wastewater effluents due to industrial inputs and NDMA-contaminated chemicals used in the manufacturing process (OCSD, 2002). However, recent studies have shown that NDMA can be formed at significant levels in both chlorinated drinking water and wastewater as reviewed in (Mitch, Gerecke *et al.*, 2003). The results suggest that NDMA is a water treatment byproduct especially associated with disinfection process. Currently, two formation pathways have been proposed to be responsible for most of NDMA formation in drinking water and wastewater: (i) formation of NDMA via *N*-nitrosation reaction; and, (Case, Darden *et al.*) formation of NDMA by oxidation of a chlorinated unsymmetrical dimethylhydrazine [UDMH] intermediate. Details of these two proposed formation mechanisms are discussed below.

2.1.2.1. *N*-Nitrosation: NDMA Formation via Nitrite

As shown in reactions (1) and (2), the *N*-nitrosation mechanism involves the formation of nitrosyl cation or similar nitrogen-containing species during acidification of nitrite. The nitrosyl cation then reacts with amine species, such as DMA, to form NDMA (Choi and Valentine, 2003; Mirvish, 1975). The nitrosation reaction undergoes most rapidly in acidic environments, especially near pH 3.4 (Mirvish, 1975). During this reaction, the demands for protonation of

nitrite [pK_a of nitrite = 3.35] and high fraction of unprotonated dimethylamine [pK_a of DMA = 10.7] counter against each other in terms of pH requirement. Overall, the need for protonation of nitrite is especially critical for the rate of the nitrosation reaction.

$$HNO_2 + H^+ \leftrightarrow H_2O + NO^+ \quad (1)$$

$$NO^+ + (CH_3)_2 NH \rightarrow (CH_3)_2 N - N = O + H^+ \quad (2)$$

The nitrosation mechanism is believed to be responsible for NDMA occurrence in many food products such as meat products cured with nitrite, cigarette smoke, malt beverages, and dried foods (Mitch and Sedlak, 2003a; Mitch and Sedlak, 2003b; Mitch, Sharp *et al.*, 2003). Although nitrosation reaction occurs slowly at neutral and basic pH, several studies have reported that photochemical reactions (Ohta, Suzuki *et al.*, 1982), formaldehyde (Keefer and Roller, 1973) and fulvic acid (Weerasooriya and Dissanayake, 1989) can catalyze nitrosation at circumneutral pH. Recently, (Choi and Valentine, 2003) reported that the formation of NDMA by the nitrosation of DMA can be greatly enhanced by the presence of free chlorine during water chlorination processes. The authors attributed the enhancement effect to the formation of a highly reactive nitrosating intermediate such as dinitrogen tetroxide (N_2O_4) during the oxidation of nitrite to nitrate by free chlorine.

2.1.2.2. Chlorinated Unsymmetrical Dimethylhydrazine (UDMH) Oxidation

Since NDMA formation in water treatment plants had been suspected to be related to chlorine-base disinfection processes, (Choi and Valentine, 2002a; Choi and Valentine, 2002c; Mitch and Sedlak, 2002b) proposed that NDMA could be preferably formed via unsymmetrical dimethylhydrazine [UDMH] intermediate during the reaction of DMA and monochloramine instead of nitrosation pathway, Figure 2.1. The authors showed that the reaction of monochloramine and DMA formed much more NDMA than that of nitrite and DMA did in circumneutral pH conditions which are encountered in drinking and wastewater treatment plants. NDMA formation from UDMH is traced back to earlier studies reporting that NDMA can be produced from oxidation of 1,1-dimethylhydrazine or unsymmetrical dimethylhydrazine [UDMH] by hypochlorite (Brubaker, Bonilla *et al.*, 1987; Brubaker, Stetter *et al.*, 1985), cupric ions (Banerjee, Pack *et al.*, 1984), hydrogen peroxide, and oxygen (Lunn, Sansone *et al.*, 1991). Contrary to nitrosation pathway, NDMA formation from UDMH is maximized at neutral and high pH (Lunn, Sansone *et al.*, 1991), which is consistent with Mitch and Sedlak's (Mitch and Sedlak, 2002b) experiment showing that NDMA formation is maximized at pH 8 from the reaction of DMA and monochloramine. However, NDMA formation mechanisms after UDMH intermediate-forming step, i.e. the oxidation pathways from UDMH to NDMA were not explicit about how the NH_2 moiety in UDMH converts to the NO moiety in NDMA.

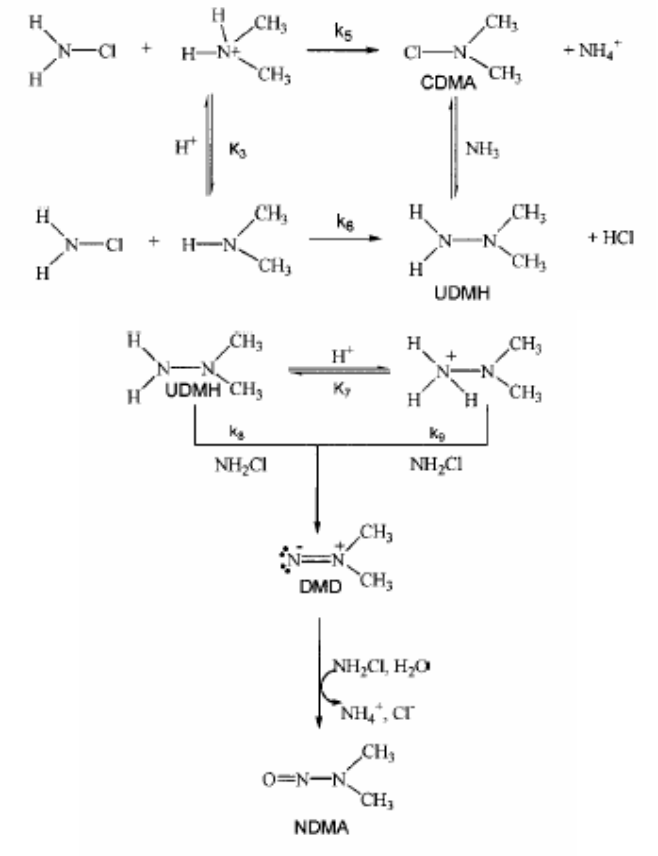


Figure 2. 1 NDMA formation from UDMH oxidation [from (Mitch and Sedlak, 2002b)]

Later on, Schreiber and Mitch (Schreiber and Mitch, 2005; Schreiber and Mitch, 2006b) refined the previous UDMH oxidation pathway by revealing the important role of dichloramine and dissolved oxygen with chlorinated UDMH intermediate rather than UDMH, Figure 2.2. The authors demonstrated that dichloramine plays a major role instead of monochloramine for NDMA formation, even in the reaction with preformed monochloramine via monochloramine disproportionation to form traces of dichloramine. The chlorinated UDMH intermediate then undergoes further oxidation by dissolved oxygen to form NDMA, which is competed with oxidation by dichloramine to form other products. The authors proposed that the low concentration of dichloramine solely contributes to NDMA formation via chlorine disproportionation even in typical chloramination conditions in which monochloramine exists as the dominant chloramine species, thereby possibly explaining the low yield of NDMA formation at the treatment plants.

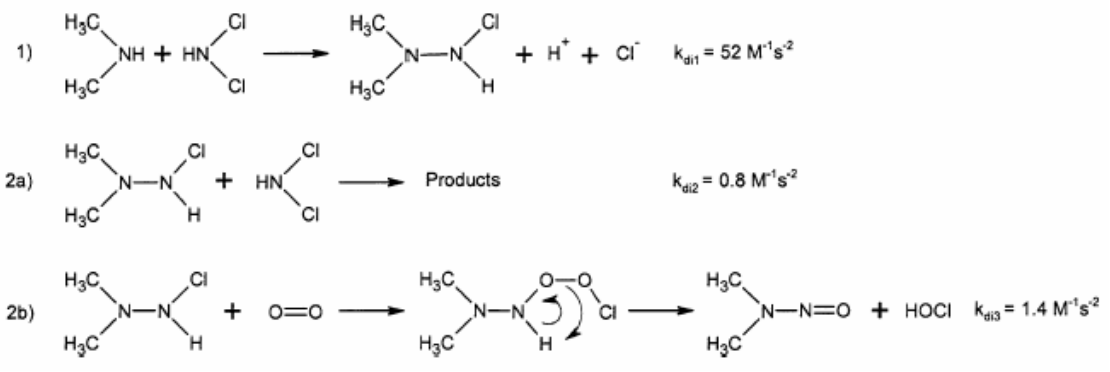


Figure 2. 2 NDMA formation from chlorinated UDMH oxidation [from (Schreiber and Mitch, 2006b)]

2.1.3. Potential NDMA precursors

On the basis of NDMA formation mechanisms via both nitrosation and chlorinated UDMH oxidation pathways, not surprisingly, DMA has been demonstrated by many studies to be the most effective organic NDMA precursor (e.g., (Choi and Valentine, 2002c; Fiddler, Pensabene *et al.*, 1972; Mitch and Sedlak, 2002a). Trimethylamine and dimethylethanolamine, in which proton is replaced by methyl and ethanol functional group respectively from dimethylamine, also have been shown to produce NDMA at lower but very comparable yields to that from DMA. The lower yield is due to the need to break a C-N bond prior to NDMA formation (Mitch and Sedlak, 2004b). According to NDMA precursor tests conducted by (Mitch and Sedlak, 2004b), the presence of DMA functional group seems to be the prerequisite to be a significant NDMA precursor and the structural relationship between DMA functional group and its adjacent group in the precursors is also an important factor to determine NDMA formation potential and rate during chloramination. For example, primary and tertiary amines which do not have DMA functional group did not form significant levels of NDMA. Dimethylaminobenzene and dimethylamides (e.g. dimethyldithiocarbamate and dimethylformamide) also did not form significant NDMA for short time chloramination (4 hrs), but formed the levels of NDMA comparable to those from DMA and tertiary amine containing DMA functional group for longer chloramination (10 days). This is because both dimethylaminobenzene and dimethylamides have structures or adjacent groups hindering electrophilic attack of chloramines to form NDMA, which did not immediately result in significant NDMA formation, but after long time exposure to chloramines, DMA was possibly released and formed comparable amount of NDMA as DMA and trimethylamine. Quaternary ammonium salt containing DMA or trimethylamine functional group also did not form significant levels of NDMA due to the absence of free lone pair electrons on the nitrogen (Fiddler, Pensabene *et al.*, 1972; Mitch and Sedlak, 2004b). Another important NDMA precursor, amine-based water treatment polymers, will be dealt with in detail in Section 2.2.1.

2.1.4. Analysis of NDMA

The analytical procedure to detect NDMA involves several steps from sample collection, preconcentration to analysis. Currently, USEPA method 521 (USEPA, 2004) is recommended as standard analytical methods for low concentrations of NDMA in drinking water. An earlier technique used for analysis of NDMA was the utilization of liquid-liquid extraction to extract NDMA from water, followed by detection using gas chromatography with tandem mass

spectrometry in the chemical ionization mode [GC/CI/MS/MS] (Mitch and Sedlak, 2002a; Mitch and Sedlak, 2002b) or gas chromatography with high resolution mass spectrometry [GC/HRMS] (Taguchi, Jenkins *et al.*, 1994a). Typical detection limits of these methods were around 1 ng/L. The liquid-liquid extraction [LLE] with dichloromethane using separatory funnels can be applied in NDMA extraction according to the US EPA Method 3510C (USEPA, 1998). However, this method often yielded low recoveries when used with wastewater effluents. The separation between effluents and dichloromethane was hindered by constituents in the effluents such as surfactants which may cause emulsion-like environments (Mitch and Sedlak, 2003b; Mitch, Sharp *et al.*, 2003). Alternatively, continuous liquid-liquid extraction [CLLE] according to USEPA Method 3520C (USEPA, 1998) could be employed to avoid problems associated with emulsions encountered in traditional LLE. The CLLE method reportedly yielded extraction efficiencies up to 60% (Mitch, Sharp *et al.*, 2003).

The LLE methods are labor intensive and require the use and disposal of large volume of methylene chloride solvent, rendering these methods inconvenient and less environmental friendly for routine analysis. As concerns over NDMA in water supplies increase, more monitoring of this contaminant is quite likely in the future. Improved analytical methods that are more sensitive, reliable, and economically attainable for measuring low concentrations (at several ppt or even lower) of NDMA in water are much needed. Solid-phase extraction (SPE) has been developed as an alternative method because it possesses several advantages over LLE such as lower costs, shorter extraction times, accommodation of more samples, ease of practice and optimization. For example, a study described by Tomkins and Griest (1996) employed a solid-phase extraction using a carbon-based Empore SPE disk which resulted as high as 60% in NDMA recovery.

Analysis of NDMA is usually based on isotope dilution, a technique that involves spiking the deuterated isotopic form of NDMA [i.e., NDMA-d_6] into the sample as a surrogate standard for quantification (Taguchi, Jenkins *et al.*, 1994a). This technique is particularly suitable for GC/MS since mass spectrometry can readily distinguish the different mass-to-charge ratios (m/z) of the parent compound and its isotopic analogue, and utilization of isotope surrogate standards precludes potential background contamination from natural sources. Detection of NDMA is typically conducted by either electron ionization [EI] or positive-ion chemical ionization [PCI] using selected ion monitoring [SIM] mode. Compared to PCI, EI may lack selectivity and yield fragmentation patterns that are not most favorable. PCI uses a softer ionization process and causes less molecular fragmentation that may enhance selectivity and sensitivity of analytes (Prest and Herrmann, 1999). Alternatively, high resolution mass spectrometry [HRMS] may be used to increase selectivity under EI mode. Utilization of large-volume injection [LVI] may also be applied to lower the concentration of NMDA detected in extracted samples.

USEPA method 521 (USEPA, 2004) is the most recent published method by EPA for the determination of nitrosamines in drinking water by solid phase extraction [SPE] and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry [MS/MS]. Coconut charcoal solid phase extraction [SPE] cartridge is used for extracting nitrosamines and surrogate standards from 0.5 L water samples. Then, the cartridges is eluted with a small quantity of dichloromethane followed by concentration with blowdown and

addition of an internal standard. Fused silica capillary column of a GC/MS/MS system equipped with a large volume injector [LVI] is used for identifying and quantifying nitrosamines by operating in the chemical ionization [CI] mode. Because the CI reagent gas such as methanol produces a mass spectrum with only one significant ion, the MS/MS mode is used for identification and quantitation.

2.2. Water Treatment Polymers

2.2.1. Water Treatment Polymers as Potential NDMA Precursors

Gough detected NDMA (Gough, Webb *et al.*, 1977) in deionized water which was made by treating tap water with mixed-bed ion exchange resins in a deionization plant. In order to identify responsible resins for NDMA formation, anion and cation exchange resins were tested separately by making resin slurries in distilled tap water followed by dichloromethane [DCM] extraction and GC analysis. The results showed that a much greater amount of NDMA as well as other nitrosamines was found in the anion exchange resin. Because the authors also found a similar amount of NDMA from the direct DCM extract of the resin which thus was not contacted with water, they concluded NDMA may originate from the anion resin itself rather than the reaction between free amines in the resin and the precursors in water. However, Kimoto (Kimoto, Dooley *et al.*, 1980b) demonstrated that tap water plays a significant role in NDMA formation from strong anion exchange resins. When tap water containing residual chlorine was passed through a column containing anion exchange resin, more NDMA was formed by three orders of magnitude than when the resin was contacted with the tap water treated by pre-cleaned activated carbon to remove any unknown NDMA precursors present in the tap water. The authors also showed that resins containing dimethyl-ethanol-benzyl ammonium functional groups formed more NDMA than those containing trimethyl-benzyl ammonium functional groups (Figure 2.3), and the increase of residual chlorine in tap water resulted in increase of NDMA formation.

Child et al. (Child, Kaa *et al.*, 2002) first reported NDMA formation from the reaction of water treatment polymers and chlorine. The authors showed that one hour reaction of high concentration [5000 ppm] poly[diallyldimethylammonium chloride] [polyDADMAC] (Figure 2.3) and high concentration [5000 ppm] hypochlorite resulted in 310 ng/L of NDMA, whereas less than detection limit levels of NDMA [~10 ng/L] resulted when 1.5 ppm hypochlorite was reacted with 0.5 ppm polyDADMAC for 20 hours at room temperature. Later on, (Najm and Trussel, 2001) tested both strong anion exchange resins and polyDADMAC as NDMA precursors after they found that NDMA is a disinfection by-product of chloramination rather than of chlorination. Resins were first soaked in deionized water containing 12 g/L salt and then filtered and washed by deionized water for NDMA formation test, during which different anion exchange resins were exposed to untreated groundwater, distilled water and distilled water at 1 mg/L nitrogen concentration. The resin of dimethyl-ethanol quaternary ammonium functional groups formed the greatest amount of NDMA followed by the resin of trimethyl quaternary ammonium functional groups. The resins containing triethyl quaternary ammonium and functional group and that of tripropyl quaternary ammonium functional groups did not form significant levels of NDMA (see Figure 2.3 for resin polymer structures). Because none of the three water samples tested contained residual chlorine, the anion exchange resins appears to be an NDMA precursor; these results correlate well with the results obtained by (Gough, Webb *et al.*, 1977). However, it

cannot be ruled out that the deionized water used for preparation of the resins contained neutral HOCl or monochloramine which cannot be removed by the deionization process and subsequently reacts with amines in the resins to make NDMA. The authors also conducted a NDMA formation test using 1.5 mg/L of Cat-Floc polymer [the trade name of polyDADMAC] and 5 mg/L of chlorine for 24 hrs. NDMA was not formed (below reporting level of 2 ng/L) from this test. This result, however, was insufficient in evaluating the NDMA formation potential of amine-based water treatment polymers because the most effective NDMA formation oxidant monochloramine was not applied to the polymers and the experiment conditions were not representative of water treatment plants.

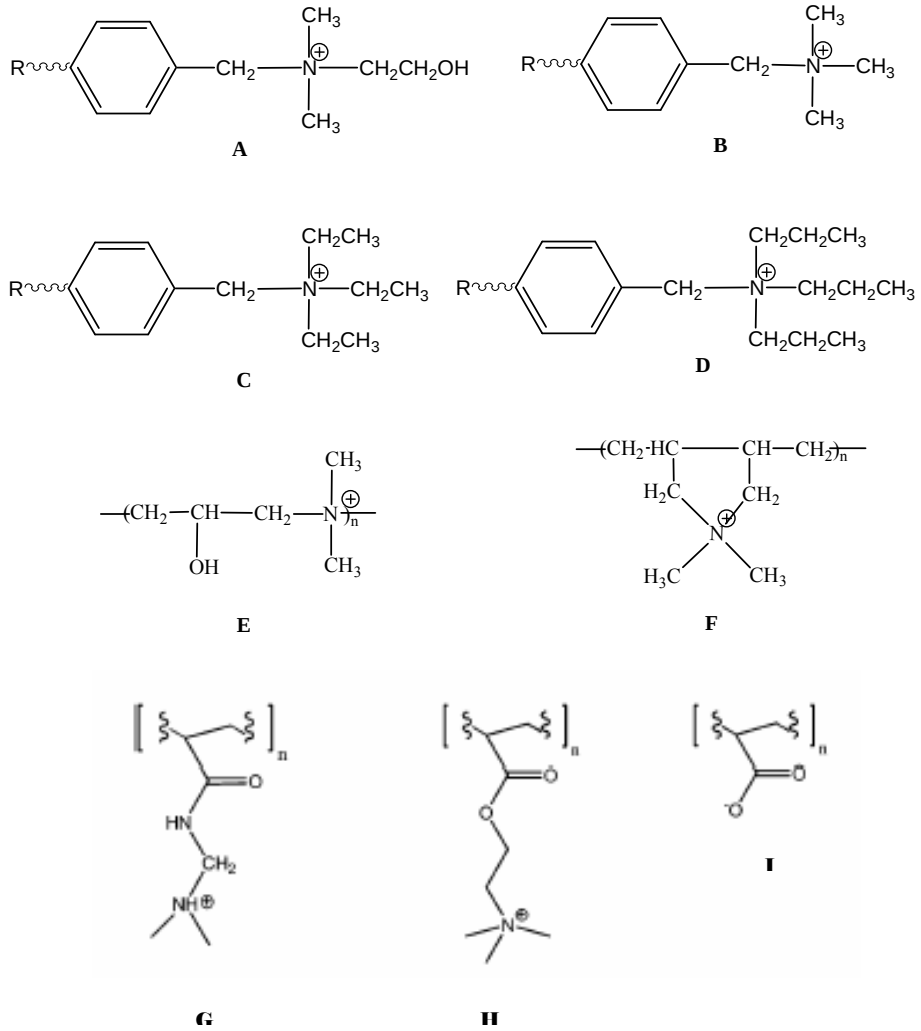


Figure 2. 3 Ion exchange resins and polymers that were examined in previous studies. A, B, C and D: strong base anion exchange resins with dimethyl-ethanol, trimethyl, triethyl and tripropyl benzyl ammonium functional groups, respectively, E: polyamine, F: polyDADMAC, G: Mannich polymer, H: trimethylamine-based cationic polyacrylate (ADAM QUAT polymer), and I: polyacrylate anionic copolymer.

Wilczak and his colleagues (Wilczak, Assadi-Rad *et al.*, 2003c) extensively tested NDMA

formation potential of polyDADMAC under several treatment conditions including laboratory, pilot plant, and water treatment plant. From NDMA screening tests in the laboratory using 10-30 times higher dosage of several water treatment chemicals (alum and cationic and nonionic polymers) and in-situ chloramination, polyDADMAC was confirmed as the only major potent NDMA precursor. The authors also showed from pilot scale tests that the sequence of chlorine and ammonia addition has profound impact on the level of NDMA formed. Then, the NDMA formation potential of polyDADMAC was tested in realistic conditions by conducting NDMA formation simulations in a pilot plant and by direct sampling from two water treatment plants and distribution systems in California. More than 10 ng/L of NDMA were observed in samples from chloraminated distribution systems having high dose (0.8-1.2 mg/L) of polyDADMAC, filter backwash recycle, and very short time or no free chlorine contact. In contrast, low polymer dose (0.2-0.4 mg/L), no recycle filter backwash, and a long free chlorine contact time resulted in around 2 ng/L of NDMA. The positive correlation between NDMA formation and polymer dosage from both pilot tests and real water treatment samples effectively demonstrated that polyDADMAC plays a significant role in NDMA formation from its reaction with chloramines.

Kohut and Andrews (2003) tested NDMA formation potential of poly[dimethylamine-epichlorohydrin] [polyamine] (Figure 2.3) as well as polyDADMAC in simulations of coagulation /flocculation/sedimentation using raw water and varying doses of polymer and chlorine. Coagulation for 30 sec at 100 rpm, flocculation for 10 min at 40 rpm, and sedimentation for 30 min were conducted for samples and then supernatants were analyzed for NDMA concentration. NDMA formation increased from around 70 to 130 ng/L when polyDADMAC dose increased from 0.1 to 10 mg/L with the fixed chlorine dose of 9 mg/L. The same dose effect test was applied to polyamine, which resulted in more significant NDMA formation in the range of around 100 – 550 ng/L. The authors also mentioned that the NDMA formation potential of the two polymers with raw water was considerably higher than that with tap water in their previous experiments, and therefore suspected that certain NDMA formation catalysts or precursors already existed in the raw water.

Mitch and Sedlak (Mitch and Sedlak, 2004b) extended NDMA formation tests to four types of water treatment polymers: DMA-based cationic polyacrylamide [Mannich polymer], trimethylamine-based cationic polyacrylate [ADAM QUAT polymer], polyDADMAC, and polyacrylate (see Figure 2.3 for structures). The Mannich polymer formed a huge amount of NDMA, while the other three polymers did not form significant levels of NDMA. It is not surprising that Mannich polymer has great NDMA formation potential if it is considered that tertiary amine-ended pendent groups attached to the polyacrylamide backbone are more vulnerable to the attack of oxidant and pH change than the quaternary ammonium groups in the other cationic polymers. The authors also suggested that quaternary ammonium functional groups are not significant NDMA precursors because the lack of lone pair electrons on nitrogen hinders the electrophilic attack of monochloramine for NDMA formation.

Najm and his colleagues (Najm, Teefy *et al.*, 2004b) tested NDMA formation potential of several polyDADMACs using 1 mg/L of active ingredient polymer and 4 mg as Cl_2/L of in-situ monochloramine for 7 days at pH 8.3-8.6. DMA concentrations were also measured before and

after 7 days of chloramination. Most of the tested polyDADMAC solutions formed 50-60 ng/L of NDMA, and two out of eight samples formed more than 130 ng/L. Residual DMA concentrations of polymer solutions before chloramination were in the range of 0.21 – 1.2 μg/mg polymer but increased to 1.9 – 3.3 μg/mg polymer after 7 days of chloramination. The amount of NDMA formed and DMA concentration measured after chloramination increased with increasing polymer and/or chloramine concentrations. The study results also showed that increased chlorine contact time prior to ammonia addition increased NDMA formation slightly. This is contrary to the results of (Wilczak, Assadi-Rad *et al.*, 2003c; Wilczak, Assadi-Rad *et al.*, 2002), although direct comparison is difficult because Najm et al. used bicarbonate buffered Nanopure water in their bench-scale tests but Wilczak et al. used the filtered raw water which might have other chlorine demands.

2.2.2. Synthesis of Amine-based Water Treatment Polymers

This project focuses particularly on four polymers: polyamine, polyDADMAC, cationic polyacrylamide and Mannich polymer. Thus, their synthetic procedures are discussed here.

Polyamine is among the polymers with quaternary ammonium ionic groups integrated all along the backbone of the polymer chain instead of in pendent positions. Polymerization usually takes place with two steps. First, at low temperature, DMA is added to epichlorohydrin, or vice versa, to make DMA-epichlorohydrin adduct. Then, the DMA-epichlorohydrin adduct undergoes condensation polymerization at high temperature to produce the polymer (Scheme 2.1) (Schwoyer, 1981).

PolyDADMAC is the first quaternary ammonium cationic polymer to be approved by the U.S. Food and Drug Administration for potable waters. As shown in Scheme 2.2, DADMAC monomer is first prepared commercially from the reaction of allyl chloride and DMA. Then, the non-conjugated diene of DADMAC undergoes cyclopolymerization to form a 5-membered ring structure of polyDADMAC (Shalaby, McCormick *et al.*, 1989).

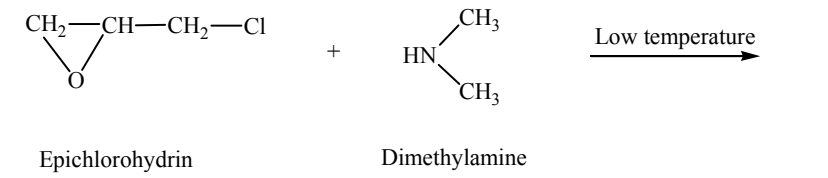
Cationic polyacrylamide [cationic PAM] is synthesized in the powder form from copolymerization of acrylamide with quarternized dimethylaminoethyl acrylate [DMAEA] after first preparing quarternized DMAEA via the reaction of DMAEA with methyl chloride (Scheme 2.3). The cationic molar proportion of the copolymer is determined by the ratio of the two monomers (i.e., acrylamide and chloromethylated DMAEA), yielding varying cationic charge density between 0% and 100% (Ishigaki, Okada *et al.*, 1981). Note that the ester group of this copolymer is sensitive to pH and may hydrolyze at pHs above 6.

Generally referred to as Mannich polymer, aminomethylated polyacrylamide is also a well known flocculating agent. Unlike the synthetic processes of the other three polymers, Mannich polymer is made by the attachment of aminomethylated tertiary amine to already-prepared polyacrylamide backbone using DMA and formaldehyde via Mannich reaction followed by acidification (McDonald and Beaver, 1979) (Scheme 2.4). However, this polymer has some drawbacks such that Mannich reaction is reversible so that DMA and formaldehyde can be reproduced during usage or storage.

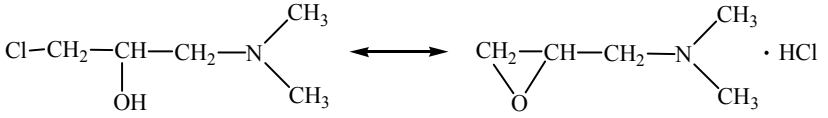
Among these polymers, polyDADMACs and polyamines are typically used as coagulants in drinking water treatment. Cationic PAMS and nonionic Mannich polymers (waste water only) are used as flocculants in treatment of potable water and waste process water, as well as sludge dewatering processes. The typical dosages of polymers in the above applications are about 0.3-1.5 mg/L in active ingredients. Higher dosages of polymers are generally not used in real practice because they lead to poor coagulation and the problem of redispersion of polymer particles. The polymers also have very strong tendency to adsorb to particulates and the formed flocs in water. Therefore, the majority of the polymers applied are expected to be removed by sedimentation and filtration processes prior to disinfection processes. As a result, direct contact of the polymers with chlorine is limited, except in cases where pre-oxidation is used prior to coagulation/flocculation processes, and for polymers remaining that are dissolved in water or bound to particulates that are not effectively removed by sedimentation and filtration. However, the time period of the above direct contact should also be taken into account for potential NDMA formation.

SCHEME 2.1. Synthesis of polyamine.

Step 1

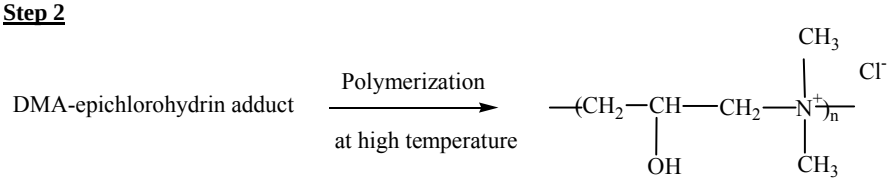


Epichlorohydrin Dimethylamine



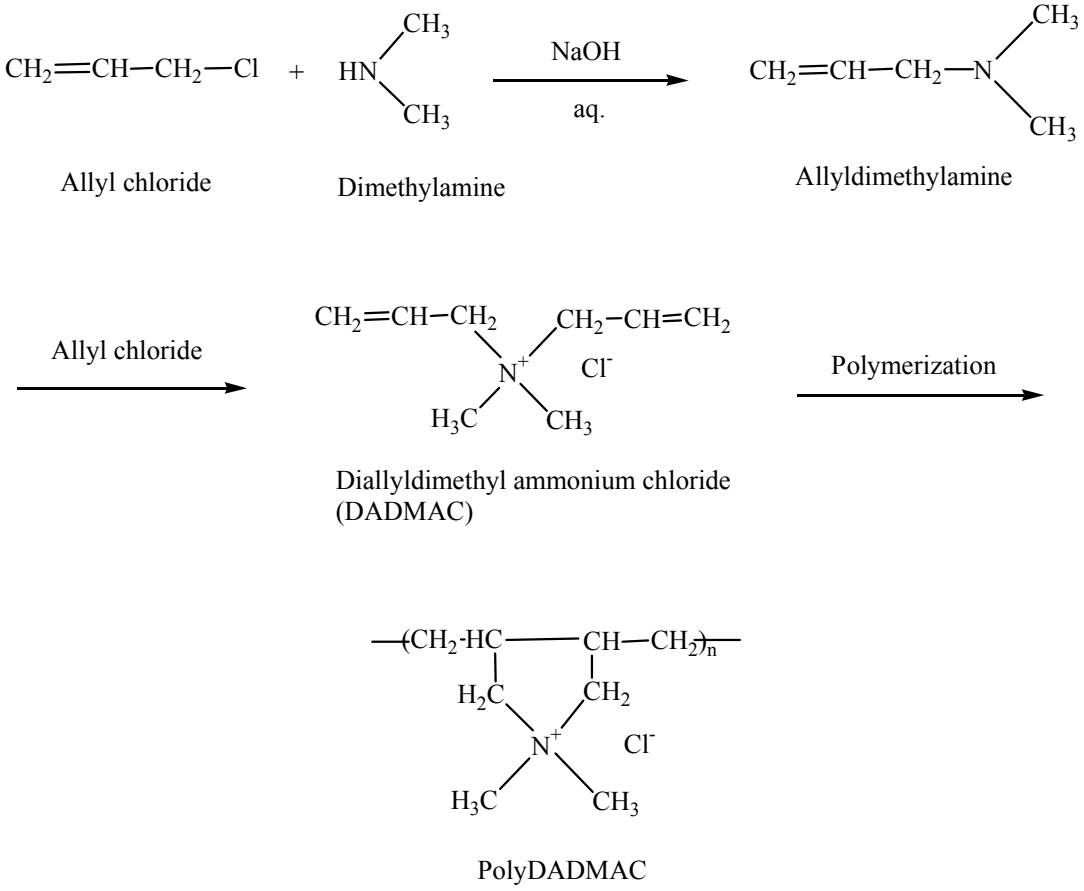
DMA-epichlorohydrin adduct

Step 2

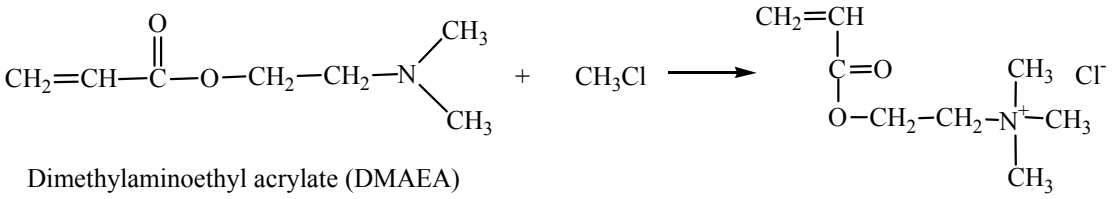


Polyamine

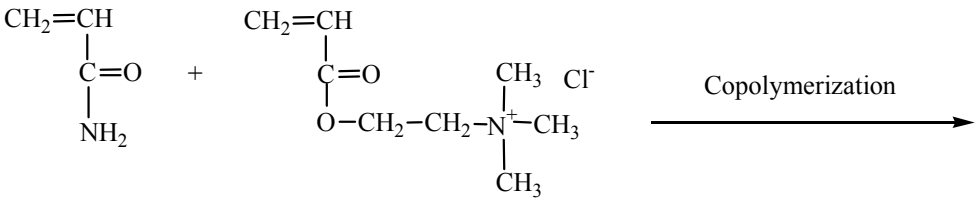
SCHEME 2.2. Synthesis of polyDADMAC.



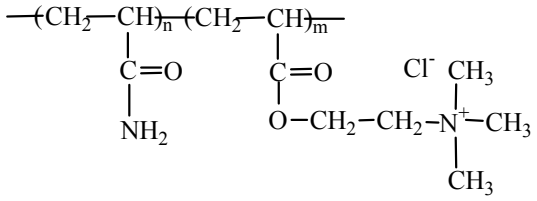
SCHEME 2.3. Synthesis of cationic polyacrylamide copolymer.



Dimethylaminoethyl acrylate (DMAEA) Chloromethylated DMAEA

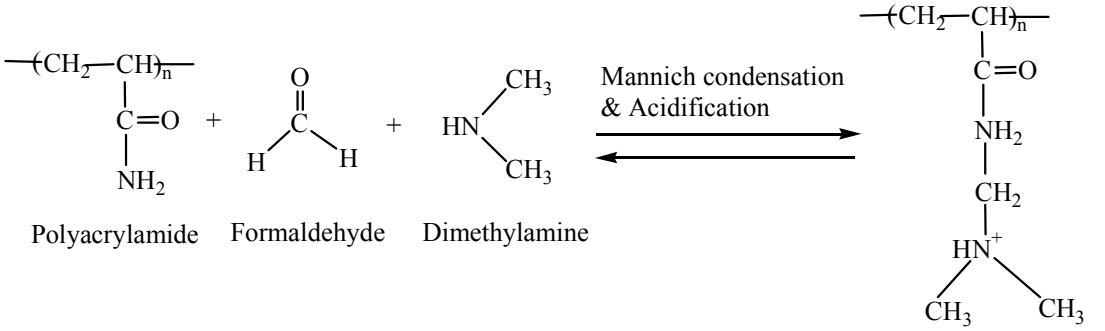


Acrylamide Chloromethylated DMAEA



Cationic Polyacrylamide Copolymer

SCHEME 2.4. Synthesis of Mannich polymer.



Polyacrylamide Formaldehyde Dimethylamine Mannich polymer

3 Analytic Chemistry: Materials, Methods and Analysis of Results

As summarized in the literature review given above, a significant number of studies have indicated that certain water treatment polymers may be NDMA precursors under water chloramination or chlorination conditions. However, the mechanisms of which NDMA is formed from the polymers and what the critical influencing factors are for the NDMA formation are still poorly understood. The purpose of the analytic chemistry studies summarized in this section is to conduct a systematic investigation to assess the potential NDMA formation from four types of commonly used water treatment polymers and probe the mechanisms of such a formation. The specific research objectives of this analytic work are:

i. Establish robust and sensitive analytical methods for detection of NDMA and DMA;
ii. Determine whether the SNF polymer products (specifically polyamine, polyDADMAC, cationic polyacrylamide copolymer, and Mannich polymer) as supplied, can form significant levels of NDMA in the conditions found in water and wastewater treatment plants;
iii. If the SNF products are significant sources of NDMA, determine whether the polymeric components or the residual raw materials (monomers, catalysts, other impurities such as residual oligomers, etc.) in the products contribute to NDMA formation. If neither are the direct sources, identify other possible causes;
iv. Evaluate whether the SNF polymers are stable during water treatment processes. Determine if degradation of polymers occurs and leads to higher levels of NDMA;
v. Assess the influence of water quality parameters on NDMA formation by applying NDMA formation test in real water treatment conditions; and,
vi. Develop the strategy to reduce NDMA formation potential of SNF polymers by modifying polymer synthetic processes and identifying treatment conditions minimizing NDMA formation.

3.1 Characteristics of General Chemicals

Deionized [DI] water used in the experiments was produced from a Millipore Milli-Q Nanopure water purification system. A.C.S. reagent grade water from Sigma-Aldrich was used to prepare dimethylamine standard solutions and preformed monochloramine stock solutions. Dimethylamine hydrochloride (99%), sodium nitrite (98+%), 4-methoxybenzenesulfonyl chloride (99%) and sodium thiosulfate were obtained from Acros. Ammonium chloride (99.9%), ferrous ammonium sulfate, sodium hypochlorite (4-6%, purified grade), potassium iodide dibasic, potassium phosphate, *N*,*N*-diethyl-*p*-phenylenediamine oxalate, disodium ethylenediamine tetraacetate [EDTA] were obtained from Fisher Scientific. The above reagents were used directly without further purification. *N*-nitrosodimethylamine from Protocol Analytical, and *N*-nitrosodimethylamine-d_6 (98%), and dimethylamine-d6 (98%) from Cambridge Isotope Laboratories were used as standards without further purification. Sodium bicarbonate (99.7+%), sodium phosphate monobasic (99%), sodium phosphate dibasic (99.7%) from Fisher Scientific, and sodium borate decahydrate from reagent ACS were used to produce buffer stock solutions. Small amounts of sulfuric acid and sodium hydroxide from Fisher Scientific were further added

to buffered solutions to adjust pH to a specific value. L-ascorbic acid (99+%) from Fisher Scientific was used for quenching. Solvents used in experiments were Fisher Scientific acetone for derivatizing solution, methanol for standard dilutions and washing, and dichloromethane for liquid-liquid extraction, solid-phase extraction and GC/MS analysis. Supelco Ambersorb 572 adsorbent was used to extract NDMA from water samples. Environmental Express TCLP non-binding borosilicate microfiber filters with a nominal pore size of 0.7 µm were used to filter water samples.

3.2 Characteristics of Polymers and Other Samples Received from SNF

Samples of polymers and other related compounds received from SNF are summarized in Table 3.2.1. The samples were kept at room temperature (23 ºC), protected from light in storage, and used directly in experiments without additional purification. General characteristics of the four polymers (polyamine, polyDADMAC, cationic PAMS and Mannich polymers) are summarized in Table 3.2.2.

Table 3.2. 1 Polymers and other samples provided by SNF

Product No:	Description	Received	Solid %
DPR 4256	80 % mole cationic powder grade polyacrylamide.	10/20/04	94.3 %
DPR 4257	40 % mole cationic powder grade polyacrylamide.	10/20/04	93.7 %
DPR 4258	Mannich solution polymer.	10/20/04	4.39 %
DPR 4259	PolyDADMAC solution polymer.	10/20/04	40.3 %
DPR 4260	PolyDADMAC solution polymer.	10/20/04	40.4 %
DPR 4261	Polyamine solution polymer.	10/20/04	49.7 %
RB2199-A	Unpurified polyDADMAC.	04/19/05	40.0 %
RB2199-B	Purified (by precipitation) polyDADMAC.	04/19/05	40.0 %
RB2202-A	Unpurified polyDADMAC.	04/19/05	40.1 %
RB2202-B	Purified (by precipitation) polyDADMAC.	04/19/05	40.1 %
RB2200-A	Unpurified polyamine.	04/19/05	49.1 %
RB2200-B	Purified polyamine.	04/19/05	49.1 %
RB2203-A	Unpurified polyamine.	04/19/05	49.1 %
RB2203-B	Purified polyamine.	04/19/05	48.7 %
	DADMAC monomer.	11/11/05	67.1 %
RB2220-A	Lowest MW polyDADMAC (No Branching).	11/11/05	36.5 %
RB2220-B	Highest MW polyDADMAC (No Branching).	11/11/05	19.7 %
RB2220-C	Lowest MW polyamine (No Branching).	11/11/05	49.5 %
RB2220-D	Lower MW polyamine (Branching).	11/11/05	49.9 %
RB2220-E	Highest MW polyamine (Branching).	11/11/05	49.5 %
AT2020-A	Undialyzed Polyamine.	01/09/06	3.4 %
AT2020-B	Dialyzed Polyamine in DI water.	01/09/06	3.4 %
AT2020-C	Dialyzed Polyamine in 5 % NaCl solution.	01/09/06	14.4 %

AT2021-A	Undialyzed PolyDADMAC.	01/09/06	5.0 %
AT2021-B	Dialyzed PolyDADMAC in DI water.	01/09/06	5.0 %
AT2021-C	Dialyzed PolyDADMAC in 5 % NaCl solution.	01/09/06	16.1 %
	Synthetic water containing DI water, 50 ppm humic acid, and 500 ppm bentonite clay.	03/07/06	
	Polyamine rain pad water.	03/07/06	
	PolyDADMAC rain pad water.	03/07/06	
RB2233-A	Artificial water that has been coagulated using 100 ppm alum and filtered	03/28/06	
RB2233-B	Artificial water that has been coagulated using 100 ppm alum/10 ppm polyamine and filtered.	03/28/06	
RB2233-C	Artificial water that has been coagulated using 100 ppm alum/10 ppm polyDADMAC and filtered.	03/28/06	
RB2233-D	(i) Filtered artificial water (50 ppm humic acid; 500 ppm bentonite Clay); (Case, Darden *et al.*) CONTROL filtered deionized water - used in the formulation for artificial water (Jar test procedure to generate RB2233-A-C).	03/28/06	
RB2237	Coagulated and filtered water sample from a municipal potable water plant using SNF polymer. (It has already been disinfected.).	04/11/06	
AT2022-A	DMA-Epi-DMA polyamine model compound. (1 mole epichlorohydrin reacted with 1 mole DMA)	04/13/06	~ 60 %
AT2022-B	Allyldimethylamine.	04/13/06	
	Filtered DI water: used on formulation for artificial water (Jar test procedure to generate RB 2233-A-C).	04/25/06	
	Humic acid: used in the formulation for artificial water (Jar test procedure to generate RB2233-A-C).	04/25/06	
	Bentonite Clay: used in the formulation for artificial water (Jar test procedure to generate RB2233-A-C).	04/25/06	
	Aluminum sulfate hydrate (Alum): used in the formulation for artificial water (Jar test procedure to generate RB2233-A-C).	04/25/06	
RB 2240-A	Raw water that has been coagulated using 75 ppm Alum and filtered.	05/26/06	
RB 2240-B	Raw water that has been coagulated using 75 ppm Alum/ 15 ppm polyamine and filtered.	05/26/06	
RB 2240-C	Raw water that has been coagulated using 75 ppm Alum/ 5 ppm polyDADMAC and filtered.	05/26/06	
RB 2240-D	Filtered raw water (No Coagulation): CONTROL.	05/26/06	
RB2241-A	Raw water that has been coagulated using 75 ppm Alum (No Filtration).	06/19/06	
RB2241-B	Raw water that has been coagulated using 75 ppm Alum/8 ppm polyamine (No Filtration).	06/19/06	
RB2241-C	Raw water that has been coagulated using 75 ppm Alum/1 ppm polyDADMAC (No Filtration).	06/19/06	
RB2241-D	Raw water (No Coagulation; No Filtration); CONTROL.	06/19/06	
RB2242-A	Artificial water that has been coagulated using 65 ppm Alum (No Filtration).	06/26/06	

RB2242-B	Artificial water that has been coagulated using 65 ppm Alum/8 ppm polyamine (No Filtration).	06/26/06	
RB2242-C	Artificial water that has been coagulated using 65 ppm Alum/6 ppm polyDADMAC (No filtration).	06/26/06	
RB2242-D	Artificial water (No Coagulation; No Filtration); CONTROL.	06/26/06	
RB 2248-A	Raw water (No Coagulation).	08/07/06	
RB 2248-B	Raw water that has been coagulated using 75 ppm Alum.	08/07/06	
RB 2248-C	Raw water that has been coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC.	08/07/06	
RB 2248-D	Raw water that has been coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 10% PD dosage after coagulation).	08/07/06	
RB 2248-E	Raw water that has been coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 20% PD dosage after coagulation).	08/07/06	
RB 2248-F	Raw water that has been coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 50% PD dosage after coagulation).	08/07/06	
RB 2248-G	Raw water that has been coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 100% PD dosage after coagulation).	08/07/06	
RB 2248-H	Raw water that has been coagulated using 37.5 ppm Alum / 0.55 ppm polyDADMAC.	08/07/06	
RB 2248-I	Raw water that has been coagulated using 37.5 ppm Alum / 0.65 ppm polyDADMAC.	08/07/06	
RB 2248-J	Raw water that has been coagulated using 37.5 ppm Alum / 0.75 ppm polyDADMAC.	08/07/06	
RB 2248-K	Raw water that has been coagulated using 37.5 ppm Alum / 1.0 ppm polyDADMAC.	08/07/06	
RB 2248-L	Raw water that has been coagulated using 37.5 ppm Alum / 0.45 ppm polyDADMAC.	08/07/06	
RB 2248-M	Raw water that has been coagulated using 37.5 ppm Alum / 0.40 ppm polyDADMAC.	08/07/06	
RB 2248-N	Raw water that has been coagulated using 37.5 ppm Alum / 0.25 ppm polyDADMAC**.**	08/07/06	
RB2269-A	Raw Lake Ontario water (No Coagulation) (CONTROL), No Filteration.	01/16/07	
RB2269-B	Raw Lake Ontario water coagulated using 38 ppm Alum, No Filteration.	01/16/07	
RB2269-C	Raw Lake Ontario water coagulated using 19 ppm Alum/3 ppm polyamine, No Filteration.	01/16/07	
RB2269-D	Raw Lake Ontario water coagulated using 19 ppm Alum/2 ppm polyDADMAC, No Filteration.	01/16/07	
RB2270-A	Raw Kitchener, Ontario River water (No Coagulation) (CONTROL), No Filteration.	01/16/07	
RB2270-B	Raw Kitchener, Ontario River water coagulated using 50 ppm Alum, No Filteration.	01/16/07	

RB2270-C	Raw Kitchener, Ontario River water coagulated using 25 ppm Alum/3 ppm polyamine, No Filteration.	01/16/07	
RB2270-D	Raw Kitchener, Ontario River water coagulated using 25 ppm Alum/1 ppm polyDADMAC, No Filteration.	01/16/07	
RB2271-A	Raw Pushlinch, Ontario aquifer water (No Coagulation) (CONTROL), No Filteration.	01/16/07	
RB2271-B	Raw Pushlinch, Ontario aquifer water coagulated using 63 ppm Alum, No Filteration.	01/16/07	
RB2271-C	Raw Pushlinch, Ontario aquifer water coagulated using 33 ppm Alum/0.5 ppm polyDADMAC, No Filteration.	01/16/07	
RB2271-D	RAW Pushlinch, Ontario aquifer water coagulated using 33 ppm Alum/1 ppm polyDADMAC (OVERDOSED), No Filteration.	01/16/07	
CR2502	19.9 % Aqueous solution of polyDADMAC synthesized in mild conditions with VA-044 and chain end capping with hypophosphite.	01/16/07	19.9 %
CR2500-A	22.9 % Aqueous solution of polyDADMAC synthesized with 0 ppm ADMA-spiked DADMAC.	01/16/07	22.9 %
CR2500-B	22.2 % Aqueous solution of polyDADMAC synthesized with ~ 500 ppm ADMA-spiked DADMAC.	01/16/07	22.2 %
CR2500-C	22.4 % Aqueous solution of polyDADMAC synthesized with ~ 5,000 ppm ADMA-spiked DADMAC.	01/16/07	22.4 %
CR2500-D	21.8 % Aqueous solution of polyDADMAC synthesized with 20,000 ppm ADMA-spiked DADMAC.	01/16/07	21.8 %
CR2505-A	51.4 % Aqueous solution of polyamine synthesized with 1 % of theoretical Quat 188.	01/24/07	51.4 %
CR2505-B	53.1 % Aqueous solution of polyamine synthesized with 10 % of theoretical Quat 188.	01/24/07	53.1 %
CR2505-C	54.0 % Aqueous solution of polyamine synthesized with 100 % of theoretical Quat 188.	01/24/07	54.0 %

Table 3.2. 2 Characteristics of polymer samples (received in October, 2004)

	Polyamine Solution Polymer	PolyDADMAC Solution Polymer	Cationic PAMS Powder	Mannich Solution Polymer
Viscosity (centipoises)	840	2,880	UL viscosity 4.26	31,750
pH	5.9	6.0	N.A.	10.5
Non-Volatile Solids	49.7%	40.3%	94.3%	4.39%
Residues	Epi = 0 ppm Glycidol = 0 ppm DCIPA = 236 ppm DCPA = 78 ppm DIOL = 34 ppm TOC = 347 ppm	Residual monomer < 0.1%	Residual acrylamide 35 ppm	N.A.

Note: N.A. = not available; Epi = Epichlorhydrin; DCIPA = 1,3-dichloro-2-propanol; DCPA = 2,3-dichloro-1-propanol; DIOL = 3-chloro-1,2-propanediol and TOC = Total Organic Content.

3.3 Reagent Preparation and Experimental Procedures

3.3.1 Preparation of Monochloramine Stock Solution

Monochloramine stock solution was prepared fresh for every experiment by adding sodium hypochlorite slowly into an ammonium chloride solution. Ammonium chloride was first dissolved in 10 mM bicarbonate or phosphate buffer solution maintaining at pH above 8.5. Bicarbonate buffer solution was made from sodium bicarbonate or Dionex sodium carbonate concentrate solution with addition of sodium hydroxide or sulfuric acid. Phosphate buffer solution was made from monobasic and dibasic phosphate. Then a predetermined amount of sodium hypochlorite solution was added by drops slowly into the rapidly stirred ammonium chloride solution at Cl/N molar ratio of 0.7. The solution pH was maintained at 9.5 or slightly higher during the reaction to minimize disproportionation of monochloramine to dichloramine. The solution was stored in an amber glass bottle and stirred for at least two hours before use. This preformed monochloramine solution was used within one day. The concentration of monochloramine was determined by the *N,N*-diethyl-*p*-phenylenediamine-ferrous ammonium sulfate [DPD-FAS] titration method specified in the Standard Methods (APHA, 1998).

3.3.2 Preparation of Chlorine Dioxide Stock Solution

Chlorine dioxide solution was generated by slowly adding 100 mL of 8.0 N sulfuric acid [H_2SO_4] to 250 mL of 160 g/L sodium chlorite [$NaClO_2$] solution under constant stirring (modified from (Pitochelli, 1995)). The reactor was set up with air continuously bubbling in through an inlet and leaving via an outlet. The reaction between sulfuric acid and sodium chlorite produced chlorine dioxide gas, which was captured in solution by passing through chilled DI water. The same reaction was repeated again and the generated chlorine dioxide gas was trapped in the same chilled DI water trapper. The final yellow solution of chlorine dioxide was then stored in an amber glass bottle and kept in a refrigerator. The concentration of chlorine dioxide was determined by titrating with sodium thiosulfate in the presence of potassium iodide, acid and starch indicator as specified in the Standard Methods (APHA, 1998).

3.3.3 Batch Reaction Setup

All NDMA formation potential tests were conducted using amber glass batch reactors continuously agitated by a platform shaker at 23±1 °C. Typically, 1 - 10 mg/L as active ingredient of fresh polymer solutions were chloraminated with 4 - 10 mg as Cl_2/L of preformed monochloramine at pH 5 - 9 using 10 mM acetate (pH 5), phosphate (pH 6-8) or borate (pH 9) buffer for several reaction times. Then, the reactions were quenched by 30 mg/L of ascorbic acid before NDMA and DMA analysis.

In the general screening of polymers for NDMA formation during the beginning phase of this project, 20 mg/L of total weight was used in preparing polymer reaction solutions that corresponded to 0.88 to 23.58 mg/L of active polymer in the reactions with preformed monochloramine (10 mg/L as Cl_2), free chlorine (10 mg/L as Cl_2), chlorine dioxide (8 mg/L as Cl_2), or nitrite (20 mg/L). In those cases, the measured NDMA concentration was divided by the corresponding polymer concentration (yielding NDMA concentration in ng NDMA per mg polymer unit) to aid comparisons among the four polymers in the general screening tests (Piyachaturawat, 2005).

For all the experiments, matrix and reagent controls as well as duplicate experiments were conducted for each condition. In addition to DI water, a real wastewater matrix was also used in order to evaluate the impact of wastewater constituents on the NDMA formation potential of the polymers. The wastewater sample used in the experiments was collected from the R. M. Clayton Wastewater Treatment Plant near Atlanta, GA - a primarily domestic wastewater treatment plant at the capacity of 120 millions of gallons per day [MGD]. The wastewater samples were collected at the point after the processes of activated sludge and the secondary clarifier. After an immediate return to the laboratory, the wastewater was filtered by glass fiber filters to remove larger particles. The characteristics of the filtered wastewater were determined to be: pH = 6.93, total organic carbon = 5.4 mg/L and total suspended solids [TSS] = 1.3 mg/L according to the Standard Methods (APHA, 1998). The wastewater samples were kept at 4 ºC in the dark and used within a week.

3.3.4 NDMA Analysis

Early experiments of this project had shown that extraction of NDMA from water by commercial solid-phase extraction cartridges (i.e., Waters Oasis-HLB, Phenomenex Strata-X, and Supelco Envi-18 cartridges) was poor. Comparatively, free Ambersorb 572 resins performed much better (Piyachaturawat, 2005). The optimal conditions (e.g., extraction time, drying time, quantify of resins, etc.) for the solid-phase extraction of NDMA by Ambersorb resins were carefully determined. The established method is briefly described below.

NDMA was determined using solid-phase extraction followed by an isotope dilution gas chromatography/mass spectrometer [GC/MS] method (modified from (Taguchi, Jenkins *et al.*, 1994a)). All glassware was cleaned with Micro brand laboratory detergent, rinsed with methanol and DI water, and prebaked at 300 °C for at least 3 hours prior to use in each analysis to eliminate any organic residues or contaminants. Typically, 10 – 300 ng/L of deuterated NDMA [NDMA-d_6] was spiked into 350 - 750-mL water samples as a surrogate standard, depending on the expected

NDMA concentrations in samples. After adding the surrogate standard, 200 mg of Ambersorb 572 beads (pre-conditioned at 300 °C for 3 hours prior to use) was added to the sample to extract NDMA. The samples were placed on a platform shaker at 175 - 200 rpm for 2 hours to extract NDMA. After extraction, the samples were filtered and the Ambersorb beads were collected on a non-binding borosilicate fiber filter, air-dried at room temperature for 2 - 4 hour and transferred to a 2-mL amber vial. Dichloromethane (400 - 500 µL) was added to the vial to desorb NDMA from the Ambersorb beads. The vials were capped and tapped for 30 min before loading onto the autosampler tray for GC/MS analyses. To prepare calibration standards, NDMA and NDMA-d_6 were dissolved in dichloromethane at 1- 1000 µg/L and 1 - 500 µg/L, respectively. In a very few cases, liquid-liquid extraction was used for extracting NDMA from the samples of very high concentration, followed by the same GC/MS analysis described above.

NDMA and NDMA-d_6 were analyzed using an Agilent GC/EI/MS [6890/5973] system with a HP-5MS column (30 m × 250 µm × 0.25 µm) or a Supelco Equity^{TM}-1701 (30m × 250µm × 0.25µm) and a large-volume-injector [LVI]. The NDMA analysis method used splitless injection of 2 µL with an injection port temperature of 200 °C or solvent vent injection of 1 µL with a programmable temperature vaporization [PTV] inlet, a transfer line temperature of 260 °C and an MSD ion source temperature of 150 °C. The GC temperature conditions modified from (Mitch, Gerecke *et al.*, 2003) were: held at 35 °C for 1 min, ramped at 10 °C/min to 70 °C, ramped at 2 °C/min to 72 °C, and then ramped at 15 °C/min to 240 °C, with a final hold at 2.4 min. NDMA and NDMA-d_6 were both quantified in selected ion monitoring mode [SIM] using m/z 74.1 as parent and m/z 42 as daughter ions for NDMA and m/z 80.1 as parent and m/z 48 as daughter ions for NDMA-d_6 (Figure 3.1). The relative abundance of the daughter ion to the parent ion is similar in both NDMA and NDMA-d_6. Calibration curves for quantification were based on the parent ion and yielded linear relationships throughout the employed concentration range ($R^2 > 0.99$). The existence of the daughter ion at the correct relative abundance and the corresponding chromatographic retention time were used, in addition to the parent ion, to verify the identities of NDMA and NDMA-d_6 in the samples.

Typical extraction recoveries of NDMA-d_6 were 30-60% depending on sample matrices, with raw water samples usually of lower recovery than DI matrices. The final concentration of NDMA was reported here after adjustment by the concentration factor (C.F. = 700 - 1500) and the corresponding NDMA-d_6 recovery in the sample. The method detection limit for NDMA analysis was approximately 1-2 ng/L or higher dependent upon the involved sample matrix.

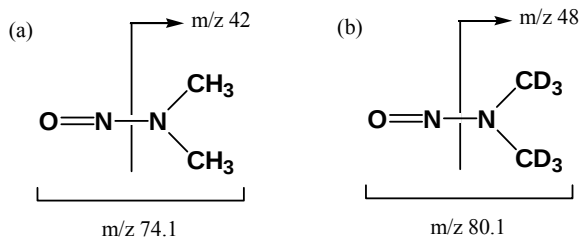


Figure 3. 1 Structures and fragmentation of (a) *N*-nitrosodimethylamine (NDMA); and, (b) *N*-nitrosodimethylamine-d_6 (NDMA-d_6)

3.3.5 Dimethylamine Analysis

Dimethylamine [DMA] was analyzed using a liquid-liquid extraction [LLE] followed by GC/MS analysis which is modified from Sacher et al (1997) and (Mitch and Sedlak, 2004b). All samples (50-100 mL) were taken to analyze for DMA before and after monochloramination. As a pretreatment of DMA for GC/MS analysis, DMA samples were derivatized with an excess amount of 4-methoxybenzenesulfonyl chloride (Figure 3.2) for 3-6 hours at pH 8.9 using 10 mM borate buffer after spiking with a surrogate standard deuterated dimethylamine [DMA-d_6]. After derivatization, the samples were extracted using 10-20 mL of dichloromethane and then the extracts were concentrated down to a final volume of 1 mL by mild heating and a gentle nitrogen gas stream. Since LVI was introduced to GC, a pre-concentration step to 1 mL was not necessary because LVI successfully conducted the pre-concentration function in the inlet enough to detect 0.1-0.2 µg/L of DMA. However, lowering MDL to less than 0.1 µg/L was unattainable due to dimethylamine contamination of the reagents rather than instrumental limit or noise resulting from environmental matrices as mentioned in (Mitch and Sedlak, 2003b). Calibration standards of DMA and DMA-d_6 were prepared by dissolving these two compounds at 0.1 - 50 µg/L in DI water, followed by the derivatization and extraction steps described above.

The samples were analyzed by an Agilent GC/EI/MS instrument as described in the previous section. The GC oven temperature conditions began at 100 °C, held for 1 min and then ramped at 8 °C/min to 250 °C and held at 250 °C for 3 min. DMA and DMA-d_6 were quantified in SIM mode using the m/z 215 parent ion and m/z 171 daughter ion for DMA, and the m/z 221 parent ion and m/z 171 daughter ion for DMA-d_6. Quantification was also primarily based on the parent ion and yielded very linear calibration curves ($R^2 > 0.98$). The typical recoveries of DMA-d_6 were 60-90% depending on sample matrices. The final reported concentration of DMA was after adjustment of the corresponding DMA-d_6 recovery in the sample. The detection limit for DMA was approximately 0.1 µg/L.

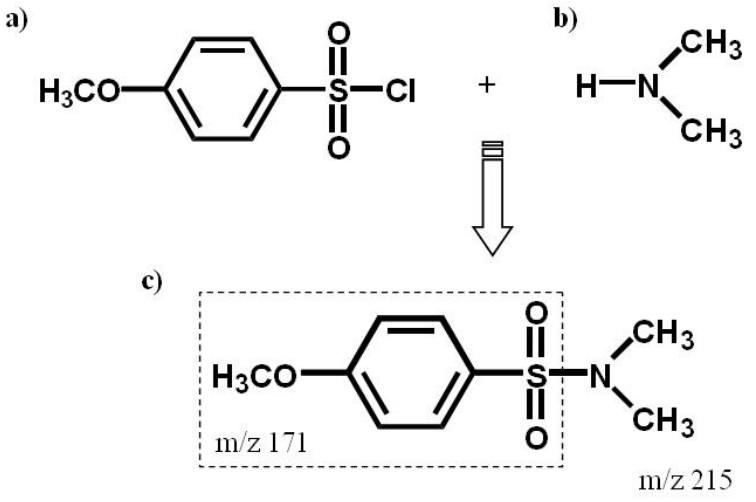


Figure 3. 2 Structures of (a) 4-methoxybenzenesulfonyl (derivatizing agent); (b) dimethylamine DMA; and, (c) derivatized DMA.

3.3.6. DADMAC Analysis

An aqueous DADMAC monomer solution was analyzed by an Agilent LC/MS system with electrosray ionization [ESI] in positive ion mode. An Agilent Zorbax RX-C18 column was used at a flow rate of 0.25 mL/min with acetonitrile and 5 mM heptafluorobutyric anhydride [HFBA] aqueous solution as the mobile phase. A gradient elution was performed as a linear gradient from 99.5% A (5mM HFBA, pH 4.2) and 0.5%B (acetonitrile) to 60% A and 40% B in 10 min and then held isocratic for 2 min, followed by a stepwise elution to 0% A and 100% B. The nitrogen gas flow rate for desolvation was at 10 L/min at 350°C, the nebulizer pressure at 25 psi, and the capillary voltage at 4000 V. DADMAC was quantified by SIM using its molecular ion (m/z 126.3).

3.4 General Screening of NDMA Formation Potential of SNF Polymers

3.4.1. Residual DMA in SNF Polymer Solutions

As DMA is directly used as a monomer in polyamine synthesis or as a starting compound in preparing monomer for polyDADMAC synthesis, the presence of residual DMA is expected in both polyamine and polyDADMAC solutions. The measured concentrations of residual DMA in the polymers solutions are shown in Table 3.4.1. A range of DMA concentration is shown because DMA measurement was conduced several times for each polymer. The DMA concentrations were divided by the corresponding concentration of active ingredient of polymer, yielding DMA concentration in μg DMA per mg polymer. As shown by the results, the Mannich polymer contained a large amount of residual DMA, likely due to the unstable tertiary amine function group at the end of pendent groups in this polymer. In contrast, cationic PAM (80% cationic) contained the lowest amount of residual DMA.

Table 3.4. 1 Residual dimethylamine concentrations in the polymer solution

Polymers	DMA [μg/mg]
Cationic PAM	0.04 - 0.14
PolyDADMAC	0.90 - 1.40
Polyamine	0.81 - 1.84
Mannich	5800 - 7800

3.4.2. NDMA Formation Potential Screening of SNF Polymers

The results of NDMA formation from cationic PAM, polyDADMAC, polyamine and Mannich polymer in the reactions with preformed monochloramine [MCA], free chlorine, chlorine dioxide and nitrite at pH 7.0 and 23 ºC for 24 hours are shown in Figure 3.3. As mentioned in Section 3.3.3, varying concentration of active polymer was used in these experiments, thus the measured NDMA concentration was divided by the corresponding polymer concentration, yielding NDMA concentration in ng NDMA per mg polymer active ingredient. The general trend of NDMA formation from the polymers is the order of Mannich polymer >> polyamine > polyDADMAC > cationic PAM, with particularly high level of NDMA from the Mannich polymer. Polyamine yielded more NDMA than polyDADMAC in the reactions with chlorine-based oxidants while polyamine and polyDADMAC produced similar amount of NDMA when they reacted with nitrite. Cationic PAM has the lowest potential of NDMA

formation as well as the least amount of residual DMA. A slightly higher level of NDMA formation was generally observed in the wastewater matrix than that compared to the DI water matrix except in the case of using both chlorine dioxide and nitrite for the reaction with polymers. Particularly, the increase was significant in the reaction with free chlorine.

Among the three chlorine-based oxidants and nitrite, monochloramine generally yielded a much higher level of NDMA than free chlorine, chlorine dioxide or nitrite. However, from the reaction with Mannich polymer did nitrite, chlorine dioxide and free chlorine also yielded significant levels of NDMA.

3.4.3. Effect of Reactant Dosage and Contact Time

Preliminary experiments on the effect of polymer dosage, monochloramine dosage and contact time on the formation of NDMA were also conducted in the screening studies. Overall, the trends were as expected that higher reactant dosage and longer contact time lead to higher NDMA formation potential as described further below.

As shown in Figure 3.4, the total molar concentration of NDMA increased with increasing polymer dosage. However, the polymer weight averaged NDMA yield (i.e., μg NDMA per mg polymer) actually decreased slightly with increasing polymer dosages. The molar concentration of DMA measured after reaction from different dosages of polymers is shown in Figure 3.5. In general, the DMA concentration was higher with higher dosage of polymer in use. Furthermore, higher DMA concentration was found after exposure to monochloramine for all of the four polymers, indicating that reaction of the polymers with monochloramine leads to release of more DMA from the polymers.

Figures 3.6 and 3.7 show that NDMA yield increased with extended monochloramine contact time (from 2 to 7 days) except for Mannich polymer, which had only slight increase in NDMA yield. A noticeable increase in DMA concentration with increasing monochloramine contact time was observed for the Mannich polymer, while only a slight increase was observed for cationic PAMS, polyDADMAC and polyamine polymers. When the polymers were exposed to two different monochloramine concentrations (4 and 8 mg/L as Cl_2) for the same contact time, both NDMA yield and DMA concentration were higher with the higher monochloramine dosage as shown in Tables 3.4.2 and 3.4.3.

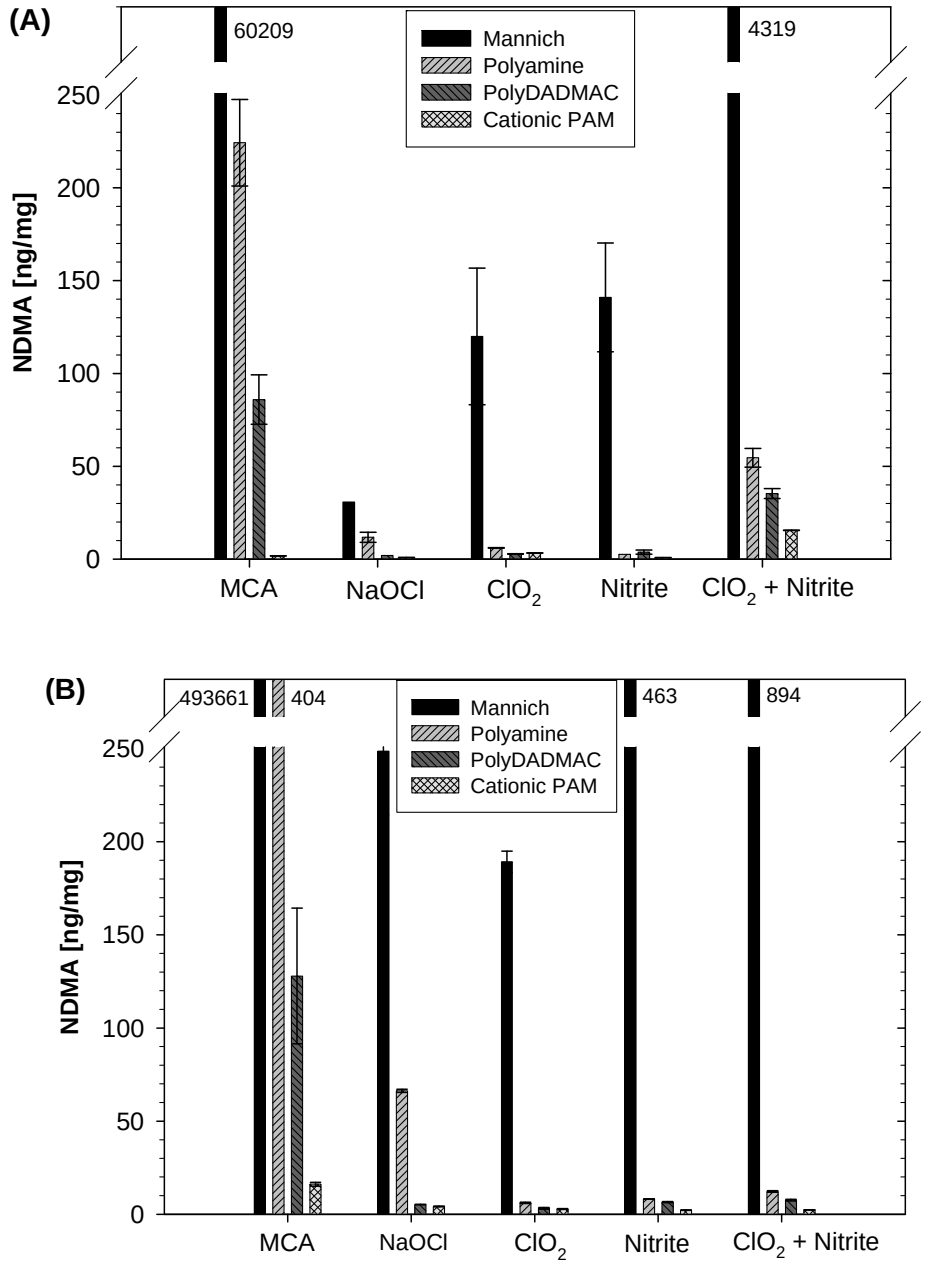


Figure 3. 3 (A) NDMA formation from polymers in reaction with oxidants and nitrite in DI water matrix: 23.58, 20.0, 9.94 and 0.88 mg/L active ingredient for cationic PAM, polyDADMAC polyamine; and, Mannich polymer, respectively, with preformed monochloramine (MCA) (10 mg/L as Cl_2), free chlorine (10 mg/L as Cl_2), chlorine dioxide (8 mg/L as Cl_2) or nitrite (20 mg/L) at pH 7.0 and 23 ºC for 24 hours. (B) Similar reactions but in a wastewater matrix.

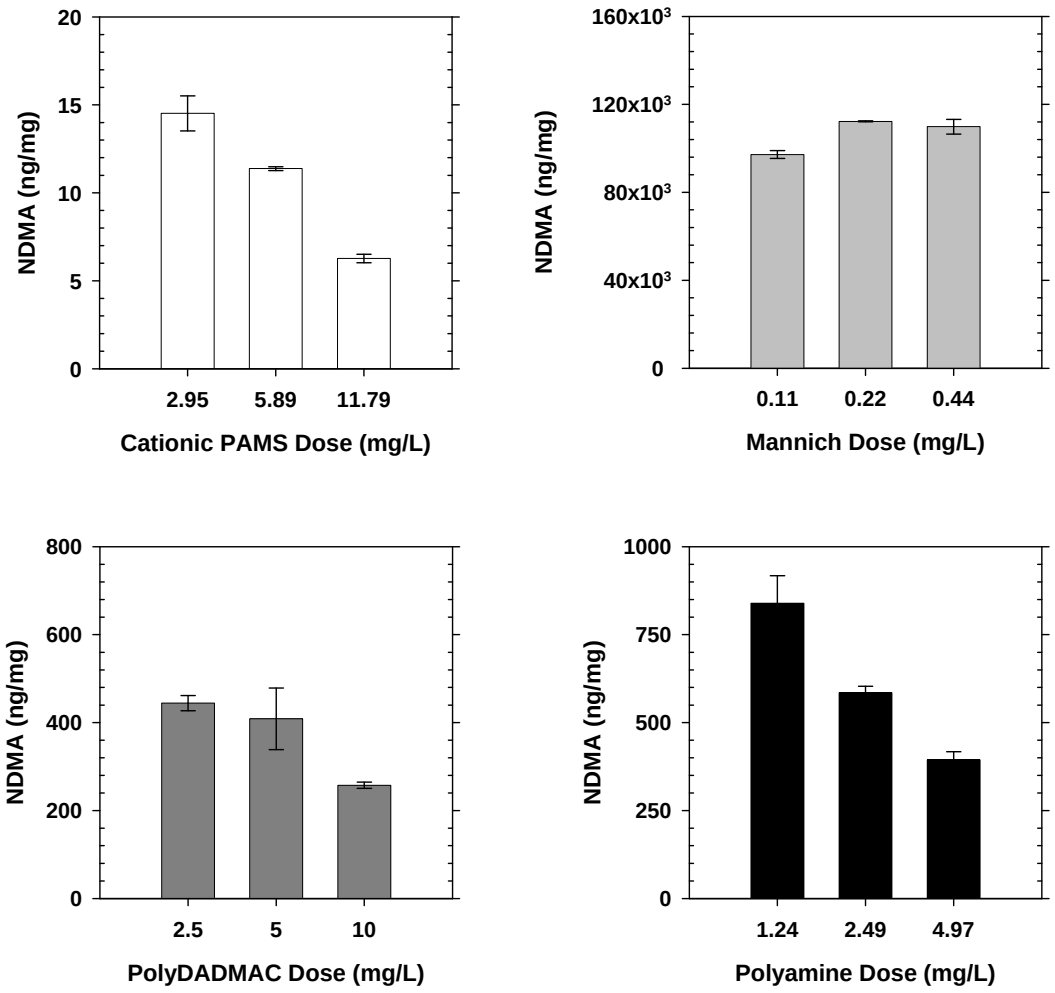


Figure 3. 4 Effect of polymer dosage on NDMA formation. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. The residual monochloramine was 2.3 - 2.8 mg/L (as Cl_2) after the reaction.

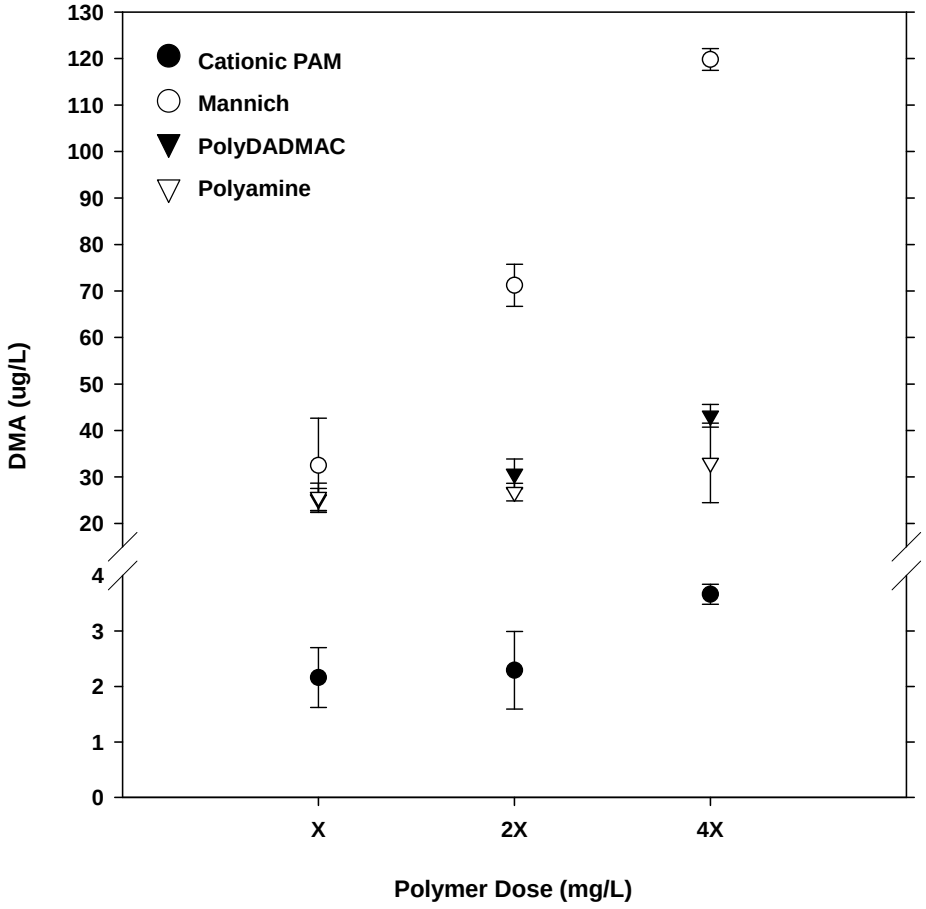


Figure 3. 5 Relationship of DMA concentration and polymer dosage after reaction with monochloramine. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2; pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer dosage x = 2.95, 0.11, 2.5 and 1.24 mg/L active for cationic PAM, Mannich, polyDADMAC and polyamine, respectively. The residual monochloramine was 2.3 - 2.8 mg/L (as Cl_2) after the reaction.

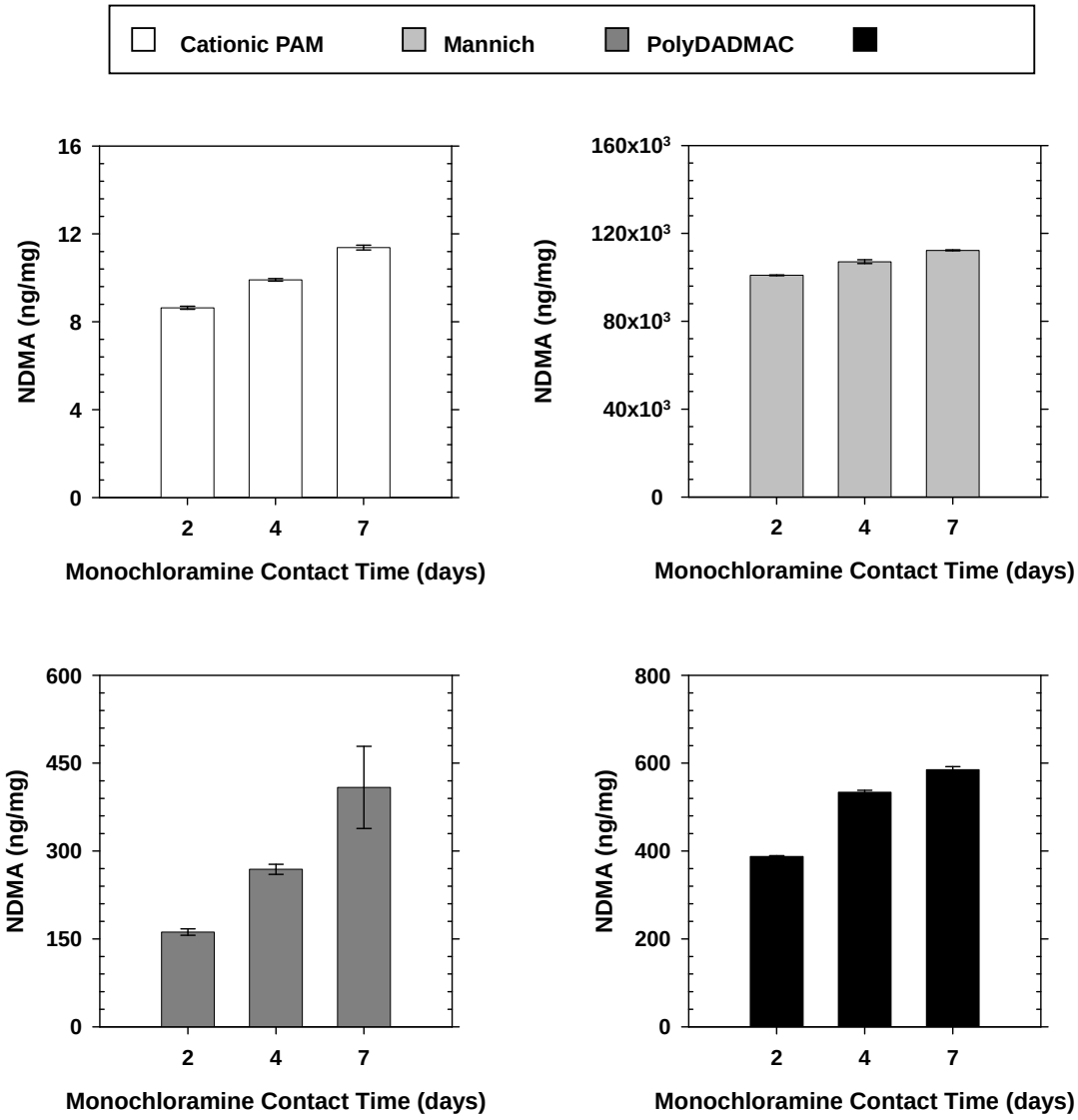


Figure 3. 6 Effect of monochloramine contact time on NDMA formation. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAM, Mannich, polyDADMAC and polyamine, respectively. The residual monochloramine in these tests was 2.1 - 2.8 mg/L (as Cl_2) after the reaction.

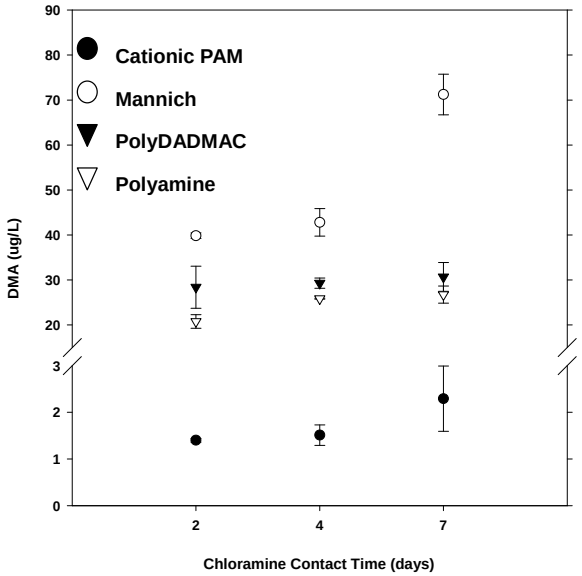


Figure 3. 7 Effect of monochloramine contact time on DMA concentration. Reaction conditions: initial [NH_2Cl] = 4 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAM, Mannich, polyDADMAC and polyamine, respectively. The residual monochloramine in these tests was 2.1 - 2.8 mg/L (as Cl_2) after the reaction.

Table 3.4. 2 Effect of monochloramine dosage on NDMA formation from the polymers. Reaction conditions: initial [NH_2Cl] = 4 and 8 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAM, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	**NDMA Yield (ng/mg polymer)**	
	[NH_2Cl] 4 mg/L as Cl_2	[NH_2Cl] 8 mg/L as Cl_2
Cationic PAM	11.38 ± 0.11	13.39 ±0.30
Mannich	> 112,000 ± 206	> 156,000 ± 24
PolyDADMAC	409 ± 70	598 ± 44
Polyamine	585 ± 18	968 ± 52

Table 3.4. 3 Effect of monochloramine dosage on DMA concentration from the polymers. Reaction conditions: initial [NH_2Cl] = 4 and 8 mg/L as Cl_2), pH = 8.6 (10 mM bicarbonate buffer), reaction time = 7 days, T = 23 ºC. Polymer concentration: 5.9, 0.22, 5 and 2.48 mg/L active for cationic PAM, Mannich, polyDADMAC and polyamine, respectively.

Polymer Type	**DMA concentration (µg/L)**	
	[NH_2Cl] 4 mg/L as Cl_2	[NH_2Cl] 8 mg/L as Cl_2
Cationic PAM	2.29 ± 0.70	2.98 ± 0.71
Mannich	71.2 ± 4.5	90.0 ± 0.2
PolyDADMAC	30.7 ± 3.2	34.9 ± 0.6
Polyamine	26.8 ± 1.9	37.2 ± 0.0

3.4.4. Effect of UV Exposure

The effect of UV irradiation on polymer's NDMA formation potential was investigated. In this study, each of the three polymer solutions (cationic PAM, polyDADMAC and polyamine) at the concentration of 1 g/L was first exposed to UV light for 24 hours. Note that unpurified cationic PAM and polyDADMAC samples and purified polyamine samples were used in these experiments (see more explanation later for polymer purification in Section 3.5.1). After UV exposure, the polymer solution was diluted with DI water to 10 mg/L and allowed to react with 10 mg as Cl_2/L of preformed monochloramine for 24 hours at pH 7.5 and 23°C.

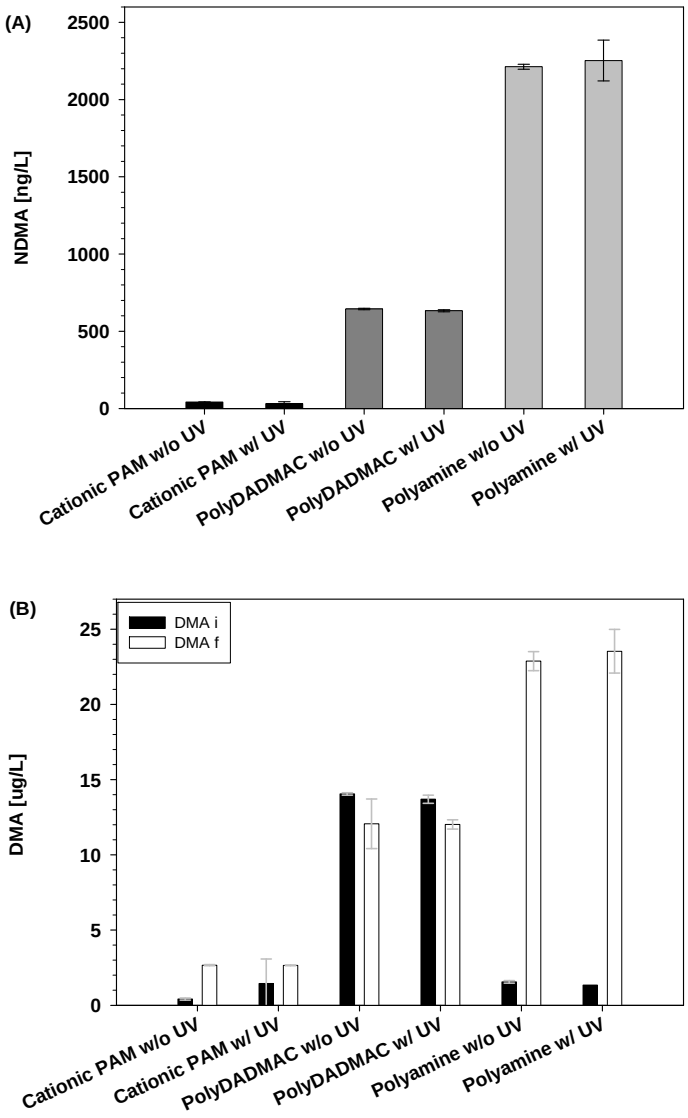


Figure 3. 8 Effect of UV irradiation on NDMA formation. 10 mg/L as active ingredient of polymers (with or without pre-exposure to UV light) were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

As shown in Figure 3.8, there was no apparent effect of UV irradiation on the polymers. No significant difference was observed in NDMA yield or DMA concentration with or without pre-exposure of polymers to UV light. Pre-exposure to UV light had negligible effect on the DMA concentration both before (DMA_i) and after (DMA_f) chloramination. This result confirms that UV irradiation does not induce polymer degradation to release DMA nor weaken the polymers' structure to be more susceptible to degradation by chloramines attack.

3.4.5. Discussion

One main reason for the exceptionally high level of NDMA formation from the Mannich polymer compared to the other polymers (Figure 3.3) is the presence of a much higher level of residual DMA in this polymer solution (see Table 3.4.1). The high level of DMA residues is likely due to reversible Mannich reaction during storage, resulting in possible polymer degradation and release of DMA (Scheme 2.4). Moreover, the Mannich polymer is likely more easily degraded during reactions with the oxidants due to its unstable tertiary amine group resulting from the Mannich reaction compared to the quaternary ammonium group present in the other polymers. As a result, a much higher level of NDMA was formed from the Mannich polymer.

The results showed that polyamine yielded more NDMA than polyDADMAC in the reactions with chlorine-based oxidants (i.e., MCA, NaOCl and ClO_2) (Figure 3.3) irrespective of the similar residual DMA concentration in both polymer solutions (see Table 3.4.1), indicating that initial DMA present in the polymer solution does not necessarily determine the NDMA formation level. The different NDMA formation potentials seem to relate more to the different structures of the two polymers. As shown in Schemes 2.1 and 2.2, the DMA-based moieties in polyamine and polyDADMAC are most probable candidates for NDMA precursors and such moieties may be released as a result of polymer degradation during reaction with strong oxidants. It is likely that the structural difference in the two polymers causes different degrees of polymer degradation and thus different amounts of NDMA formation. In contrast to the chlorine-based oxidants, nitrite yielded similar amounts of NDMA from these two polymers (Figure 3.3). One possible explanation is that nitrite cannot cut off polymer chains like chlorine-based oxidants, which prevents the release of NDMA precursors such as DMA from the polymer chains. Thus, NDMA formation potential depended primarily on the initial DMA residues in the polymer solution, which were similar between polyamine and polyDADMAC.

The lowest amount of NDMA formation was from cationic PAM (80% cationic) (Figure 3.3). This is probably a result of both very low residual DMA and the structure of this polymer. In the synthesis of cationic PAM (Scheme 2.3), DMA is not directly used in the polymerization or in monomer preparation which may explain cationic PAM's lowest amount of residual DMA among the four polymers. Another possible reason for the lowest NDMA formation potential may be due to the presence of noncationic polyacrylamide functional group [$-CONH_2$] in cationic PAM. The $-CONH_2$ linkage should be more susceptible to electrophilic attack or chlorine transfer of the oxidants than quaternary ammonium linkage [$-N^+(CH_3)_3$] present in all polymers due to the pair of unshared valence electrons on the nitrogen atom. Thus, oxidants like monochloramine can be consumed by the noncationic polyacrylamide part even though it accounts for only 20% of the

total polymer structure. As a result, less oxidant is available for reacting with the cationic DMA-based moiety of the polymer to generate NDMA.

Furthermore, the overall tendency of much higher NDMA formation potential with monochloramine than with free chlorine, chlorine dioxide or nitrite (Figure 3.3) is in good agreement with previous studies by other researchers (Choi and Valentine, 2002a; Mitch and Sedlak, 2002b). Monochloramine is the most efficient NDMA generator compared to other chlorine-based disinfectants and nitrite because monochloramine undergoes the unsymmetrical dimethylhydrazine [UDMH] pathway which is much more favorable than *N*-nitrosation pathway (Mirvish, 1975) for NDMA formation at circumneutral pH. In the case of Mannich polymer, high NDMA formation was also observed with nitrite addition (Figure 3.3). This is likely due to the high DMA concentration in Mannich polymer solution that renders formation of NDMA via *N*-nitrosation mechanism still significant even at circumneutral pH. Moreover, previous studies have reported *N*-nitrosation at circumneutral to alkaline pH may be enhanced by the presence of formaldehyde (Keefer and Roller, 1973). Such enhancement may be in work here since reverse Mannich reaction yields formaldehyde in the solution.

Lastly, the result of more NDMA formation from the wastewater matrix (Figure 3.3) is also consistent with expectation since the wastewater matrix contains other constituents such as natural organic matter that may also behave as NDMA precursors in the sample, adding to the overall amount of NDMA formed. Notably, NDMA formation from particularly polyamine and Mannich polymers in the reaction with free chlorine in wastewater matrix is remarkably higher than that in DI water matrix. This result may be due to the existence of ammonia in wastewater which can produce the efficient NDMA generator monochloramine *in situ* from the reaction with free chlorine.

3.5. Probing Mechanisms of NDMA Formation from Polyamine and PolyDADMAC

The Section 3.4 shows that the cationic PAM, polyDADMAC, polyamine, and Mannich polymers from SNF are all potential NDMA precursors, although at different tendencies and that the polymers appear to degrade and release DMA in reaction with chlorine-based oxidants. In this section, more experiments were conducted to probe the NDMA formation mechanisms from SNF polymers, with particular emphasis on polyDADMAC and polyamine. These two polymers were particularly targeted because they are commonly applied in potable water treatment and thus of higher urgency to evaluate the potential risk associated with them. To probe the reaction mechanisms involved in the formation of NDMA from polyDADMAC and polyamine during chloramination, systematic studies were conducted to evaluate the effect of polymer purification, the effect of polymer molecular weight [MW] and structure, the role of polymer synthetic intermediate compounds, and the effect of solution pH.

3.5.1 Effect of Polymer Solution Purification

Because polymer solutions contain residual DMA (Table 3.4.1) as well as other impurities including monomers, oligomers, intermediate compounds, catalysts, etc., removing the residues from the polymers allows discerning the relative contribution of polymer itself versus the

residues to the overall NDMA formation potential. Polymer samples were purified by either solvent precipitation or by dialysis to remove low MW impurities such DMA and oligomers. The MW cut-off for the dialysis membranes was 6,000-8,000 Dalton and salt was used for some polymer samples to increase the efficiency of dialysis. The purified polymer solutions were then tested for NDMA formation potential using conditions similar to those described in Figure 3.8.
As shown in Figure 3.9 (purification by precipitation) and Figure 3.10 (purification by dialysis), the amount of initial DMA (i.e., DMA_i) was effectively reduced in the purified polymer solutions, especially to less than 1 μg/L in 10 mg/L polymer solution when dialysis was used. Compared to the unpurified samples, NDMA formation potential was also decreased. This is because the purification process removes DMA as well as other oligomers which are NDMA precursors in the polymer solutions. However, despite lower DMAi, the NDMA formation potential of the polymers was not eliminated by polymer purification. Significantly, a considerable amount of DMA was still released from the polymers as seen by the DMA concentration measured after the reaction (i.e., DMA_f) to levels almost comparable to those in unpurified polymers. This result strongly indicates the occurrence of polymer degradation and that leads to DMA release.

The inserted graph in Figure 3.10A shows NDMA formation from the reaction of 1 – 50 μg/L DMA with preformed monochloramine under conditions similar to those used for polymer samples. Note that the DMA concentrations employed here were within the similar range of DMA_i found in the polymer samples. Evidently, the levels of NDMA formed from the DMA precursor were orders of magnitude lower than those from polymers. In other words, DMA_i plays a rather minor role in the polymer's NDMA formation potential.

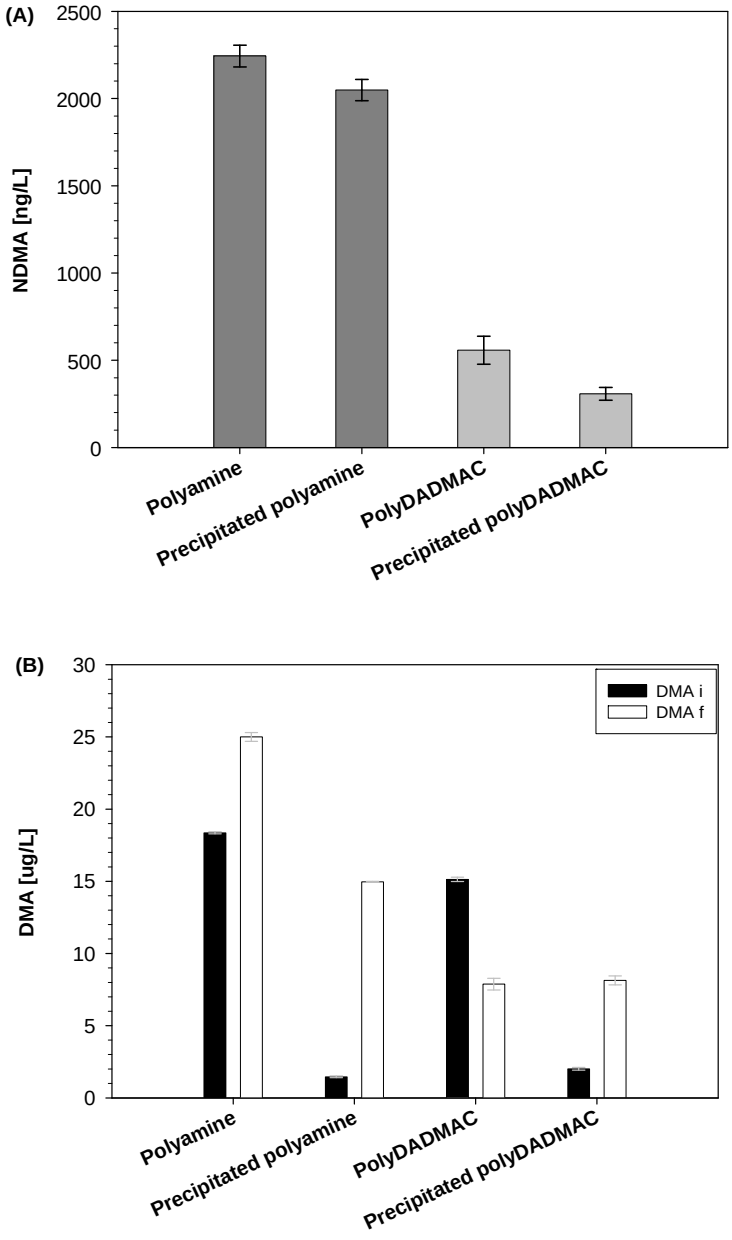


Figure 3. 9 Effect of polymer purification (by precipitation) on NDMA formation. 10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

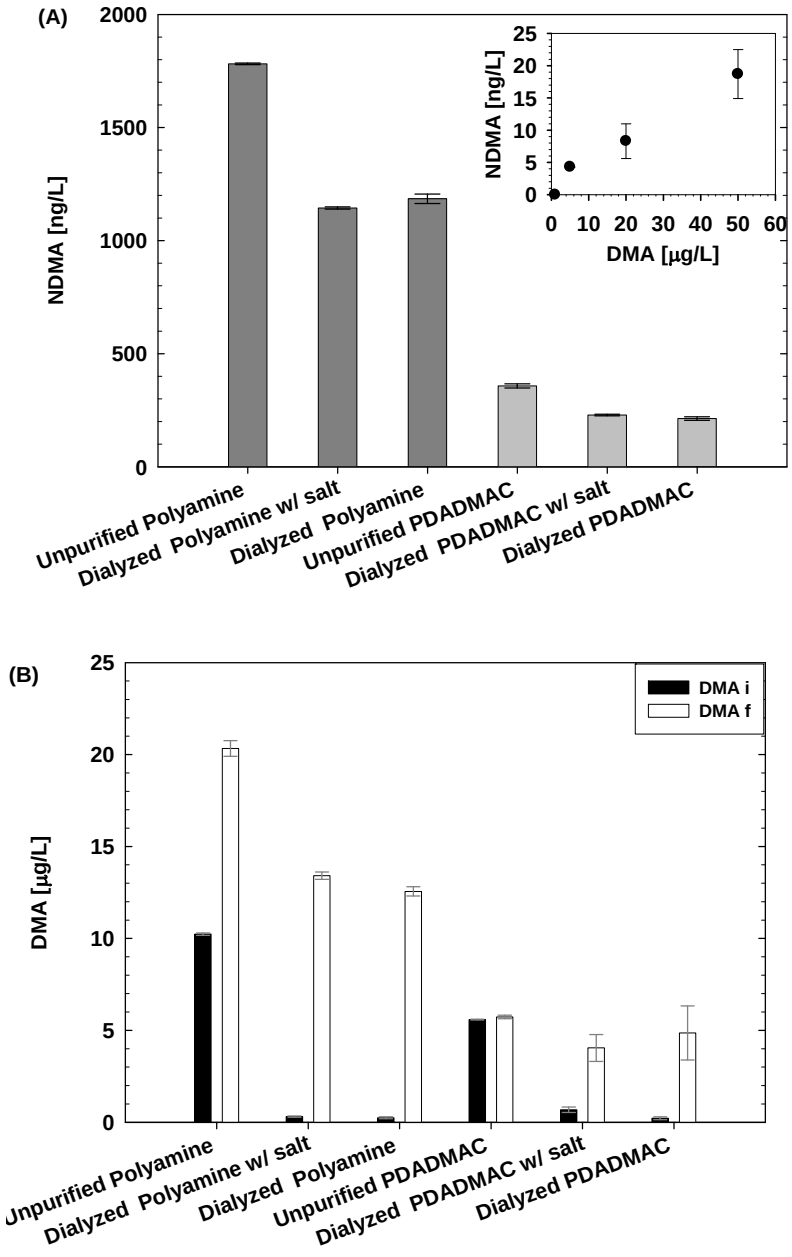


Figure 3. 10 Effect of polymer purification (by dialysis) on NDMA formation. Reaction conditions the same as those in Figure 5.2. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction. Inserted graph in (A) shows NDMA formation from the reaction of 1 – 50 µg/L DMA with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C.

3.5.2. Effect of Polymer Molecular Weight

Polyamine and polyDADMAC were prepared at several different MW ranges and evaluated for the impact on NDMA formation potential. This investigation allows evaluation of the role of polymer chain ends versus polymer backbone in the overall NDMA formation potential. For the same mass of a certain polymer, polymers with lower MW are of shorter chain length and thus contain a greater number of chain ends compared to polymers of higher MW and longer chain length.

As shown in Figure 3.11, the Lowest MW polyamine sample yielded the highest amount of NDMA as well as the highest DMA concentration (both DMA_i and DMA_f). The particularly high DMA_i (i.e., initial residual DMA) in this sample is likely due to shorter polymerization time to reduce the degree of polymerization in making the lowest MW polyamine. The Low MW and High MW samples did not differ greatly, with DMA_f a little higher for the Low MW polyamine. The DMA concentration for all polyamine samples was increased after chloramination, while almost the same DMA concentration was observed in polyDADMAC before and after chloramination. The high NDMA yield of the Lowest MW polyamine sample could be the result of several factors including high initial DMA impurity and more tertiary amine chain ends in the polyamine solution and will be discussed further in Section 3.5.6.

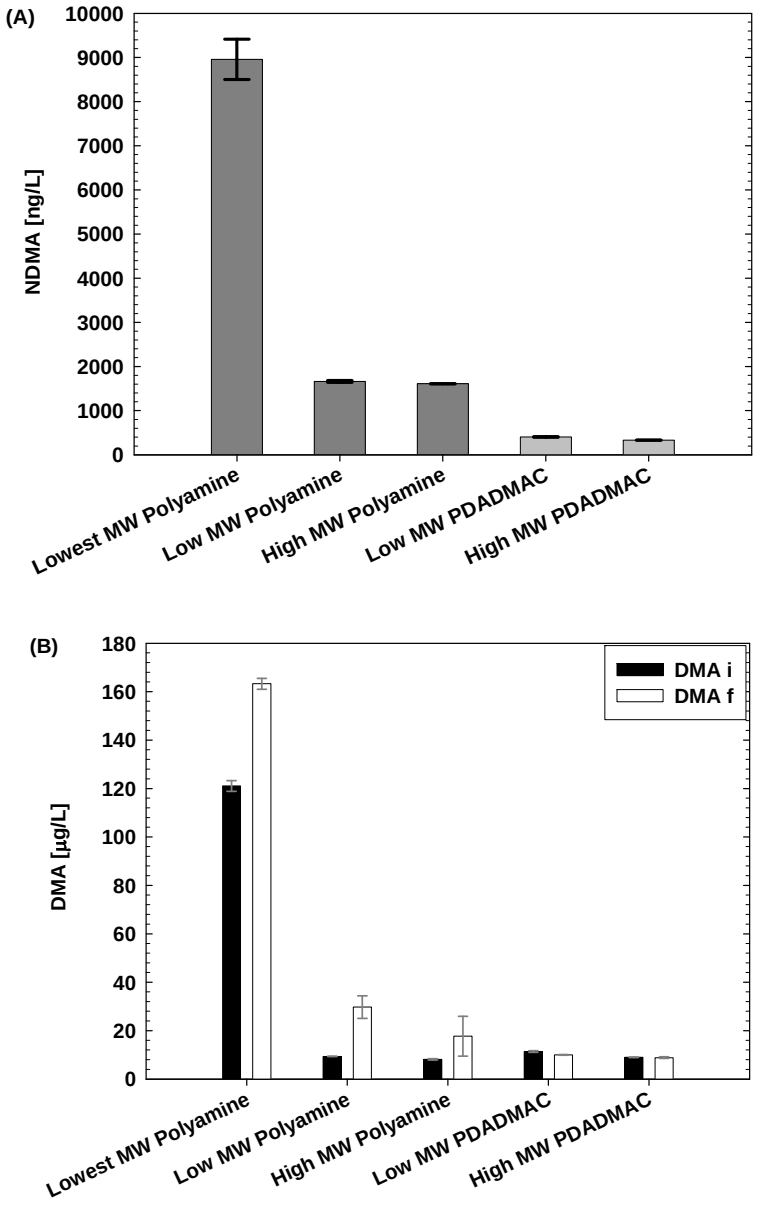


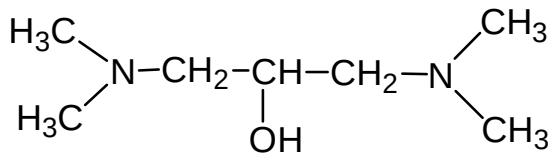
Figure 3. 11 Effect of polymer molecular weight on NDMA formation. Reaction conditions the same as those in Figure 3.4. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

3.5.3. Investigation of Polymer Intermediate Compounds

3.5.3.1. DMA-epi-DMA, ADMA, and DADMAC

To further elucidate the effect of polymer structural moieties and other potential residues in the polymer solutions on the overall NDMA formation potential, three model compounds representing intermediate compounds during synthesis of polyamine and polyDADMAC were investigated. The model compound DMA-epichlorohydrin-DMA (DMA-epi-DMA) (Figure 3.12) was investigated for the case of polyamine. DMA-epi-DMA is the DMA-epichlorohydrin

intermediate compound shown in Scheme 2.1 condensed with another DMA molecule. The intermediate compounds allyldimethylamine [ADMA] and DADMAC monomer, both structures shown in Scheme 2.2, were investigated for the case of polyDADMAC.



DMA-epichlorohydrin-DMA

Figure 3. 12 Structure of DMA-epi-DMA.

As shown in Figure 3.13A, DMA-epi-DMA formed significantly more NDMA than polyamine and than, polyDADMAC, and polyDADMAC's model compounds. This result indicates that the chain ends of polyamine are responsible for NDMA formation since DMA-epi-DMA represents an extreme case of a short-chain polyamine. PolyDADMAC's model compound ADMA formed the second highest amount of NDMA, higher than both polyDADMAC and polyamine. This result further confirms that DMA-based chain ends are a significant source of NDMA formation. Notably, both DMA-epi-DMA and ADMA released much more DMA than the polymers (Figure 3.13B). In contrast, DADMAC monomer formed the least amount of NDMA among all of the tested samples. DADMAC monomer also showed much lower levels of DMA_i and DMA_f, suggesting that monochloramine does not degrade DADMAC monomer to yield the release of DMA. A DADMAC monomer stability test was conducted by using higher monochloramine concentration (20 mg as Cl_2/L) and monitoring DADMAC concentration change during chloramination over time by LC/MS. After exposing 50 μM (6.3 mg/L) of DADMAC to 20 mg as Cl_2/L of preformed monochloramine for three days, 90% of DADMAC still remained in the solution (Figure 3.14). The allyl functional groups of DADMAC were found to be rather unreactive to monochloramine.

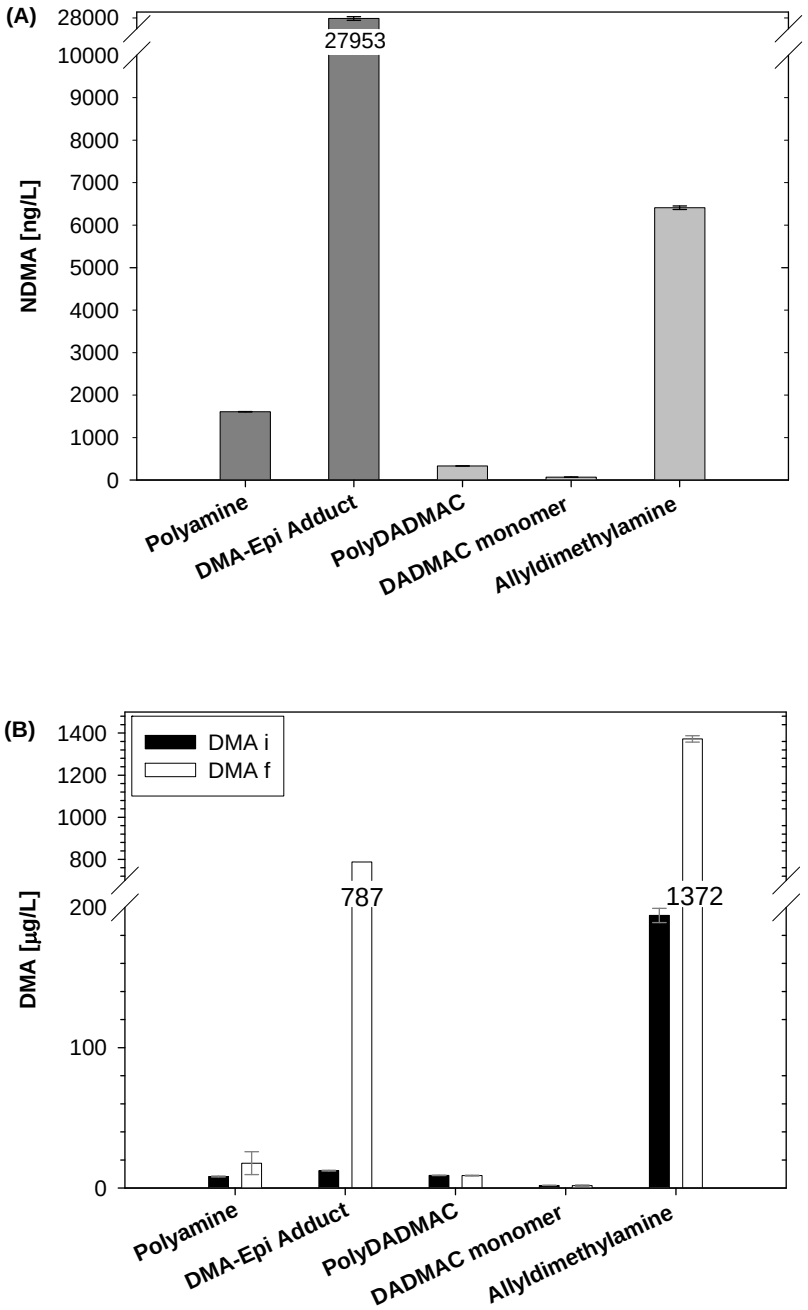


Figure 3. 13 NDMA formation potential of intermediate compounds. 10 mg/L of DMA-epichlorohydrin-DMA, allyldimethylamine, polyamine and polyDADMAC were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

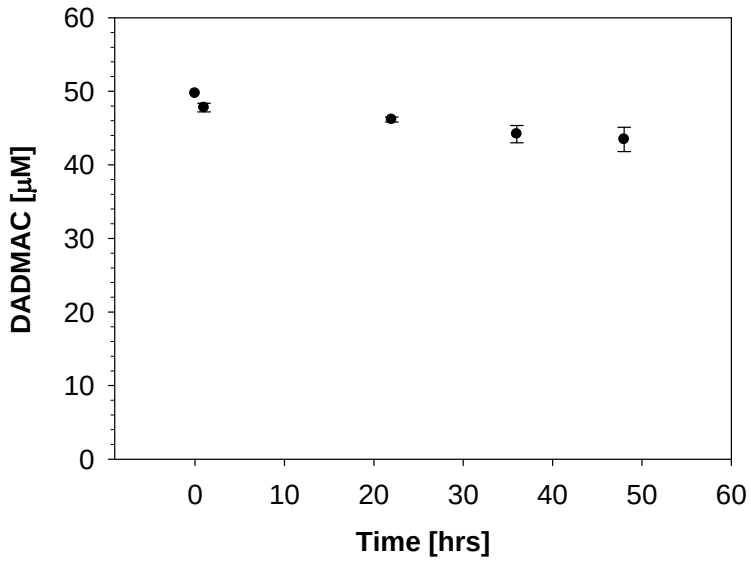


Figure 3. 14 Monitoring DADMAC concentration under monochloramination. 50 μM (6.3 mg/L) of DADMAC were reacted with 20 mg as Cl_2/L of preformed monochloramine for 36 h at pH 7.5 and 23°C.

3.5.3.2. PolyDADMAC synthesized with ADMA-spiked DADMAC

Previous results indicate that ADMA could be a major contributor to polyDADMAC's NDMA formation potential. Therefore, several polyDADMACs were synthesized with ADMA-spiked DADMAC to evaluate whether increase of ADMA in the synthesis would lead to higher NDMA formation potential. In general, the more ADMA-spiking in the synthesis of polyDADMAC, the more NDMA was formed despite that the degree of increase was not very significant (Figure 3.15). In addition, DMA_i and DMA_f were not proportional to the amount of ADMA spiked into DADMAC. Instead, they were roughly the same among the four different polyDADMACs.

3.5.4. Effect of pH

The effect of pH was evaluated by conducting NDMA formation tests at the pH range of 5 – 9 for both polyamine and polyDADMAC. Dialyzed polymer samples were used in this case to minimize potential interference of low MW impurities such as DMA on the pH dependency. The amount of NDMA formed and DMA measured at the end of the reaction are shown in Figure 3.16. NDMA formation was maximized at pH near 8 in both polyamine and polyDADMAC solutions. DMA concentration measured at the end of reaction had a trend (highest at pH 8) similar to NDMA formation throughout the pH range in the case of polyamine. However, DMA concentration in polyDADMAC appeared to be comparable from pH 6 to 8, but lower at pH 5 or 9, different from the pH trend observed for NDMA formation.

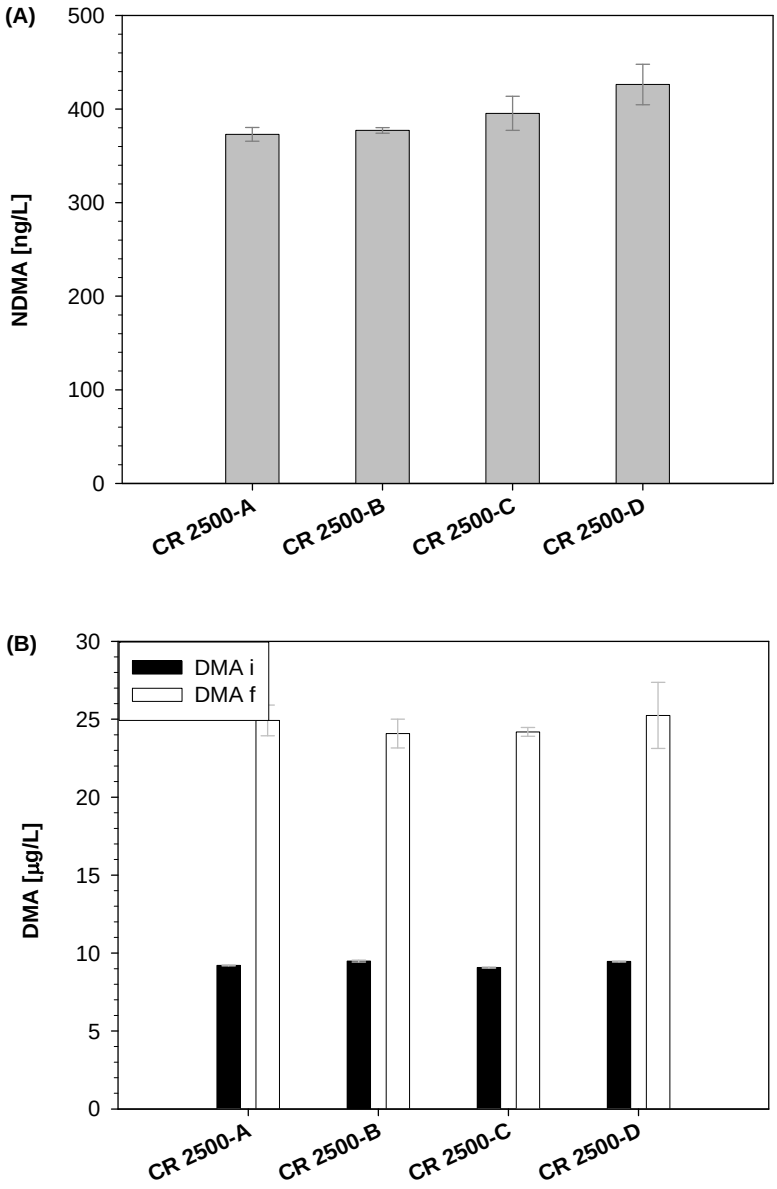


Figure 3. 15 NDMA formation potential of polyDADMAC made of ADMA-spiked DADMAC. 10 mg/L as active ingredient polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. The polyDADMAC was synthesized with DADMAC that was spiked with 0 ppm (CR 2500-A), ~500 ppm CR (2500-B), ~5000 ppm CR (2500-C) or ~20000 ppm (CR 2500-D) of ADMA. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

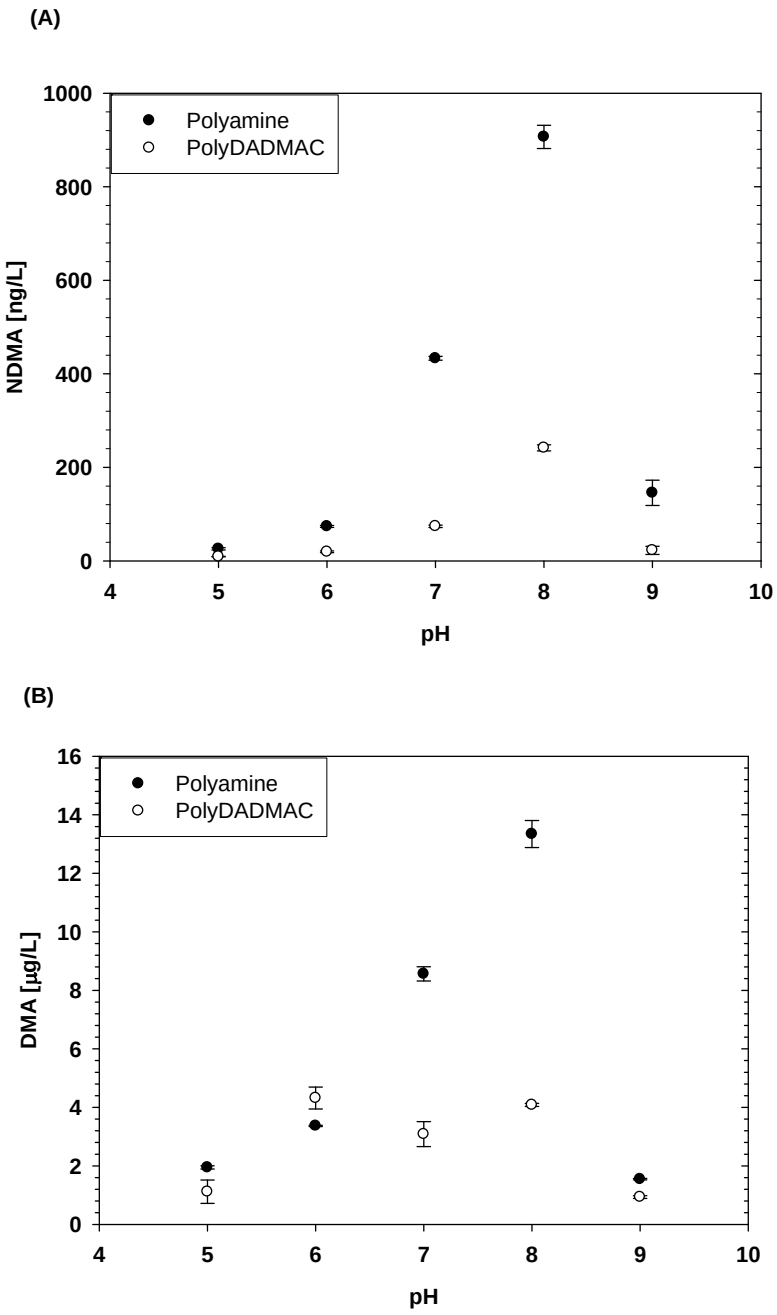


Figure 3. 16 Effect of pH on NDMA formation from polymers. 10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 hrs at the pH range of 5-9 and 23 °C. 10 mM buffers of acetate for pH 5, phosphate for pH 6, 7, and 8, and borate for pH 9 were used. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured at the end of reaction (DMA_f).

3.5.5. Kinetics of NDMA and DMA Formation from SNF Polymers

Kinetic studies were conducted for up to 144 hours using the same reaction conditions as previous NDMA formation tests in order to observe NDMA formation and DMA concentration variation during the initial 24 hours and beyond. The residual monochloramine concentration was

determined to be 5.8 mg as Cl_2/L in polyamine solution and 7.2 mg as Cl_2/L in polyDADMAC solution at the end of 144 hours of reaction time. As shown in Figures 3.17A and 3.18A, NDMA formation in both polyamine and polyDADMAC solutions increased continuously during the 6 days of exposure to monochloramine, and the formation potential did not appear to be exhausted after 6 days although the formation rate became slower after 5 days. In contrast, the DMA concentration change was more complex. For polyamine, DMA concentration increased continuously in the first 24 hours and decreased afterwards except for a second maximum at about 72 h (Figure 3.17B). For polyDADMAC, DMA concentration fluctuated even more along the exposure time and at a lower concentration in general than that in polyamine solution (Figure 3.18B).

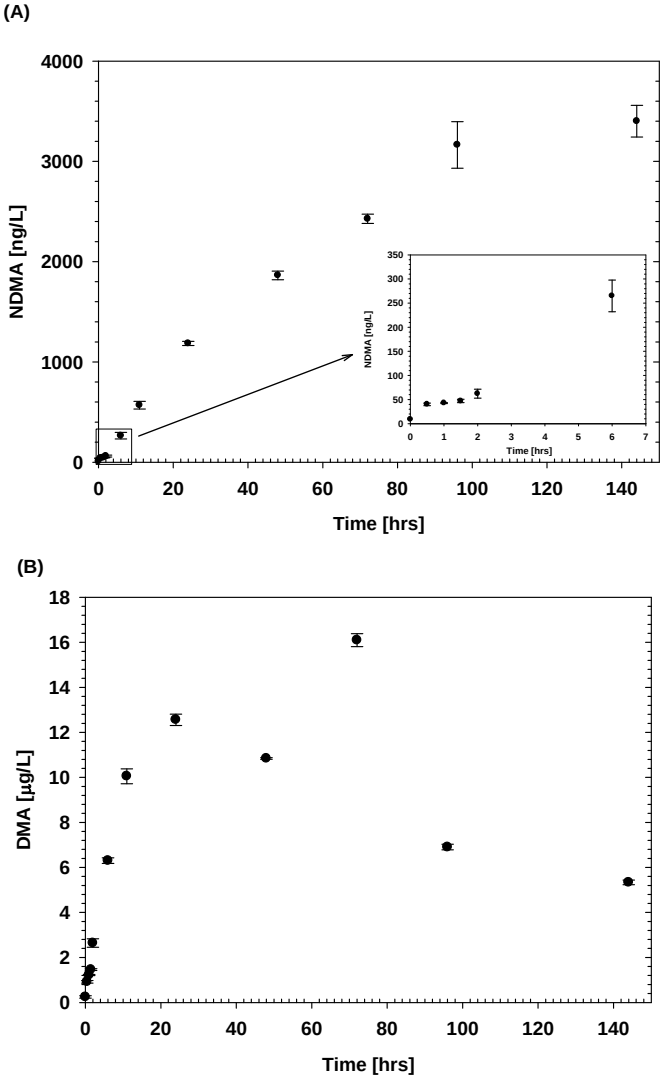


Figure 3. 17 NDMA formation and DMA measurement as a function of time. 10 mg/L as active ingredient of purified polyamine were reacted with 10 mg as Cl_2/L of preformed monochloramine for 0 - 144 h at pH 7.5 and 23 °C. (A) NDMA formation; and, (B) DMA measurement from polyamine as a function of time.

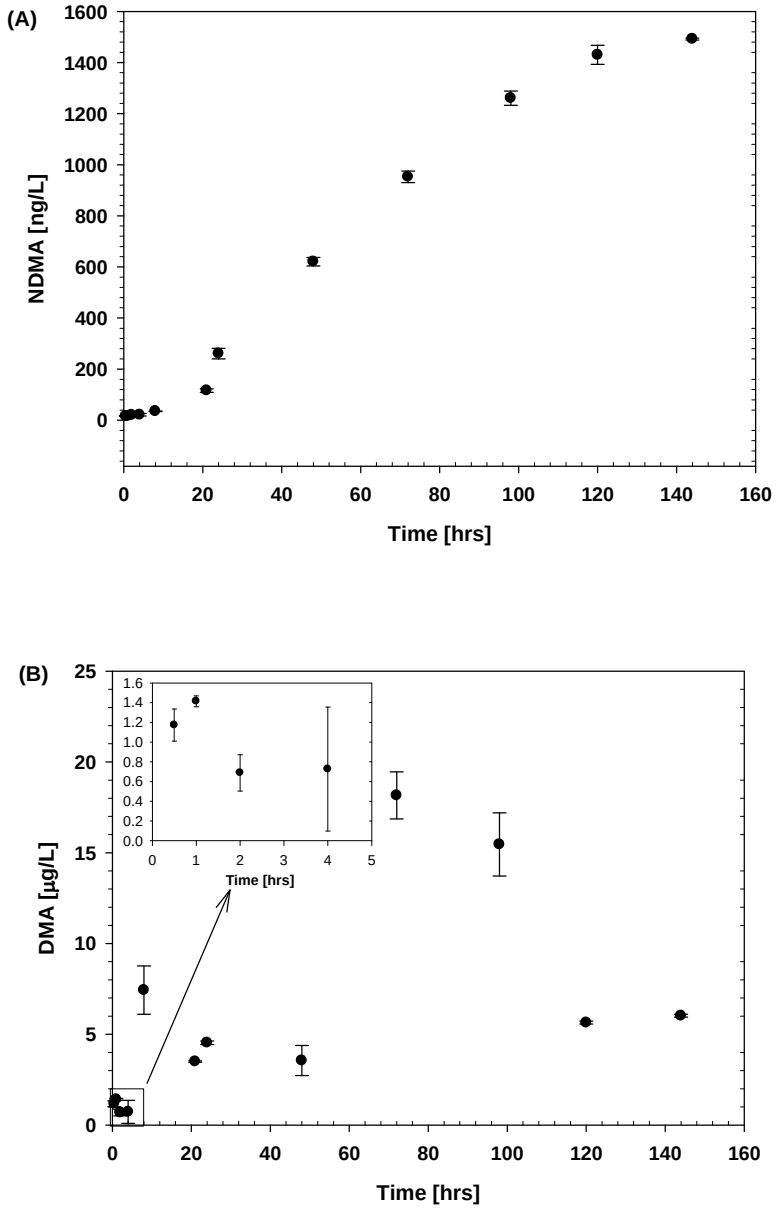


Figure 3. 18 NDMA formation and DMA measurement as a function of time. 10 mg/L as active ingredient of purified polyDADMAC were reacted with 10 mg as Cl_2/L of preformed monochloramine for 0 - 144 h at pH 7.5 and 23 °C. (A) NDMA formation from polyDADMAC, and (B) DMA measured in polyDADMAC.

3.5.6. Discussion

Polymer Degradation and DMA release. It is evident that reaction of polyamine and polyDADMAC with monochloramine results in polymer degradation and release of DMA from the polymers. This is clearly demonstrated by the increase of DMA concentration after monochloramination (i.e., DMA_f versus DMA_i) in many cases (Figures 3.9-3.11 and 3.15) and particularly in the studies involving purified polymer samples (Figure 3.9 and 3.10), because if

polymers did not degrade and release DMA, the DMA concentration would have decreased due to oxidation by monochloramine to yield NDMA and other products. The results of IR and Raman analysis of high dosages of polymers after monochloramination also support polymer degradation with structural change evidence such as leaving of $-N(CH_3)_2$ group and ring opening in polyDADMAC, and cleavage of CH_2-N bond and polymer backbone change in polyamine (results shown in Chapter 4). Polyamine appears to be more easily degraded than polyDADMAC in terms of DMA release (Figures 3.9-3.11). Furthermore, the degradation of polyamine depends significantly on polymer molecular weight: polyamine of lower MW is more susceptible to degradation than polyamine of higher MW. In contrast, polymer MW does not have significant impact on the degradation of polyDADMAC (Figure 3.11). The difference between these two polymers can be explained by their structures and is discussed further in the next section.

Since DMA is a good NDMA precursor, residual DMA initially present in the polymer solution [DMA_i] and new DMA released from polymer degradation (related to DMA_f) will impact the overall NDMA formation potential of the polymers. The measured DMA_f reflects the sum of initial DMA, newly released DMA and loss of DMA by reaction with chloramines within the selected time period. The results with purified polyamine samples show that the solution's DMA_i could only account for a very small fraction of the total NDMA that was formed (Figure 3.10A and Section 5.2.1). If normalizing the molar concentration of NDMA formed by the molar concentration of DMA_i or DMA_f for the range of experiments that were conducted, a much more consistent NDMA to DMA molar ratio is obtained with DMA_f than with DMA_i (Table 3.5.1), indicating that NDMA formation correlates much more strongly to DMA_f than with DMA_i. In other words, NDMA formation potential depends more strongly on released DMA by polymer degradation than on the initial residual DMA in the polymers.

Table 3.5. 1 Calculated molar ratio of NDMA and DMA

Polymer type	**Molar Ratio (in %)**	
	NDMA/DMA_i	**NDMA/DMA_f**
Lowest MW polyamine	4.5	3.3
Low MW polyamine	10.8	3.4
High MW polyamine	12.0	5.5
Low MW polyDADMAC	2.2	2.5
High MW polyDADMAC	2.3	2.3
Undialyzed Polyamine	10.6	5.3
Dialyzed polyamine w/o salt	291.4	5.7
Dialyzed polyamine w/ salt	229.4	5.2
Undialyzed PolyDADMAC	3.9	3.8
Dialyzed polyDADMAC w/o salt	58.6	2.7
Dialyzed polyDADMAC w/ salt	20.5	3.4

Note: NDMA formation tests were conducted under the same conditions for all of the polymer types.

The importance of polymer degradation and released DMA on polymers' overall NDMA formation potential is also supported by the results of pH effect experiments. As shown in Figure 3.16, NDMA formation in both polyamine and polyDADMAC was maximized at near pH 8 but lower at either higher or lower pH, consistent with the pH dependence of NDMA formation from DMA under chloramination conditions reported by previous studies (Mitch and Sedlak, 2002a). Furthermore, the results also show that, in general, at the pH values where higher NDMA formation was observed, higher DMA concentration measured at the end of chloramination was also found. These results suggest that degradation of polymer and formation of NDMA are both most significant at circumneutral pH range that is commonly encountered in water and wastewater treatment plants.

The kinetic study indicates that NDMA formation from the polymers has slow kinetics and the reactions can continue for many days and continue to release NDMA (Figures 3.17 and 3.18). Similarly slow kinetics were also reported for NDMA formation from reaction of DMA with monochloramine (Mitch and Sedlak, 2002a). The complicated trend of DMA_f over time is most likely results from the different rate of oxidation of DMA by chloramines, oxidation of polymers by chloramines, degradation of polymer to release DMA, and decay of chloramines.

Effect of Polymer Structures. In regard to DMA-based moieties on the polymers as NDMA precursors, polyamine has tertiary amine [$–N(CH_3)_2$] chain ends and quaternary ammonium groups [$–N^+(CH_3)_2$-] along the backbone, while polyDADMAC has quaternary ammonium groups [$–N^+(CH_3)_2$-] in a ring structures along the polymer chain. Some chain ends of polyDADMAC are capped by the initiator radical (e.g., persulfate) used in the polymerization process (Figure 3.19). For reaction with chloramines, tertiary amine groups are expected to be more reactive than quaternary ammonium groups because tertiary amines have less steric hindrance and, even if protonated, can loose the positive charge via reversible deprotonation, both favorable for electrophilic attack by chloramine oxidants. In contrast, the greater steric hindrance and permanent positive charge on the nitrogen of quaternary ammonium groups are less favorable for chloramine attack. In terms of releasing DMA, tertiary amine groups are also expected to have a higher tendency than quaternary ammonium groups because tertiary amine groups require breaking only one C-N bond to release DMA while quaternary ammonium groups require breaking two C-N bonds.

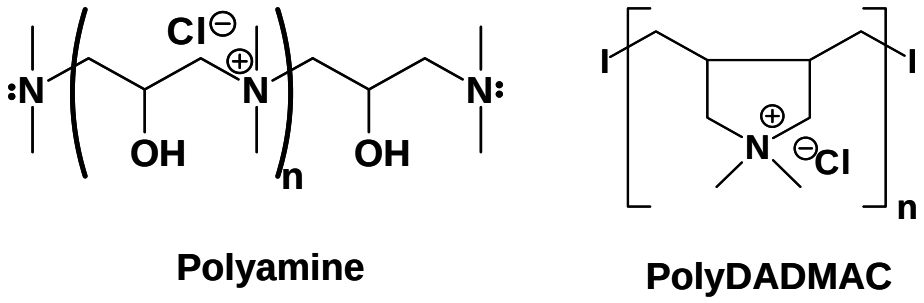
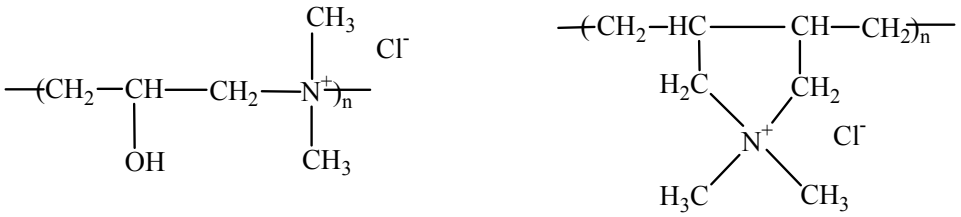


Figure 3. 19 Repeating units of polyamine and polyDADMAC, respectively.

On the same mass basis, polyamines of lower MW have shorter chain length and thus a greater number of total tertiary amine chain ends than polyamines of higher MW. The model intermediate compound DMA-epi-DMA (Figure 3.12) represents an extreme case of short-chain polyamine that contains only the tertiary amine chain ends. The results that DMA-epi-DMA releases a large amount of DMA and yields very high NDMA formation (Figure 3.13), and that lower MW polyamines generate more DMA and NDMA (Figure 3.11) suggest the significant role of tertiary amine chain ends in the NDMA formation potential of polyamines. These results also point to the greater susceptibility of lower MW polyamines to degradation during chloramination due to the greater number of vulnerable tertiary amine chain ends. It is also worthwhile to point out that purification of polyamines decreases the NDMA formation potential (Figures 3.9 and 3.10). This is mostly due to removal of low MW polyamine oligomers that are potent NDMA precursors for the above reasons and the amount of DMA decreased (from tens of μg/L to <1 μg/L) would only lead to less than 10 ng/L of NDMA formation decrease and that is inadequate to explain the magnitude of almost 600 ng/L of NDMA formation decrease that was observed.

For polyDADMAC, the model intermediate compound ADMA yields significant NDMA formation and DMA release (Figure 3.13). Since ADMA also contains a tertiary amine end (see Scheme 2.2), this result further confirms the significant potential of tertiary amine groups for NDMA formation. In contrast, the DADMAC monomer has little NDMA formation or DMA release potential (Figure 3.14). The very low NDMA formation potential of DADMAC monomer can be attributed to its cationic charge and greater steric hindrance on the quaternary ammonium nitrogen, which hinder electrophilic attack of monochloramine. For polyDADMACs synthesized with ADMA-spiked DADMAC, NDMA formation increases only slightly with more spiked ADMA. This NDMA formation potential increase becomes significant only when a relatively high spiking concentration of ADMA is used (Figure 3.15). Such result is not surprising since most of the spiked free ADMA is incorporated into polyDADMAC during polymerization process. Only when a relatively high concentration of ADMA is used, the amount of residual ADMA may become appreciable.

Based on the above discussion on tertiary amine group versus quaternary ammonium group, the fact that polyamine consistently exhibits higher NDMA formation potential and more DMA release than polyDADMAC in all of the experiments agrees well with the reasoning. If the repeating unit or monomer is broken off from the polymer backbone during chloramination, DMA or DMA-epichlorohydrin would be released from polyamine while DADMAC would be released from polyDADMAC. This leads to a significant difference in NDMA formation potential for the two polymers since DMA and DMA-epichlorohydrin are very efficient NDMA precursors while DADMAC monomer is not. A second possible reason for the lower NDMA formation potential of polyDADMAC than polyamine is that polyDADMAC has a lower mass fraction of DMA moiety per repeating unit in the polymer structure as shown in Figure 3.20. Because the experiments exposed the same mass of polyDADMAC and polyamine to monochloramination, polyDADMAC has lower DMA precursor content per mass basis than polyamine. This may partly contribute to the overall observation that less NDMA is formed from polyDADMAC.



Polyamine repeating unit MW: 102+35.5
DMA moiety % = 44/137.5 = 32 %

PolyDADMAC repeating unit: 126+35.5
DMA moiety = 44/161.5 = 27.2 %

Figure 3. 20 Fraction of DMA moiety in Polyamine and PolyDADMAC (The reason of including chloride ion for fraction calculation is chloride ion always exists as counter ion in polymer solution or in salt-form polymer product).

Apart from the above chemical properties concerning the microscopic structures of polymers, a third possible reason related to the behavior of polymer chains as string-like objects in aqueous solutions can be considered. These properties of polymers, referred to as mesoscopic structures, concern larger scale structure than atomic scale. The chains of both polyamine and polyDADMAC have bond angle and torsional angle restricting their chain flexibility. The local stiffness of a polymer chain due to bond angle and steric hindrance is usually expressed by Flory's characteristic ratio (C_∞), which is higher in the polymer containing bulkier side groups (Rubinstein and Colby, 2003; Shalaby, McCormick *et al.*, 1989). Based on this understanding, the polymer chain of polyDADMAC is stiffer and bulkier than that of polyamine because of the ring structure in polyDADMAC. Thus, polyamine is more flexible and moves more freely in aqueous solution than polyDADAMC. This greater flexibility may allow the polyamine chain to react with monochloramine more easily, leading to increased polymer chain degradation and thus higher DMA release and NDMA formation.

Overall, the results strongly indicate that direct reaction of polyamine and polyDADMAC with monochloramine can result in degradation of several functional groups and release of DMA. NDMA formation potential is closely related to these two phenomena. Polymer chain ends play the major role in polyamine's NDMA formation potential, while degradation of quaternary ammonium groups of the cyclic structures in polyDADMAC are responsible for its NDMA formation.

3.6. Reducing Polymers' NDMA Formation Potential

Based on the experimental findings presented so far, three strategies were developed and tested to reduce the NDMA formation potential of polyamine and polyDADMAC. The test results are discussed below.

3.6.1 Polyamine Manufactured with Chain End Capping

Because polyamine's tertiary amine chain ends are identified to be the major contributor to NDMA formation potential, capping the chain ends with a quaternary ammonium functional group that is a less efficient NDMA precursor will likely reduce the NDMA formation potential. Polyamines were prepared by capping chain ends with quaternary ammonium functional group

[QUAT 188] (Figure 3.21). As shown in Figure 3.22A, such chain end capping effectively reduces polyamine's NDMA formation potential to almost the same level of polyDADMAC with NDMA formation reduction efficiency of nearly 70% compared to undialyzed, uncapped polyamine. The reduction in NDMA formation potential is more efficient than that by dialysis. Capping the chain ends also lowers the amount of DMA release compared to undialyzed, uncapped polyamine (Figure 3.22B). This result further emphasizes the critical role of tertiary amine chain ends of polyamine in NDMA formation during chloramination.

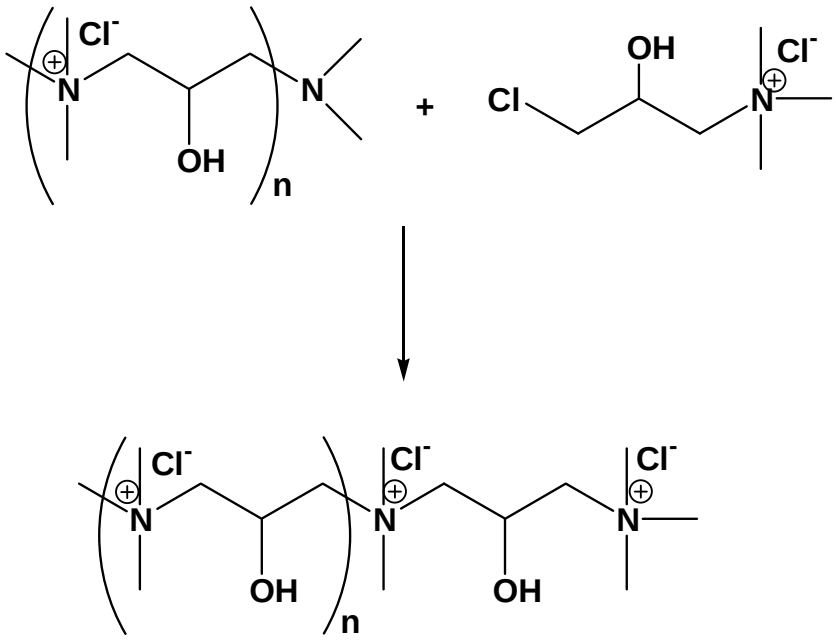


Figure 3. 21 Preparation of "chain-end capped" polyamine.

3.6.2. PolyDADMAC manufactured in Mild Conditions and with Chain End Capping

The experimental results indicate that degradation of ring quaternary ammonium group and the presence of residual DMA-containing intermediates such as ADMA are the likely reasons for polyDADMAC's NDMA formation potential. It was hypothesized that synthesizing polyDADMAC under milder conditions and capping the chain ends may reduce the presence of residual DMA-containing intermediates and minimize the tendency of polyDADMAC for degradation. As shown in Figure 3.23, this polyDADMAC forms slightly less NDMA compared to undialyzed polyDADMAC, but not to dialyzed polyDADMAC. The release of DMA was not reduced, in contrast, was increased in this particular experiment. Overall, the efficiency of this strategy to reduce NDMA formation is low.

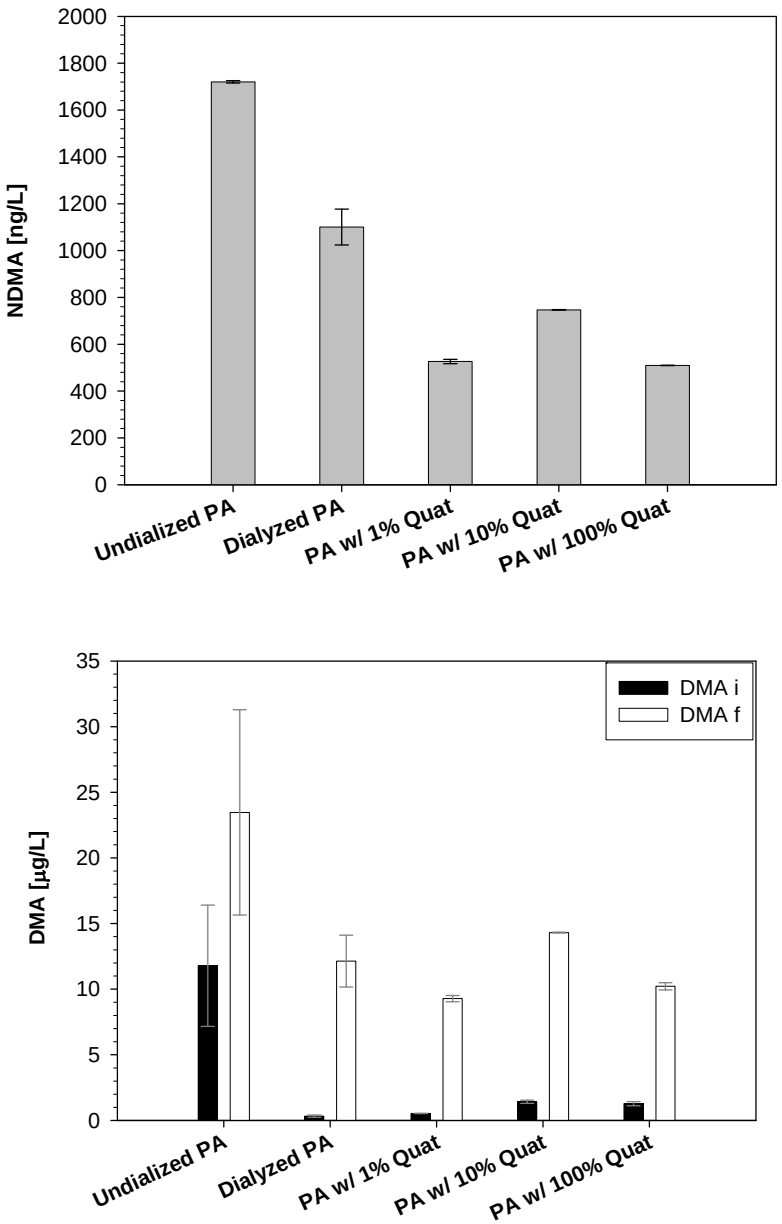


Figure 3. 22 NDMA formation of undialized, dialyzed and "capped" polyamines.10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction. The "capped" polyamines were prepared by capping chain ends with Quat 188.

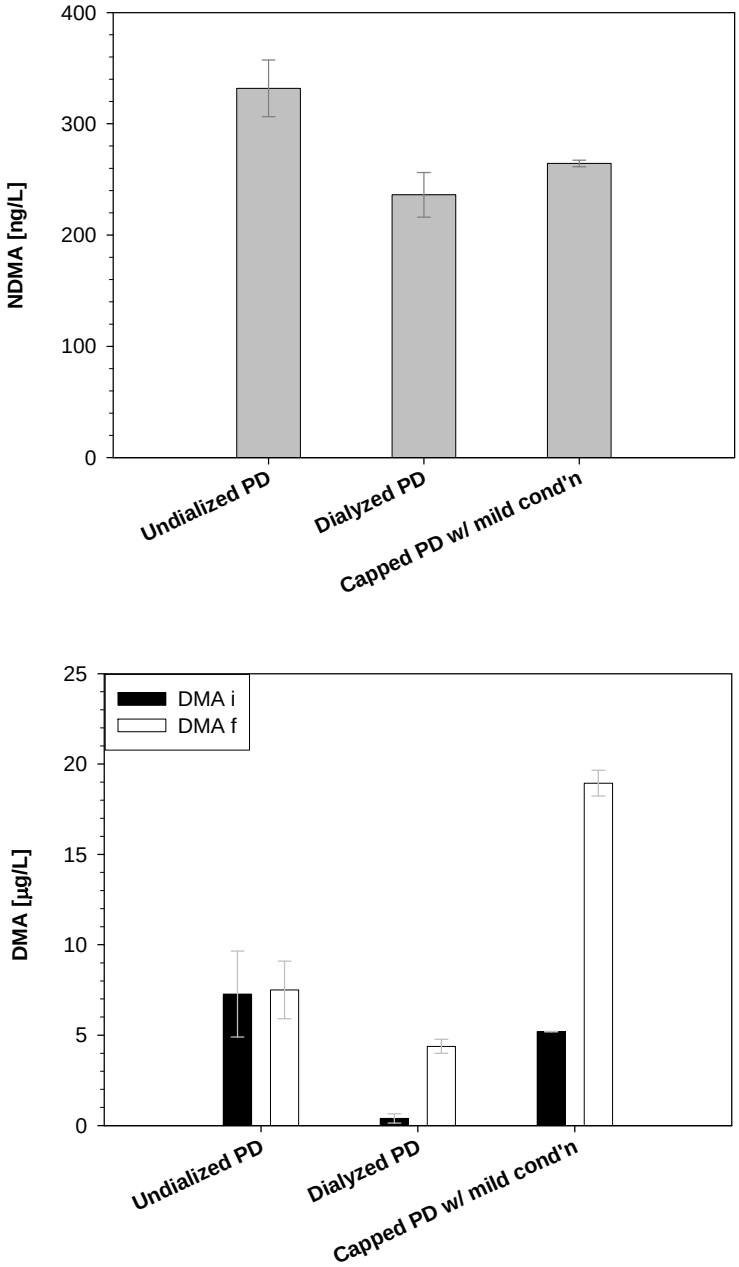


Figure 3. 23 NDMA formation potential of polyDADMAC manufactured in mild conditions and with chain end capping. 10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C. (A) NDMA concentration measured at the end of reaction. (B) DMA concentration measured before (DMA_i) and after (DMA_f) the reaction.

3.6.3 Effect of Ionic Strength

Although the experimental results show that DADMAC monomer has little reactivity to monochloramine and thus very low NDMA formation potential (Figures 3.13 and 3.15), polyDADMAC spiked with varying concentration of DADMAC monomer, surprisingly, showed decreased NDMA formation, and as the concentration of spiked DADMAC increased, the greater

the decrease in NDMA formation (Figure 3.24). Since DADAMC monomer is not expected to consume monochloramine nor react with polyDADMAC polymer, it was hypothesized that this trend may be due to increased ionic strength in these experiments since DADMAC monomer was added in chloride salt form. Spiking a higher concentration of DADMAC chloride salt would lead to a higher ionic strength in the solution. The ionic strength might affect polymer's conformation and interaction with oxidants in solutions.

To test the above hypothesis, sodium chloride was added to polyamine, polyDADMAC, as well as DMA solutions to see the effect of ionic strength on NDMA formation. As shown in Figure 3.25, the addition of salt effectively reduced NDMA formation potential of both polymers, although a relatively high amount of salt is needed to obtain a significant reduction. Adding 0.1 M NaCl resulted in a modest decrease in NDMA formation, while adding 1.0 M NaCl resulted in approx. 4-fold decrease in NDMA formation for polyamine and DMA, and more than 13-fold decrease in NDMA formation for polyDADMAC.

It is necessary to point out that the polyDADMAC sample used in the experiments here was different from those in the experiments in Section 3.5. The polyDADMAC sample used here contained lower percentage active weight 3-5% as apposed 40-60% typically in other polymer stocks and more than one year of storage time. The greater dilution and longer storage time may have facilitated hydrolysis of some polymers. As a result, a higher than typically observed level of NDMA formation was seen in these experiments

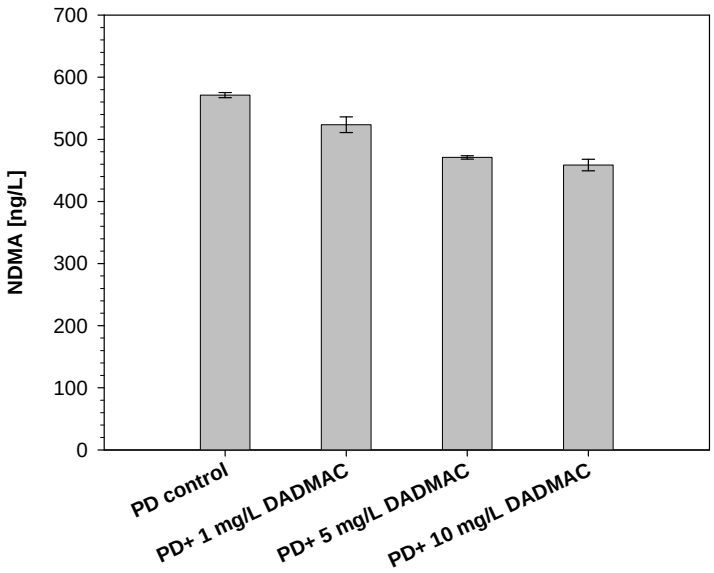


Figure 3. 24 NDMA formation from polyDADMAC spiked with varying concentration of DADMAC monomer chloride salt. 10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C.

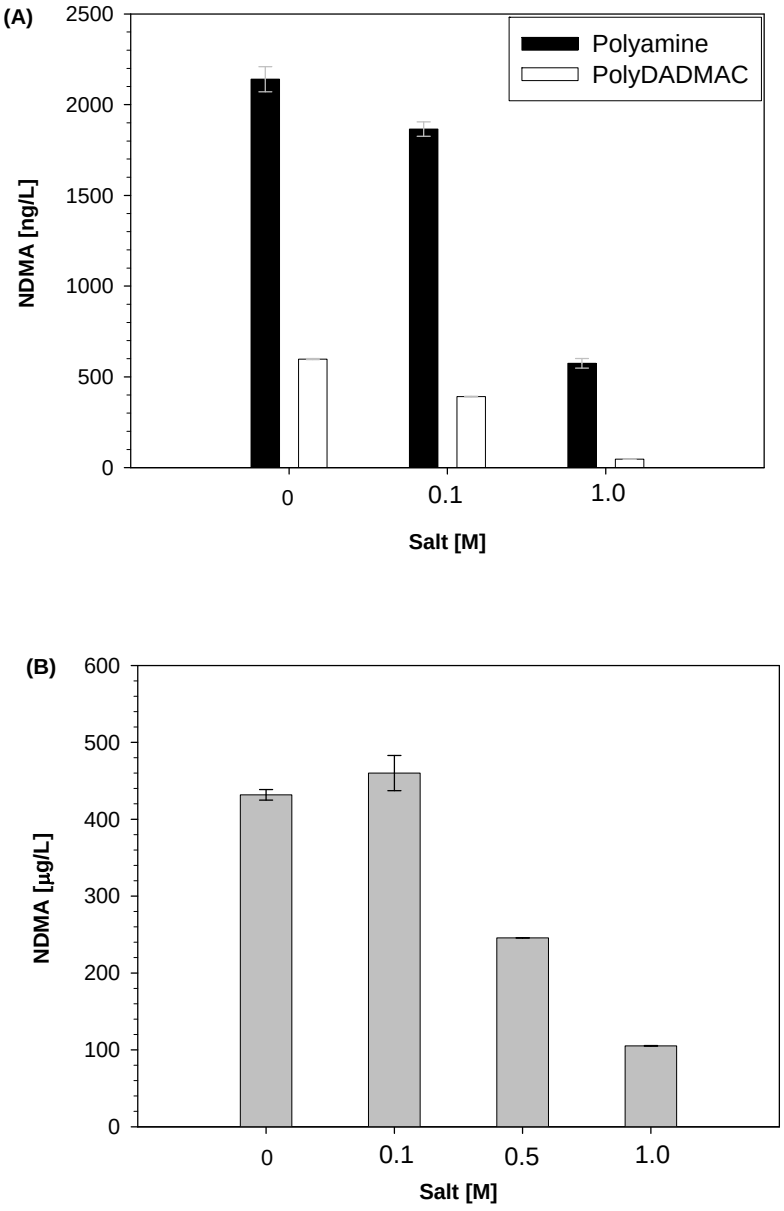


Figure 3. 25 Effect of ionic strength on NDMA formation from (A) polymer solutions and from (B) DMA solutions. Reaction conditions: (A) 10 mg/L as active ingredient of polymers were reacted with 10 mg as Cl_2/L of preformed monochloramine for 24 h at pH 7.5 and 23 °C with and without adding NaCl; (B) 1 mM of DMA was reacted with 1 mM of preformed monochloramine for 24 h at pH 7.5 and 23 °C with and without adding NaCl.

3.7 NDMA Formation Potential of SNF Polymers under Representative Water Treatment Conditions

The previous sections report the results from mechanistic studies, in which experiments were conducted under conditions that maximize NDMA formation (i.e., high polymer dosage, high monochloramine dosage and long contact time) in order to gain insights for the mechanisms

via which amine-based polymers can act as NDMA precursors. This section reports the results from studies that employed reaction conditions more representative of those that are likely encountered in water and wastewater treatment plants.

3.7.1. Coagulated Artificial Water Samples

In these experiments, artificial water samples were subject to coagulation/flocculation by Alum with or without polymers in jar tests followed by filtration at SNF's labs in Pearlington, MS (PolyChemie Inc.). These samples were then shipped to Georgia Tech (Dr. Huang's Analytical Chemistry Lab.) for monochloramination under conditions representative of water treatment plants (i.e., 4 mg as Cl_2/L of preformed monochloramine (MCA) and 2 hours of contact time) and analyzed for NDMA formation after the contact time and DMA concentrations before [DMA_i] and after [DMA_f] the reaction. Table 3.7.1 summarizes the results from the first batch of samples received from SNF. Although the two samples [RB2233 B & C] in which polymers were used in coagulation/flocculation did contain a higher concentration of DMA than the sample [RB2233 A] in which polymers were not used, the amount of NDMA formed in the three samples were almost the same. There was no significant increase in DMA concentration after reaction with MCA, possibly due to the relatively short time of chloramination. NDMA was detected in the RB2233-A sample but not in the control experiments conducted at Georgia Tech, suggesting that background NDMA contamination might have occurred for the RB2233-A sample at the SNF facility.

Further experiments were conducted to assess potential background contamination and the results are shown in Table 3.7.2. Compared to the control samples [C1-C3], the RB2233-A and RB2233-D were contaminated with DMA; this could explain why these two samples had higher NDMA formation after reaction with MCA. Comparing the RB2233-D and C3 samples, DMA contamination seems to have happened during filtration. More DMA contamination seems to come from the coagulation with Alum, based on the DMA results from the RB2233-A sample by both sets of experiments (Table 3.7.1 and Table 3.7.2). Comparing the results of RB2233-A in Table 3.7.1 and Table 3.7.2, the DMA results were similar, but the NDMA results showed a difference of about 3 ng/L. The NDMA results in Table 3.7.2 are likely more accurate because the NDMA formation potential is expected to be in the order of polyamine > polyDADMAC > Alum, according to the measured DMA concentrations.

Another set of tests was conducted using synthetic water samples from SNF prepared by adding 50 ppm of humic acid and 500 ppm bentonite clay to DI water. This synthetic water was diluted to 20 ppm humic acid and 200 ppm bentonite clay, then dosed with 1 mg/L as active of undialyzed polyamine [AT2020-A] and polyDADMAC [AT2021-A], respectively. These samples were directly subject to monochloramination without filtration. As shown in Table 3.7.3, the SNF synthetic water (containing humic acid and bentonite clay) and Analytic Chemistry Lab DI water showed the level of NDMA formation close to the method detection limit (1-2 ng/L), while the samples amended with either polyamine or polyDADMAC formed more NDMA. These results suggest that utilization of polymers can increase the level of NDMA formation under relevant water treatment conditions, although the concentration of NDMA formed is still quite low (mostly less than 10 ng/L). In addition, these results point to the need to assess whether Alum or

other chemicals used in the coagulation process is contaminated with DMA or NDMA as discussed in the following section.

Table 3.7. 1 NDMA and DMA measurements for chloramination of coagulated and filtered artificial water samples.

Sample ID	Sample Description	Replicate	NDMA [ng/L]	DMA_i [ug/L]	DMA_f [ug/L]
RB2233-A	SNF artificial water + 100 ppm Alum + filtration	1	9.3	5.5	7.1
		2	10.2	5.7	7.3
RB2233-B	SNF artificial water + 100 ppm Alum / 10 ppm polyamine + filtration	1	9.8	17.7	18.6
		2	9.3	17.4	18.9
RB2233-C	SNF artificial water + 100 ppm Alum / 10 ppm polyDADMAC + filtration	1	7.3	13.9	14.6
		2	7.8	13.7	14.9
C0	Huang Lab DI water only (no chloramination)		ND		ND
C1	Huang Lab DI water + buffer + preformed monochloramine		ND		ND

Note: Samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.5. NDMA was measured at the end of chloramination and DMA was measured before (DMA_i) and after (DMA_f) the reaction. ND = not detected.

Table 3.7. 2 NDMA and DMA measurements for chloramination of coagulated and filtered artificial water samples (repeated experiments for Table 3.7.1)

Sample ID	Water Matrix Description	NDMA [ng/L]	DMA_i [ug/L]	DMA_f [ug/L]
C1	Huang Lab DI water	1.3	0.07	0.07
C2	SNF control filtered DI water	2.6	0.10	0.13
RB2233-A	SNF artificial water + 100 ppm Alum + filtration	6.7	6.07	7.29
RB2233-D	SNF artificial water + 50 ppm humic acid/500 ppm bentonite clay + filtration	2.9	1.96	2.01
C3	Huang Lab DI water + 50 ppm humic acid/500 ppm bentonite clay (without filtration)	1.5	0.11	0.31

Note: Samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.5. NDMA was measured at the end of chloramination and DMA was measured before (DMA_i) and after (DMA_f) the reaction.

Table 3.7. 3 NDMA and DMA measurements for chloramination of SNF synthetic water samples.

Sample Description	Replicate	NDMA [ng/L]	DMA_i [ug/L]	DMA_f [ug/L]
Synthetic water (20 ppm humic acid/200 ppm bentonite clay) + 1 mg/L polyamine	1	3.1	-	1.60
	2	2.2	-	1.61
Huang Lab DI water + 1 mg/L polyamine	1	7.6	1.48	4.02
	2	7.7	2.07	4.58
Synthetic water (20 ppm humic acid/200 ppm bentonite clay) + 1 mg/L polyDADMAC	1	11.1	-	1.04
	2	2.5	-	0.96
Huang Lab DI water + 1 mg/L polyDADMAC	1	3.1	1.54	2.23
	2	-	-	2.25
Synthetic water control (20 ppm humic acid/200 ppm bentonite clay)		1.8	-	0.25
Huang Lab DI water control		1.9	-	0.20

Note: Samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.5. NDMA was measured at the end of chloramination and DMA was measured before (DMA_i) and after (DMA_f) the reaction.

3.7.2. Effect of Alum, Humic Acid, and Bentonite Clay

From the previous experiments, filtered artificial water samples containing Alum, bentonite clay, or humic acid had measurable amounts of NDMA after monochloramination, suggesting that NDMA precursors may be present in these commercial chemicals. To evaluate whether this was the case, samples were prepared by the following steps. First, solutions of 100 ppm Alum, 500 ppm bentonite clay, and 50 ppm humic acid, respectively, were prepared in the lab using the provided dry chemicals. After sufficient shaking, each solution was allowed time for particle settling, and then filtered through 0.7 μm borosilicate glass fiber filters. The filter bases were rinsed with detergent and acid washed prior to use. Secondly, control samples (i.e., lab DI water filtered by the clean filtration system) were also analyzed for comparison. Next, the above samples were monochloraminated (4 mg as Cl_2/L of monochloramine for 2 hours at pH 7.5 and 23°C) and the NDMA concentration was measured after the reaction. As shown in Table 3.7.4, NDMA formation in all of the samples was very low, either non-detectable or below the method quantification level (1.0 ng/L). Therefore, the Alum, bentonite clay, and humic acid chemicals are not sources of NDMA precursors. The background contamination of NDMA and DMA in the previous experiments was not from these three commercial chemicals, and was from other unknown sources or human errors.

Table 3.7. 4 NDMA formation potential of Alum, humic acid and bentonite clay.

No	Product No	NDMA [ng/L]
1	Control 1	ND
2	Control 2	ND
3	Control 3	ND
4	Alum 1	<1.0
5	Alum 2	<1.0
6	Bentonite clay 1	<1.0
7	Bentonite clay 2	<1.0
8	Humic acid 1	<1.0
9	Humic acid 2	<1.0

Note: The samples were reacted with 4 mg as Cl_2 /L of preformed monochloramine for 2 h at pH 7.5.
ND: Not detected

3.7.3 Effluents of Water Treatment Plants Using SNF Polymers

An effluent sample after free chlorine disinfection was collected from a municipal drinking water treatment plant where SNF polymers were used along with ferric sulfate in the coagulation and flocculation process. The sample was received from SNF on 4/12/2006 and stored in a 4°C room within enclosed container (no light exposure). NDMA analysis was conducted on 6/19/2006 with addition of the surrogate standard NDMA-d_6 at 10 ng/L. The residual chloramine concentration of the sample was determined to be 0.3 mg/L as Cl_2. The concentration of NDMA was found to be 12.3 ± 0.3 ng/L from triplicate analyses. Because the sample was stored at 4°C in the dark for about two months and there was residual monochloramine in the sample, the measured NDMA concentration here is probably not the actual NDMA concentration at the time of sampling, but instead the maximum amount of NDMA that could be formed after prolonged reaction time. For a more accurate analysis of NDMA concentration at the time of sampling, a quenching agent (e.g., ascorbic acid) should be added to eliminate any residual oxidants. Information for the plant treatment parameters such as polymer concentrations and disinfectant type, concentration and contact time can also help interpret the results.

3.7.4. Coagulated Raw Water Samples and Artificial Water Samples (with and without filtration)

A series of experiments were conducted to evaluate NDMA formation from raw water samples (drinking water intake) as well as artificial water samples in reaction with monochloramine. The water samples were first coagulated with Alum with or without addition of polymers in jar tests followed by filtration or no filtration. The samples were then shipped to Georgia Tech for monochloramination (4 mg as Cl_2/L of preformed monochloramine (MCA) and 2 hours of contact time). NDMA concentration was measured at the end of the contact time and the results are summarized in Tables 3.7.5 and 3.7.6. Based on the results of Sample 1 vs. Sample 5 (raw water coagulated with Alum only) and the results of Samples 4 vs. Sample 8 (raw water controls), there is no apparent effect of filtration on NDMA formation. For the samples in which

polymers were used (Samples 2, 3, 6, and 7), it was not possible to evaluate the effect of filtration because different dosages of polymers were used. The results of Samples 2 vs. 6 indicate that NDMA formation is proportional to polyamine dosage. When the results of Samples 3 vs. 7 are compared, the results show that lower dosage of polyDADMAC results in less NDMA formation, although the proportionality is not as strong as that in case of polyamine. Samples coagulated with polyamine produced more NDMA than those with polyDADMAC, in good agreement with the previous mechanistic studies for polyamine and polyDADMAC. Slightly more NDMA was formed in the raw water matrix than in the artificial water matrix.

Table 3.7. 5 NDMA formation in raw water samples that were coagulated followed by filtration or no filtration prior to monochloramination.

Sample No	Product No	Sample description	NDMA [ng/L]
1	RB 2240-A	75 ppm Alum w/ filtration	2.0
2	RB 2240-B	75 Alum + 15 PA w/ filtration	13.0
3	RB 2240-C	75 Alum + 5 PD w/ filtration	2.8
4	RB 2240-D	Control (raw water) w/ filtration	<2.0
5	RB 2241-A	75 ppm Alum w/o filtration	2.0
6	RB 2241-B	75 Alum + 8 PA w/o filtration	6.3
7	RB 2241-C	75 Alum + 1 PD w/o filtration	<2.0
8	RB 2241-D	Control (raw water) w/o filtration	<2.0
9	Lab DIW_1	Huang lab Nanopure water	<2.0
10	Lab DIW_2	Huang lab Nanopure water	<2.0

Note: The samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.5; PA = polyamine, PD = polyDADMAC

Table 3.7. 6 NDMA formation in artificial water samples that were coagulated followed by filtration or no filtration prior to monochloramination.

Sample No	Product No	Sample description	NDMA [ng/L]
11	RB 2242-A	65 ppm Alum w/o filtration	<2.0
12	RB 2242-B	65 Alum + 8 PA w/o filtration	4.1
13	RB 2242-C	65 Alum + 6 PD w/o filtration	<2.0
14	RB 2242-D	Control artificial water w/o filtration	<2.0

Note: The samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.5. PA = polyamine, PD = polyDADMAC

3.7.5. Effect of Polymer Dosage

The impact of polymer dosage on NDMA formation was also evaluated under representative water treatment conditions. Table 3.7.7 summarizes the results from evaluating the effect of polyDADMAC dosage on NDMA formation in artificial water samples. RB2248_C was an artificial water sample that was subject to coagulation by Alum and 0.5 ppm (optimum) of

polyDADMAC in jar tests followed by filtration at SNF's labs. RB 2248_D–G samples were similar to RB2248_C but spiked with additional varying amounts of polyDADMAC after coagulation. In contrast, RB 2248_H–N samples were coagulated by Alum and varying concentrations of under- (< 0.5 ppm) and overdosages (> 0.5 ppm) of polyDADMAC in jar tests at SNF's labs. After allowing the particles to settle, the water was decanted into a bottle and shipped to Georgia Tech for monochloramination (4 mg as Cl_2/L of preformed monochloramine and 2 hours of contact time) and analyzed for NDMA formation after the reaction time. The results of RB 2248_D – G show that NDMA formation increased when additional polymers was spiked into the sample after coagulation, indicating that residual polymers present in the solution will increase NDMA formation. In contrast, the results of RB 2248_H – N show that polymer dosage used in coagulation (in the range of 0.25 ppm to 1.0 ppm) had little effect on NDMA formation. One possible reason for this outcome could be that, despite the varying concentration of polyDADMAC used, all of these samples actually have similar residual polyDADMAC concentration in the solutions after coagulation since most of the polymers were attached to flocs and removed by filtration. This result also suggests that slight overdosing of polymers during coagulation is unlikely to cause significant increase in NDMA formation at the treatment plants.

Table 3.7. 7 NDMA formation in artificial water samples that were coagulated with Alum and varying dosage of polymer followed by filtration prior to monochloramination.

Sample Number	**Raw Water Sample Description**	**NDMA [ng/L]**
RB 2248_A	Control (No coagulation)	<2.0
RB 2248_B	Coagulated using 75 ppm Alum	Analysis failed
RB 2248_C	Coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC	3.6
RB 2248_D	Coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 10% PD dosage after coagulation)	3.4
RB 2248_E	Coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 20% PD dosage after coagulation)	4.6
RB 2248_F	Coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 50% PD dosage after coagulation)	5.1
RB 2248_G	Coagulated using 37.5 ppm Alum / 0.5 ppm polyDADMAC (spiked with 100% PD dosage after coagulation)	5.5
RB 2248_H	Coagulated using 37.5 ppm Alum / 0.55 ppm polyDADMAC	3.4
RB 2248_I	Coagulated using 37.5 ppm Alum / 0.65 ppm polyDADMAC	3.5
RB 2248_J	Coagulated using 37.5 ppm Alum / 0.75 ppm polyDADMAC	3.3
RB 2248_K	Coagulated using 37.5 ppm Alum / 1.0 ppm polyDADMAC	4.3
RB 2248_L	Coagulated using 37.5 ppm Alum / 0.45 ppm polyDADMAC	3.3
RB 2248_M	Coagulated using 37.5 ppm Alum / 0.40 ppm polyDADMAC	3.7
RB 2248_N	Coagulated using 37.5 ppm Alum / 0.25 ppm polyDADMAC	3.8

Note: The samples were reacted with 4 mg as Cl_2 /L of preformed monochloramine for 2 h at pH 8.0.
PA = polyamine, PD = polyDADMAC

Table 3.7.8 summarizes the results from assessing the effect of coagulation polymer dosage on NDMA formation in raw water samples. For these experiments, the MDL of NDMA for 450 mL of water samples was around 4 ng/L (increased from 1-2 ng/L typically) due to some problems with the GC/MS column. Most samples (except for RB 2269-C and RB 2270-C) showed NDMA formation at near or less than 4 ng/L. Only when a relatively high polymer dosage was used (3 ppm polyamine in both RB 2269-C and RB 2270-C sample), higher NDMA formation was observed, but still below 10 ng/L. Overall, the results of this section strongly suggest that the NDMA formation potential of SNF polymers under conditions in line with those in typical water treatment plants was lower than the current advisory level (i.e., 10 ng/L in CA, MA; 9 ng/L in Ontario).

Table 3.7. 8 NDMA formation in raw water samples that were coagulated with varying concentration of Alum and polymer followed by filtration prior to monochloramination.

Sample No	Product No	Sample description	NDMA [ng/L]
1	RB 2269-A	Raw Lake Ontario water (No Coagulation) (CONTROL)	Below MDL
2	RB 2269-B	Raw Lake Ontario water coagulated using 38 ppm Alum	Below MDL
3	RB 2269-C	Raw Lake Ontario water coagulated using 19 ppm Alum/3 ppm PA	8.2
4	RB 2269-D	Raw Lake Ontario water coagulated using 19 ppm Alum/2 ppm PD	4.3
5	RB 2270-A	Raw Kitchener, Ontario River water (No Coagulation) (CONTROL)	Below MDL
6	RB 2270-B	Raw Kitchener, Ontario River water coagulated using 50 ppm Alum	Below MDL
7	RB 2270-C	Raw Kitchener, Ontario River water coagulated using 25 ppm Alum/3 ppm PA	7.5
8	RB 2270-D	Raw Kitchener, Ontario River water coagulated using 25 ppm Alum/1 ppm PD	Below MDL
9	RB 2271-A	Raw Pushlinch, Ontario aquifer water (No Coagulation) (CONTROL)	Below MDL
10	RB 2271-B	Raq Pushlinch, Ontario aquifer water coagulated using 63 ppm Alum	Below MDL
11	RB 2271-C	Raq Pushlinch, Ontario aquifer water coagulated using 33 ppm Alum/0.5 ppm PD	Below MDL
12	RB 2271-D	Raw Pushlinch, Ontario aquifer water coagulated using 33 ppm Alum/1 ppm PD (OVERDOSED)	Below MDL

Note: The samples were reacted with 4 mg as Cl_2/L of preformed monochloramine for 2 h at pH 7.9; PA = polyamine, PD = polyDADMAC; Because of some column wearing problem in GC/MS, MDL of NDMA for 450 mL water sample was increased from 1-2 ng/L to 4 ng/L in these experiments.

4 Spectroscopy Studies: Material, Methods and Analysis of Results

4.1 Background and Literature Survey

Cationic polyacrylamide copolymer (cationic PAM), poly(diallyldimethylammonium chloride) (polyDADMAC) and poly(epichlorhydrin dimethylamine) (quaternary polyamine), whose structures are shown in Figure 4.1, are water-soluble synthetic polymers most commonly used as primary coagulants or flocculants in drinking water treatment plants.

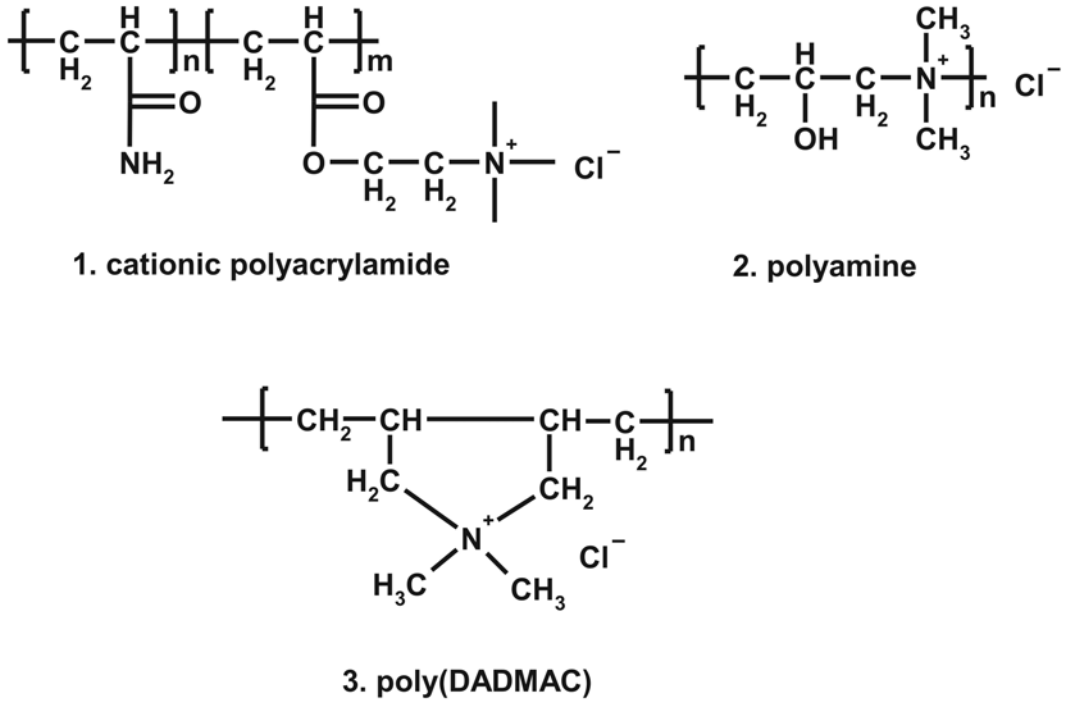


Figure 4. 1 The structure of the quaternary ammonium polymers in the present study.

It is reported in the literature that the polymers used in the water treatment plants are suspected as NDMA precursors (Graham, Andrews *et al.*, 1996b). NDMA has been classified as a probable human carcinogen (Sedlak, Pinkston *et al.*, 2003; USEPA, 1997) and has been found in highly purified wastewaters as well as some treated drinking waters in California and Canada after chlorine disinfection (California, 2000; Choi and Valentine, 2002b; Mitch and Sedlak, 2002a; MOE, ; Najm and Trussel, 2001). The EPA cancer risk of 10^{-6} in humans is 0.7 ng/L, which is the currently accepted drinking water guideline (Child, Kaa *et al.*). The current investigations reported the formation of NDMA after chlorine disinfection, which suggests a possible link between NDMA formation and treatment practices (Kohut and Andrews, 2003; Mitch and Sedlak, 2004a; Najm, Teefy *et al.*, 2004a). The most probable NDMA formation mechanism is the reaction of polymers containing DMA functional groups with chlorine-based disinfectants (Mitch and Sedlak, 2004a). However, there are some investigations revealing detectable levels of NDMA after discontinuing use of the polyelectrolyte coagulant (Jobb, Hunsinger *et al.*, 1993a; Wilczak, Lai *et al.*, 2004b), which suggests that the polyelectrolyte is not the only source of NDMA. It is reported in the literature that the cationic PAM gave significant production of trimethylamine (TMA) at high pH with lime addition, but the epichlorhydrin

dimethylamine copolymers didn't generate TMA (Chang, Abu-Orf *et al.*, 2005). Although the quaternary ammonium groups in the polymers are believed to be the NDMA precursors (Kimoto, Dooley *et al.*, 1980a), the mechanism of the polymer degradation and the effect of the degradation of those polymers on NDMA yields are poorly understood. Degradation of amine-based polymers in aqueous solutions can occur in the course of synthesis, storage, and use of polymers under the separate or combined action of heat, light and chemical interaction. In the natural conditions, many factors simultaneously influence the aging of polymer materials. The combination of all those effects can cause changes in chemical structure of polymers, leading to loss of chemical properties and release of harmful chemicals to the environment. Therefore, it is necessary to develop reliable, simple and quick procedures to understand the degradation mechanism of those polymers at the molecular level under environmental conditions.

A possible way to monitor the structure changes upon environmental conditions is via infrared spectroscopy (Chin, Aouadi *et al.*, 2001; Kim, Park *et al.*, 2003; Marchant, Zhao *et al.*, 1987; Pal, Singh *et al.*, 2004; Sammon, Yarwood *et al.*, 1999; Yang, Vang *et al.*, 2001) and Raman spectroscopy (Amer, Koczak *et al.*, 1995; Jones, Carr *et al.*, 1998; Maquet, Boccaccini *et al.*, 2003; Williams, Melendez *et al.*, 2004). FT-IR and FT-Raman are complementary techniques in characterization of chemical structure of polymer materials. FT-IR spectroscopy is now an established technique for nondestructive qualitative and quantitative analysis for polymer materials. The advantage of Raman spectroscopy for studying polymer materials is that it is nondestructive and gives strong bands for nonpolar functional groups. Structural information is provided by C-N stretch, C-C skeletal vibration and C-H stretch, which is weakly active (C-N, C-C) or covered by the broad O-H band (C-H) in the infrared absorption spectrum of polymers.

In this study, using spectroscopic analysis, we evaluated the degradation mechanism of the amine-based polymers during various water treatment processes including the effects of temperature and pH of water on the degradation. Furthermore, the effects of chloramination were studied both by chemical structure analysis and NDMA formation tests. The amount of NDMA formed from monochloramination was measured with GC/MS and compared. The relationship of NDMA formation with the molecular weight of polymers was also investigated. FT-IR and FT-Raman spectroscopy were used in combination to investigate the chemical structure change of amine-based polymers. The configuration of the polymers in water was simulated by molecular modeling method. The difference in rigidity of the polymer chains could contribute to the reactivity of the polymer in the NDMA formation.

4.2 Methodology

Chemicals: Cationic polyacrylamide (PAM, DPR 4257), poly(diallyldimethylammonium chloride) (polyDADMAC, RB 2199B, RB 2202B) and quaternary polyamine (RB2200B, RB2203B) were provided by SNF Floerger and SNF Polychemie. Sodium bicarbonate, sodium nitrite and sodium hypochlorite (10-13%, purified grade) were obtained from Sigma-Aldrich (St. Louis, MO) and used without further purification. Fisher Scientific ammonium chloride (99.9%), dibasic potassium phosphate, disodium ethylenediamine tetraacetate (EDTA), ferrous ammonium sulfate, *N,N*-diethyl-p-phenylenediamine oxalate, potassium iodide (certified ACS), sodium phosphate monobasic (99%) and sodium phosphate dibasic (99.7%) were used as supplied.

Deionized water produced from a Millipore Milli-Q Nanopure water purification system was used for the experiments. Monochloramine stock solution was prepared by adding sodium hypochlorite slowly into a rapidly stirred ammonium chloride solution with Cl/N molar ratio of 0.7 at pH > 9 (Connell, 2000a).

Temperature Dependence of Degradation: The polymers were prepared in 1g/L deionized water solutions in 25 ml glass vials. The vials were placed in water bath for 24 h at 22 ^{o}C, 42 ^{o}C and 62 ^{o}C. The polymers were dried and analyzed using IR and Raman spectroscopy. The samples were scanned 100 times at 2 cm^{-1} on IR and 500 times at 2 cm^{-1} on Raman with 550 mW laser power.

The pH Dependence of Degradation: The polymers were prepared in 1g/L water solutions in 25 ml glass vials. The pH of the solutions was adjusted to pH 5, 7 and 9 by 5 mM sodium bicarbonate buffer. The solutions were left intact for 24 h. The polymers were dried and analyzed using IR and Raman spectroscopy. The samples were scanned 100 times at 2 cm^{-1} on IR and 500 times at 2 cm^{-1} on Raman with 550 mW laser power.

The effect of different oxidant on Degradation: The polymers were prepared in 1g/L water solutions in 25 ml glass vials. Different oxidants ($NaNO_2$, NaOCl, NH_2Cl) were added to solution in 1:1 mass ratio with polymers. The reactions were continued for 24 h. The polymers were dried and analyzed using IR and Raman spectroscopy. The samples were scanned 100 times at 2 cm^{-1} on IR and 500 times at 2 cm^{-1} on Raman with 550 mW laser power.

The polymer Degradation by monochloramination and NDMA analysis: For the purpose of polymer structure analysis by IR/Raman spectroscopy, the high concentration of polymer solutions (1g/L as active ingredient in deionized water) were reacted with 200 mg as Cl_2/L of preformed monochlroamine for 24 hours. The polymers were dried and analyzed using IR and Raman spectroscopy. The samples were scanned 100 times at 2 cm^{-1} on IR and 500 times at 4 cm^{-1} on Raman with 550 mW laser power. After the monochloramination, the analyses of NDMA and residual monochloramine were conducted with GC/MS as mentioned previously and the DPD-FAS titration method specified in the Standard Methods for the Examination of Water and Wastewater (APHA, 1998), respectively and then were compared with IR/Raman spectroscopy results.

NDMA was extracted using the solid-phase extraction method adapted from Taguchi et al. (Taguchi, Jenkins *et al.*, 1994b). NDMA-d_6 was spiked into each water sample as an internal standard, and 200 mg of Ambersorb 572 resins (from Supelco) prebaked at 300 °C for 3 h was added to extract NDMA. After shaking for 2 hours, the Ambersorb resin was collected on a filter, air-dried at room temperature for 2 hours and transferred to a 2 mL amber vial. Dichloromethane (400 μL) was added to the vial, which was tapped before GC/MS analysis. NDMA was analyzed using an Agilent GC/MS (6890/5973) system with a HP-5MS column (30m × 250μm × 0.25μm). NDMA and NDMA-d_6 were quantified using m/z 74.1 parent and 42 daughter ions for NDMA and m/z 80.1 parent and 48 daughter ions for NDMA-d_6.

The degradation of polymers with different MW by monochloramination: Polymer solutions with different MWs (1g/L as active ingredient in deionized water) were reacted with 200 mg as Cl_2/L of preformed monochloramine for 24 hours. The polymers were dried and analyzed using IR and Raman spectroscopy. The samples were scanned 100 times at 2 cm^{-1} on IR and 500 times at 4 cm^{-1} on Raman with 550 mW laser power. After the monochloramination, the analyses of NDMA and residual monochloramine were conducted with GC/MS as mentioned previously and the DPD-FAS titration method specified in the Standard Methods for the Examination of Water and Wastewater (APHA, 1998), respectively and then were compared with IR/Raman spectroscopy results.

Molecular Dynamics Simulations: The molecular modeling results reported in this study were obtained with the AMBER-8 package (Case, Darden *et al.*, 2004). The polyamine/polyDADMAC (10 monomer units) was immersed in a periodic box of water (TIP3PBOX water model (Jorgensen, Chandrasekhar *et al.*, 1983)) which was subject to periodic boundary conditions with water added around the polymers at the same concentration (30.6 g/L). Energy minimization and equilibration steps in explicit solvent were performed with PMEMD, a software component from the AMBER-8 package.

4.3 Spectroscopy Study Results and Discussion

Temperature and pH dependence of degradation: The degradation of quaternary ammonium-based water soluble polymers was monitored under a variety of conditions by Raman and FT-IR spectroscopy. The dependence of polymer degradation on the temperature and pH of the water solution was studied. The temperatures chose in this study range from 22 ^oC to 62 ^oC, which is close to the raw water temperature. The change of physical properties like intrinsic viscosity and temperatures stability under different temperature would affect the activity of polymer. Figure 4.2 represents the difference IR/Raman spectra in absolute absorbance scale for the PAM samples treated at difference temperatures (22 ^oC-62 ^oC).

Firstly, a group of several new bands emerge in the spectra as a consequence of chemical degradation that appear at 1569 cm^{-1} and 1071/1020 cm^{-1} (Raman), which are associated with the carboxylate anion (CO_2^-). The new band at 1222 cm^{-1} (IR) due to the C-O stretch arises from the change of the ester group. Secondly, the decreases in intensity of 3354/3180 cm^{-1} (N-H stretching of NH_2), 1734 cm^{-1} (C=O stretching of ester), 1667 cm^{-1} (C=O stretching of amide, amide I band), 1617 cm^{-1} (N-H bending of NH_2, amide II band), 1414 cm^{-1} (IR, C-N stetching, amide III band), 1338 cm^{-1} (Raman, C-O-C stretching), 1167 cm^{-1} (the mixture N-H wagging of NH_2 and C-O stretch) are associated with the change in -$CONH_2$ and -COO moieties. In addition, the decreases in intensity of 1480/1450 cm^{-1} (C-H bending of CH_2), 1264 cm^{-1} (IR, C-C stretching), 952/844 cm^{-1} (CH_3 rocking) may indicate the leaving of the -CH_2-CH_2-$N(CH_3)_3$ group.

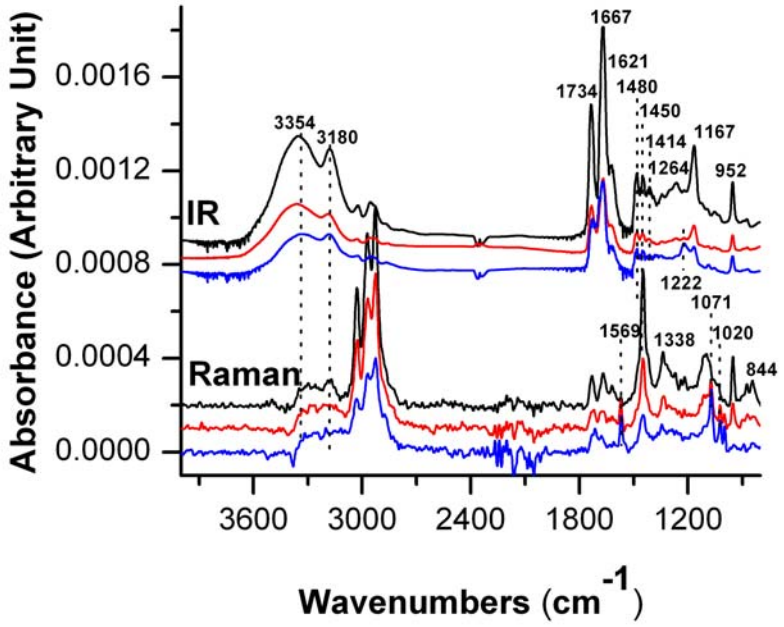


Figure 4. 2 FT-IR [up] and Raman [down] spectra of PAM after heat treatment at 22 ^{o}C [black], 42 ^{o}C [red] and 62 ^{o}C [blue]. All the IR spectra were divided by 1000.

All of the above changes can plausibly be depicted as the hydrolysis of the ester linkage with a detachment of the chain containing the $CH_2CH_2N(CH_3)_3$ group as a consequence of increasing temperature. The proposed reaction pathway is illustrated in Figure 4.3. Both the amide and ester group hydrolyzed when the temperature increased. No obvious chemical structure change was observed on the IR/Raman spectra of polyDADMAC and polyamine samples, which indicates that polyDADMAC and polyamine are stable from 22^{o}C to 62 ^{o}C. These results indicate that the long side chain of cationic PAM is more susceptible to detachment when the temperature increases.

The rate of polymer degradation strongly depended on the pH of the water solution. At pH values greater than 9, cationic PAM precipitated from water solution after 24 h. This suggests a physical and chemical structural change in the polymer. Figure 4.4 represents the different IR/Raman spectra of cationic PAM upon exposure to different pH solutions. The bands associated with the -NH_2 group at 3349/3178 cm^{-1} (N-H stretching of NH_2) and 1167 cm^{-1} (the mixture N-H wagging of NH_2 and C-O stretch) decreased when the solution pH increased from 5 to 9. The decreases in intensity of 3026/2972 cm^{-1} (C-H stretching of CH_3 and –CH_2-O-), 1450 cm^{-1} (C-H bending of CH_2), and 952/844 cm^{-1} (CH_3 rocking) are associated with the leaving of the -CH_2-CH_2-N$(CH_3)_3$ group. A new band emerged in the spectra at 1713 cm^{-1} (C=O stretching of –CO-NH-CO-) with the decrease of bands at 1731 cm^{-1} (C=O stretching of ester), 1669 cm^{-1} (C=O stretching of amide, amide I band), and 1623 cm^{-1} (N-H bending of NH_2, amide II band), which is consistent with changes expected as a consequence of the hydrolysis of the COO and $CONH_2$ groups and the formation of the –CO-NH-CO- group (Figure 4.3).

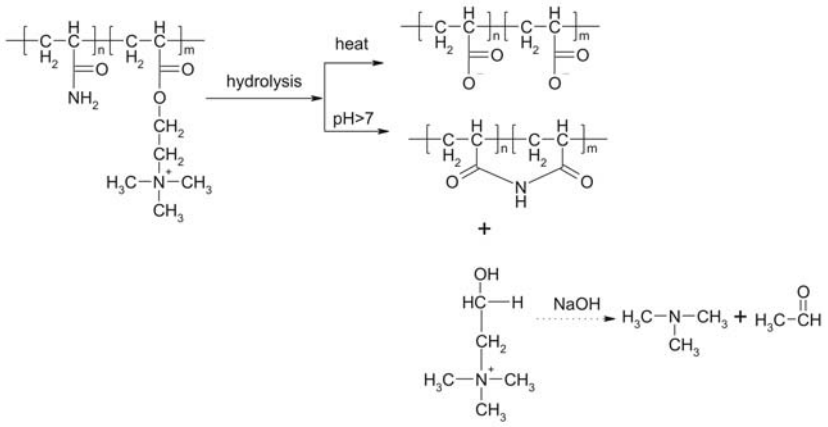


Figure 4. 3 The proposed TMA generation pathway from the degradation of PAM in solution.

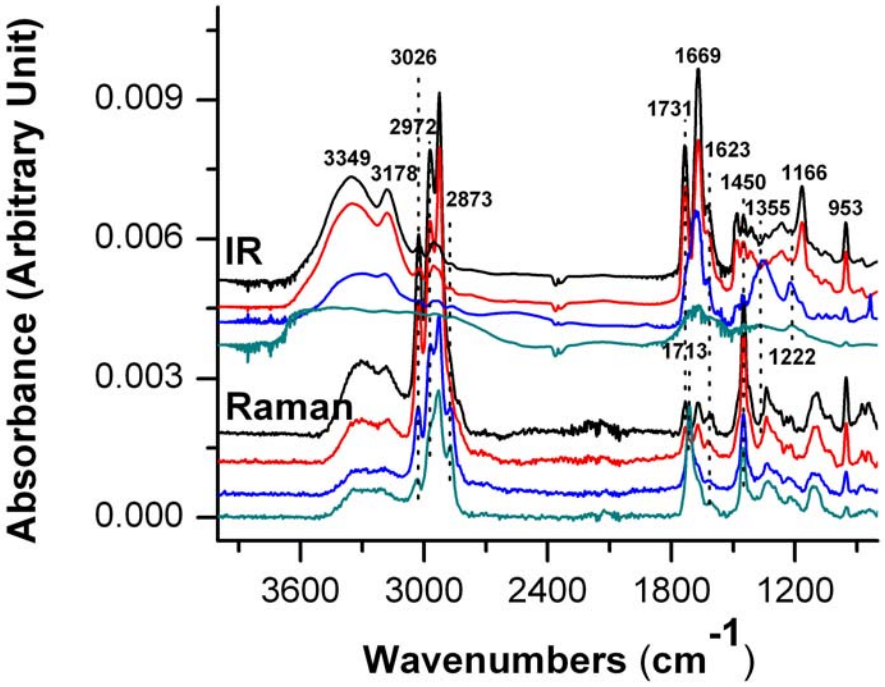


Figure 4. 4 FT-IR [up] and Raman [down] spectra of polyacylamide in solutions of different pH. All the IR spectra were divided by 100, original solution [black], pH 5 [red], pH 7 [blue], pH 9 [dark cyan].

The degree of PAM degradation increased with the solution temperature and the pH increases. The breakdown of the polymers was likely to result in the production of TMA. The polymer breakdown resulted in the production of protonated TMA, $(CH_3)_3NH^+$. With the increase of temperature or pH, TMA was deprotonated. It has been reported that one of the steps of this process is biologically mediated (Chang, Abu-Orf *et al.*, 2005). TMA can react with NH_2Cl/HOCl to form DMA and DMA can further react with NH_2Cl/HOCl to form NDMA (Figure 4.5).

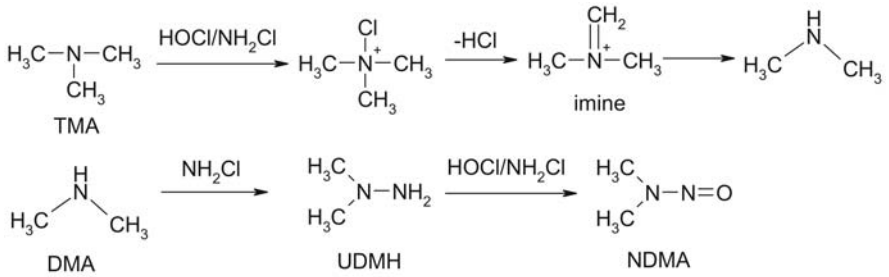


Figure 4. 5 The NDMA generation pathway from TMA or DMA in the presence of chlorine or chloramine.

The IR/Raman spectra of PolyDADMAC show pH dependence (Figure 4.6). The mechanism is shown in step 1 of Figure 4.7. It is proposed that upon Hofmann elimination under basic conditions, the quaternary amine is converted to tertiary amine. The weak CH_3 symmetric deformation at 1419 cm^{-1} from the quaternary amine (Harmon, Gennick *et al.*, 1974) disappears and the media strong CH_3 symmetric deformation at 1374 cm^{-1} from tertiary amine(Durig and Cox, 1982) appear when the solution pH is increased to 7 and 9. The quaternary amine group exhibits an absorption band at 1137 cm^{-1} (C-N stretching), whose intensity also decreases when the solution pH is increased to 7 and 9. In addition, the band at 906 cm^{-1} arises and the ring vibration disappears when the solution pH is increased. The pH 7 and 9 samples show a new band at 1734 cm^{-1} attributed to the C=C stretching vibration and a sharp peak at 834 cm^{-1} associated with the out-of-plane vibration of $R_2C=CH_2$. The evident of changing in C-H stretch and arising in C=C support the mechanism that the polymer undergos Hofmann elimination when the pH of the solutions increases.

The IR/Raman spectra of polyamine in different pH solutions are shown in Figure 4.8. The changes in the 3234 cm^{-1} region reflect the changes of the O-H group in different pHs. The bands in the region of 1462 cm^{-1} arise from CH_3 asymmetric deformation of tertiary amine groups. The new band at 1734 cm^{-1} is evidence of C=O group formation from Hofmann elimination. There is no obvious change observed from the Raman spectra. The suggested degradation mechanism of polyamine in buffer solutions is shown in step 1 of Figure 4.9.

The effect of different oxidants on Degradation: From previous pH and temperature dependence studies, it can be seen that the change of pH and temperature affect the chemical structure of the polymers, but these changes didn't result in the formation of NDMA. These results suggested that there is another factor which facilitates the formation of NDMA. The environmental impurities are one of the most possible sources for polymer degradation and NDMA formation. The use of Cl_2 as a disinfectant to kill bacteria and thus make water potable is well established (Burrows, 2003; Connell, 2000b; Galal-Gorchev, 1996; Morris, 1986; Wang, Yuan *et al.*, 2005).

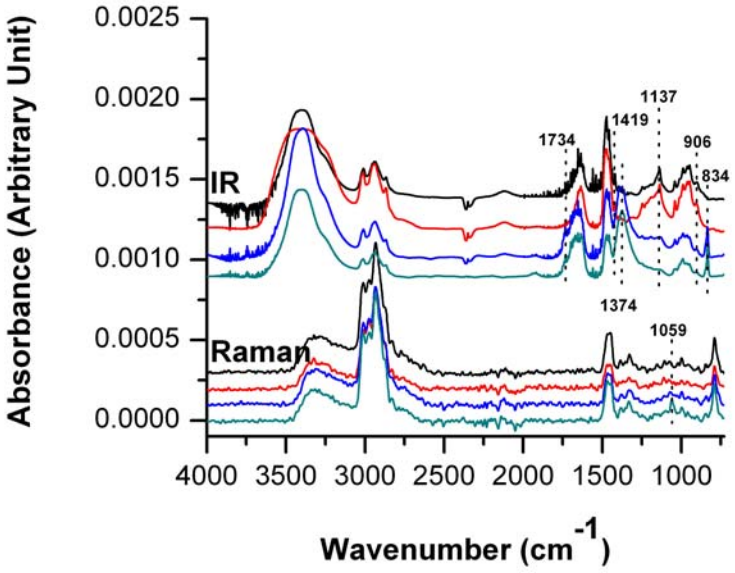


Figure 4. 6 FT-IR [up] and Raman [down] spectra of polyDADMAC in solutions of different pH. All the IR spectra were divided by 250, original solution [black], pH 5 [red], pH 7 [blue], pH 9 [dark cyan].

It is known that many polymeric materials used in chlorinated water degrade at rates that can adversely influence the functionality of the polymer and the water quality (Gill, Knapp *et al.*, 1999; Glater, Hong *et al.*, 1994; Singh, 1994). To find out the effect of oxidants on polymer degradation, $NaNO_2$, NaOCl and NH_2Cl were used to compare their reactivity with the studied polymers studies because these oxidants are potential reactants to form NDMA (Wilczak, Assadi-Rad *et al.*, 2003b). PAM (1g/L) remained stable after contact with a $NaNO_2$ solution (1g/L) for 24 h. But the polymer was difficult to recover after the reaction with NaOCl and NH_2Cl, so there is no data about the oxidant effect of chlorine and monochloramine on PAM. The oxidant effect on polyDADMAC was observed by Raman spectra (Figure 4.10). It can be seen that the peak intensities of the major peaks of the polymer decrease in the order of NH_2Cl > NaOCl > $NaNO_2$. Specifically, the decrease in intensity of 3027/2934 cm^{-1} (cyclic CH_2 stretch) and 791 cm^{-1} (ring vibration) indicates that some of the rings were opened upon oxidation. In addition, the bands associated with the N-CH_2 group decreased at 2828/2771 cm^{-1} (C-H stretch), 1448 cm^{-1} (CH_2 bending) and 573 cm^{-1} (CH_2 rocking). In the sample reacted with $NaNO_2$ (Figure 4.10, red), new peaks at 1326 and 826 cm^{-1} are associated with the NO_2 group. In the sample reacted with NH_2Cl (Figure 4.10, dark cyan), the new peak at 931 cm^{-1} can be assigned to the C-O-C symmetric stretch in ether.

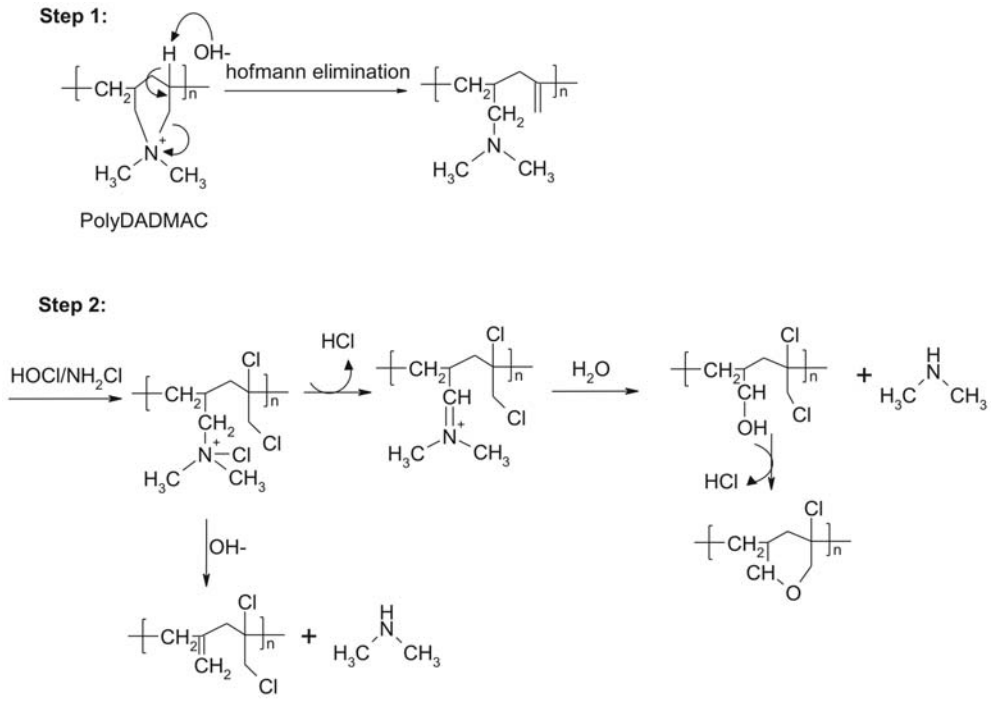


Figure 4. 7 The degradation mechanism of polyDADMAC in solution.

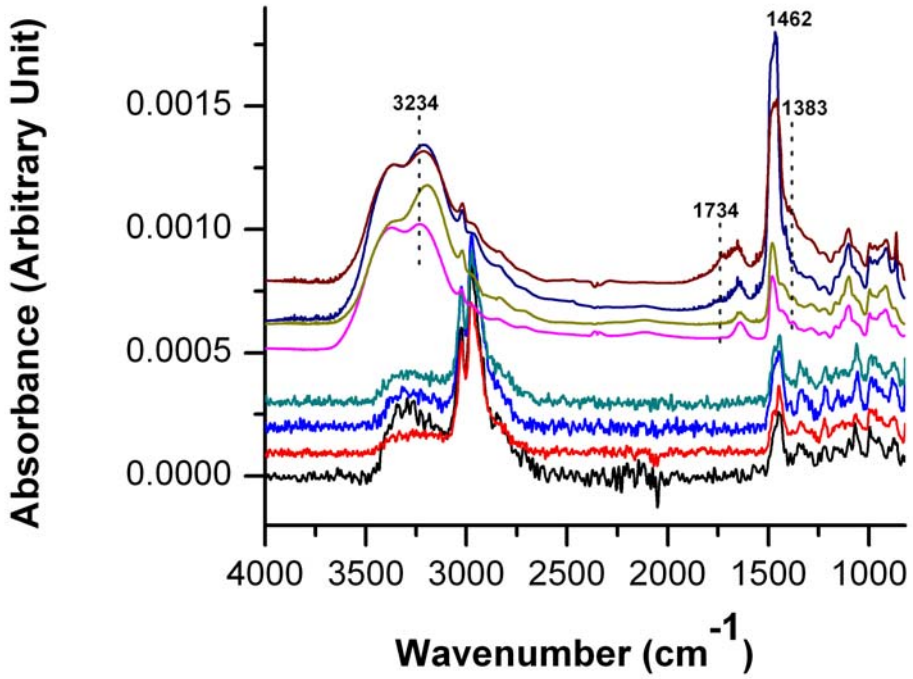


Figure 4. 8 FT-IR [up] and Raman [down] spectra of polyamine in solutions of different pH. All the IR spectra were divided by 500.

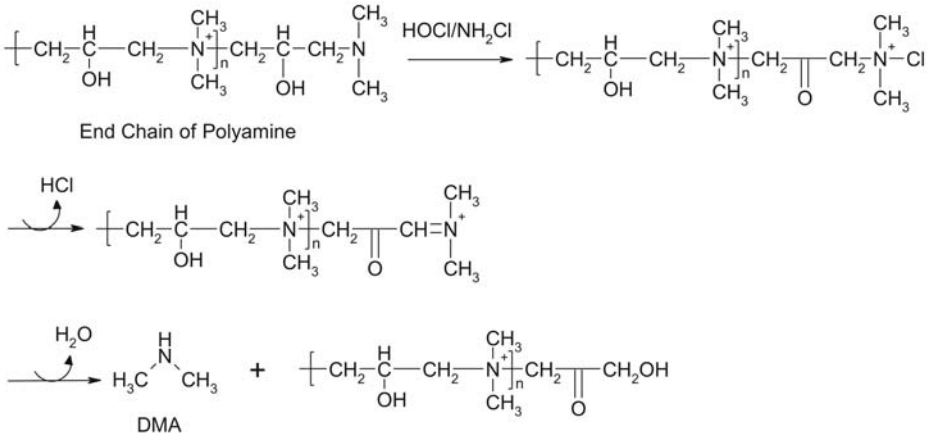


Figure 4. 9 The proposed degradation mechanism of polyamine after monochloramination.

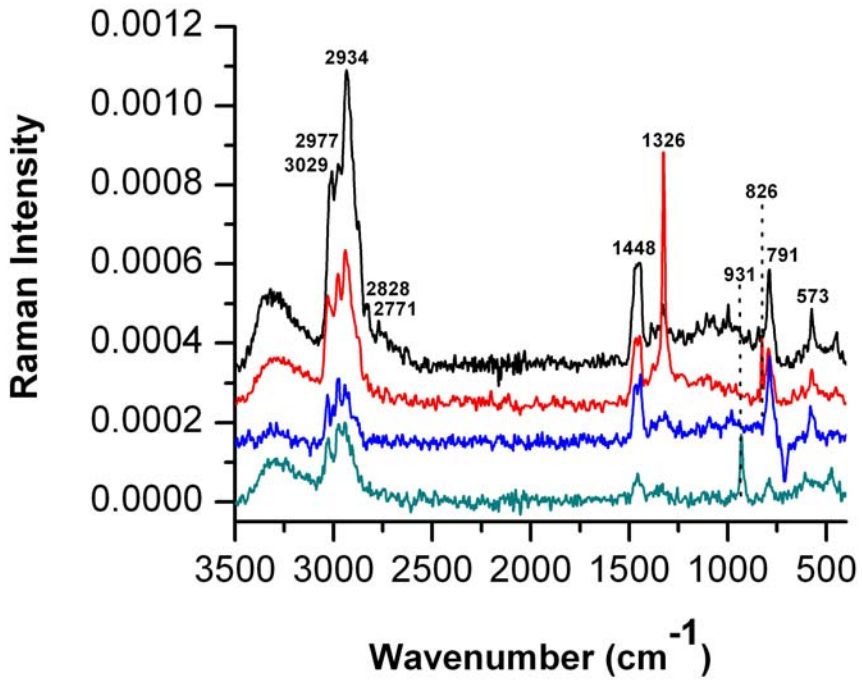


Figure 4. 10 FT-Raman spectra of polyDADMAC react with different oxidants for 24 h. Untreated polymer [black]; reacted with $NaNO_2$ [red]; reacted with NaOCl [blue]; reacted with NH2Cl [dark cyan]. The polymer and oxidants concentration are 1g/L.

Compared to Figure 4.6 (pH effect on degradation), it can be seen that there is no C= C signal after the oxidation reaction. Its absence indicates that there is further reaction with chlorine or monochloramine after the Hofmann elimination. The proposed pathway of oxidation is shown in Figure 4.7. Raman spectra of polyamine were recorded after oxidation with different oxidants

(Figure 4.11). The polymer sample (after reacting with NaOCl, blue line) was difficult to recover from solution, so the Raman signal is very weak. It can be seen that the peak at 2936 cm^{-1} (C-H asymmetric stretch in -CH_2OH) arises and the peak at 2831 cm^{-1} (C-H stretch in N-CH_2) disappears from the sample reacted with NH_2Cl, which is associated with cleavage of the polymer chain at the CH_2-N position by hydrolysis. The intensity of the peak at 1450 cm^{-1} decreases after interaction with NaOCl and NH_2Cl, which is associated with the C-H deformation in the N-CH_2 group. The new band at 931 cm^{-1} from the NH_2Cl is attributed to the C-O stretch in the newly formed alcohol group. A possible mechanism is that the polyamine releases dimethylamine after the reaction with NaOCl and NH_2Cl. Figure 4.9 shows the possible degradation pathway of the polyamine. The rleased DMA can react to form NDMA as shown in Figure 4.5.

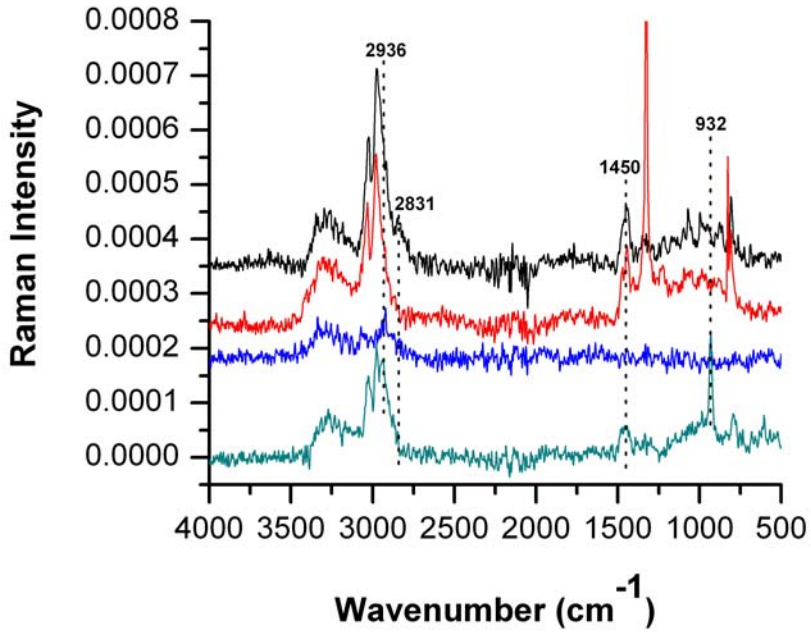


Figure 4. 11 FT-Raman spectra of polyamine react with different oxidants for 24 h. Untreated polymer [black]; reacted with $NaNO_2$[red]; reacted with NaOCl [blue]; reacted with NH_2Cl [dark cyan]. The polymer and oxidants concentration are 1g/L.

The polymer Degradation by monochloramination and NDMA analysis: To understand the relationship of polymer degradation with NDMA formation, a series of polymer samples were prepared for the monochloramination reaction at concentrations high enough for the IR/Raman measurement. The polymer samples were prepared at 1g/L with monochloramine was at 200 mg as Cl_2/L, which is less than that of oxidant effect experiments (1000 mg Cl_2/L). After the reaction, NDMA concentrations were determined by GC/MS. The polymer samples were recovered from the reaction mixture for the FT-IR and FT-Raman analysis to monitor the change of the chemical structure. PolyDADMAC samples showed changes in the C-H and C-N region after the monochloramination (Figure 4.12). In the IR spectra, a decrease in the peaks at 1478/1383 cm^{-1} (CH_3 deformation), 1268 cm^{-1} (CH_3 rocking) and 794 cm^{-1} (N-C stretch) indicates the leaving of the $N(CH_3)_2$ group. The arising of the peak at 1156 cm^{-1} is attributed to

the asymmetric C-O-C stretch. The peak at 1351 cm^{-1} is an unknown impurity in the sample. In the Raman spectra, the decrease at 1480 cm^{-1} (CH_3 asymmetric deformation) and 791 cm^{-1} (N-C stretch) supports the IR result of the $N(CH_3)_2$ group leaving. The arising of the peak at 932 cm^{-1} is attributed to the symmetric C-O-C stretch. The change of the C-C skeletal vibration at 573 cm^{-1} also supports the degradation mechanism outlined in Figure 4.7.

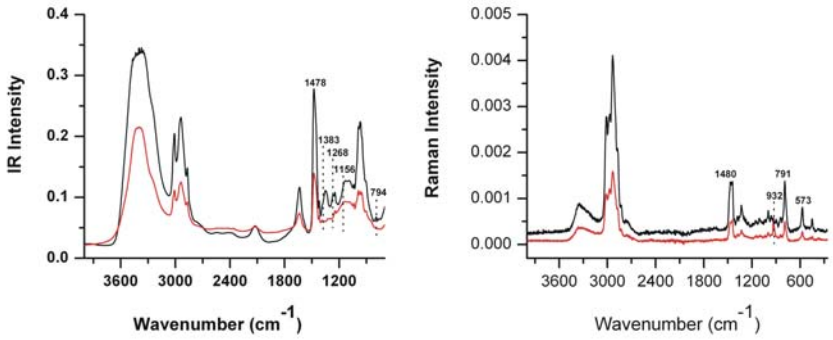


Figure 4. 12 FT-IR [right] and Raman [left] spectra of polyDADMAC before [black] and after [red] monochloramination. Polymer concentration is 1g/L and MCA concentration is 200 mg/L

For polyamine samples, a new peak at 1722 cm^{-1} emerges in the IR spectra (Figure 4.13) as a consequence of the oxidation of the OH group (Figure 4.9). And the peak at 1377 cm^{-1} from O-H in-plane deformation increases due to the formation of a new primary alcohol group after monochloramination. In the Raman spectra, it can be seen that a decrease in intensity of 1134 cm^{-1} (C-N stretch) and 1065 cm^{-1} (C-O stretch), support cleavage of the CH_2-N bond and oxidation of the OH group. The band at 948 cm^{-1} is an unknown signal. The CH/CH_2 rocking at 572/512 cm^{-1} shows the backbone change after oxidation by NH_2Cl. Compared to previous oxidant effect experiments, the absence of the symmetric C-O stretch at 931 cm^{-1} from the new alcohol group of this experiment could result from: (i) In this experiment lower amount of NH_2Cl (1/5 compared to Figure 4.11) is used; and, (ii) the peak at 931 cm^{-1} is buried in the peak of 948 cm^{-1}.

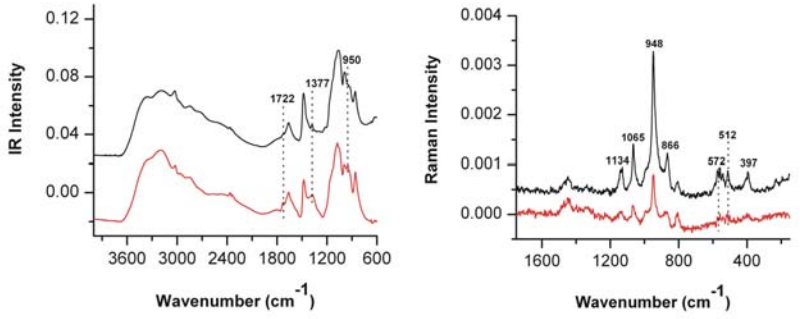


Figure 4. 13 FT-IR [right] and Raman [left] spectra of polyamine before [black] and after [red] monochloramination. Polymer concentration is 1g/L and MCA concentration is 200mg/L.

Furthermore, the reaction residue (monochloramine, MCA) and product (NDMA) were qualitatively determined by GC/MS method. It can be seen from Table 4.1 that the NDMA

amount after monochloramination is in the order of polyamine > polyDADMAC > PAM. After reaction polyDADMACs have similar amounts of residual MCA compared to PAMs after reaction but much more than that of polyamines. So there is more MCA involved in the reaction with polyamine and more NDMA produced after the reaction. Apart from chemical properties dealing with the microscopic structure of polymers, another consideration can be introduced regarding the mesoscopic structure of polymer chains.

Table 4. 1 NDMA formation and residual MCA from the reaction of 1 g/L polymers and 200 mg/L MCA

No.	Polymer Type	Polymer concentration (mg/L)	MCA_i* (mg/L)	MCA_f** (mg/L)	NDMA (μg/L)
1	PolyDADMAC	1000	200	32.5	81.3
2	PolyDADMAC	1000	200	36.0	85.9
3	PolyDADMAC	1000	No (control)		0.26
4	PolyDADMAC	1000	No (control)		0.24
5	PAM	100	200	26.0	5.17
6	PAM	100	200	28.0	5.40
7	PAM	100	No (control)		ND
8	PAM	100	No (control)		ND
9	Polyamine	1000	200	4.2	121.3
10	Polyamine	1000	200	5.0	120.3
11	Polyamine	1000	No (control)		0.51
12	Polyamine	1000	No (control)		0.64

* MCA_i: The initial concentration of monochloramine.

** MCA_f: The final concentration of residual monochloramine after 24 hrs.

It can be expected that the aliphatic straight chain structure in polyamines is more flexible than the ring structure in polyDADMACs. The conformation of the polymer chains was estimated by molecular computational modeling studies. PolyDADMAC and polyamine were put in periodic water box. After energy minimization and energy equilibration, it can be seen that the polyamine chain is more flexible and less bulky than that of polyDADMAC (Figure 4.14). The chain lengths of polyamine and polyDADMAC decrease to 49% and 90% of the initial structure, respectively. In the production run, the bending polyamine chain is open, exposing more reaction sites (quaternary ammonium groups) to the solution, while the bending polyDADMAC chain encloses more reaction sites inside the polymer chain, decreasing the chance of the polymer chain to meet other species in the solution. (The following production movies support this information: PAM_MD is the production run of polyamine, and PDM_MD is the production run of polyDADMAC). As the polyDADMAC chain is more rigid, we can expect that polyDADMAC is less active in solution because of limited mobility. This fact may provide additional clues to the reason for its different NDMA formation potential. More detailed discussion of this topic can be provided after further research involving characterization of polymer physical properties. It is quite interesting that there is only a very small amount of NDMA produced from cationic PAM. It can be seen from the IR/Raman results of pH dependence of PAM that part of the side chain containing a quaternary ammonium group was released into solution when the solution pH was

increased to 9. The NDMA formation mechanism involves chlorine reacting with the nitrogen atom on TMA followed by elimination of hydrochloric acid to form an iminium ion. Hydrolysis would results in the formation of TMA that could then react to form NDMA (Mitch and Sedlak, 2004a). However, the decomposition of choline (the released side chain of PAM) to release TMA is very slow even with a strong base in the solution. Heating of choline chloride at 60 ^{o}C in the presence of NaOH for 14 days would only produce TMA in ppm quantities (Chafetz and Philip, 1982). This explains why there is only a very small amount of NDMA produced from the reaction of cationic PAM with monochloramine.

The degradation of polymers with different MW by monochloramination: To understand the degradation of polymers with different molecular weight, a series of polymer samples were prepared for the monochloramination reaction at a concentration high enough for the IR/Raman measurement. The polymer samples were prepared at 1g/L with monochloramine was at 200 mg as Cl_2/L, which is less than that of in oxidant effect experiments (1000 mg Cl_2/L). The polymer samples were recovered from the reaction mixture for FT-IR and FT-Raman analysis to monitor changes of the chemical structure.

For PolyDADMAC samples, the tertiary amine group is absent in the highest MW polyDADMAC (Figure 15B, black) but is present after the monochloramination (Figure 15B, red), which indicates the break of one CH_2-N bond during the reaction. The tertiary amine group can be observed in the lowest MW polyDADMAC (Figure 4.15A, black) because the end group of the short polymer chain could be tertiary amine (Child, Kaa *et al.*, 2002). After monochloramination, evidence of the amine group leaving is confirmed by disappearance of the peak associated with the tertiary amine (Figure 4.15A, red).

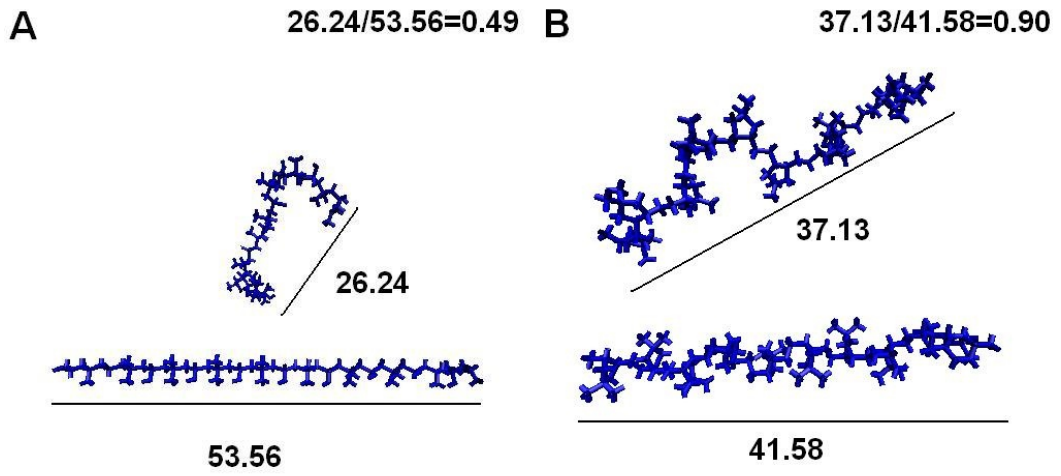


Figure 4. 14 Molecular structure of polyamine (A) and polyDADMAC (B) at initial state [lower] and energy equilibrated state [upper] from molecular dynamic simulation of polymers (10 monomer units) in water. The molecular chain length was monitored with ViewLite by measuring the distance of the head of the first monomer units and the tail of the last monomer units.

The change of CH_2 and CH_3 stretching and bending also agree with this hypothesis. In the DADMAC monomer, it is hypothesized that the allylic double bonds in allyl group could act as a monochloramine sink by being subject to electrophilic attack by monochloramine, which is supported by the decrease of C-H stretching of the C=C and increase of C-H bending from the aliphatic group (Figure 4.15C, black and red). However, the LC-MS data in Figure 3.14 shows that the monomer concentration slowly decreases upon addition of monochloramine, which indicates that the reaction of DADMAC monomer is concentration dependent as the Raman studies are based on reaction with high concentration of monomer (1000 times higher than the reaction performed in Figure 3.14).

The tertiary amine group is absent in the lower and highest MW polyamine (Figure 4.16B, black; Figure 4.16C, black) and is present after the monochloramination (Figure 4.16B, red; Figure 4.16C, red), which indicates the break of one CH_2-N bond during the reaction. The tertiary amine group can be observed in the lowest MW polyamine (Figure 4.16A, black) because the end groups of the short polymer chains should be tertiary amines, and are at detectable concentrations. After monochloramination, the tertiary amine group disappears which indicates its loss from the chain end (Figure 4.16A, red). Because of the weak signal observed, this hypothesis is confirmed by the IR spectra of the polymer samples (Figure 4.17). Also, in the IR spectra, $CH{=}CH_2$ peak information indicates the oxidation for C=C bond happens (see the other pathway added in Figure 4.7). The decrease of the CH_2-N and CH_3 peaks in all spectra (Figure 4.16, black vs. red) supports the hypothesis that part of the amine groups leaves the polymer chain after the reaction.

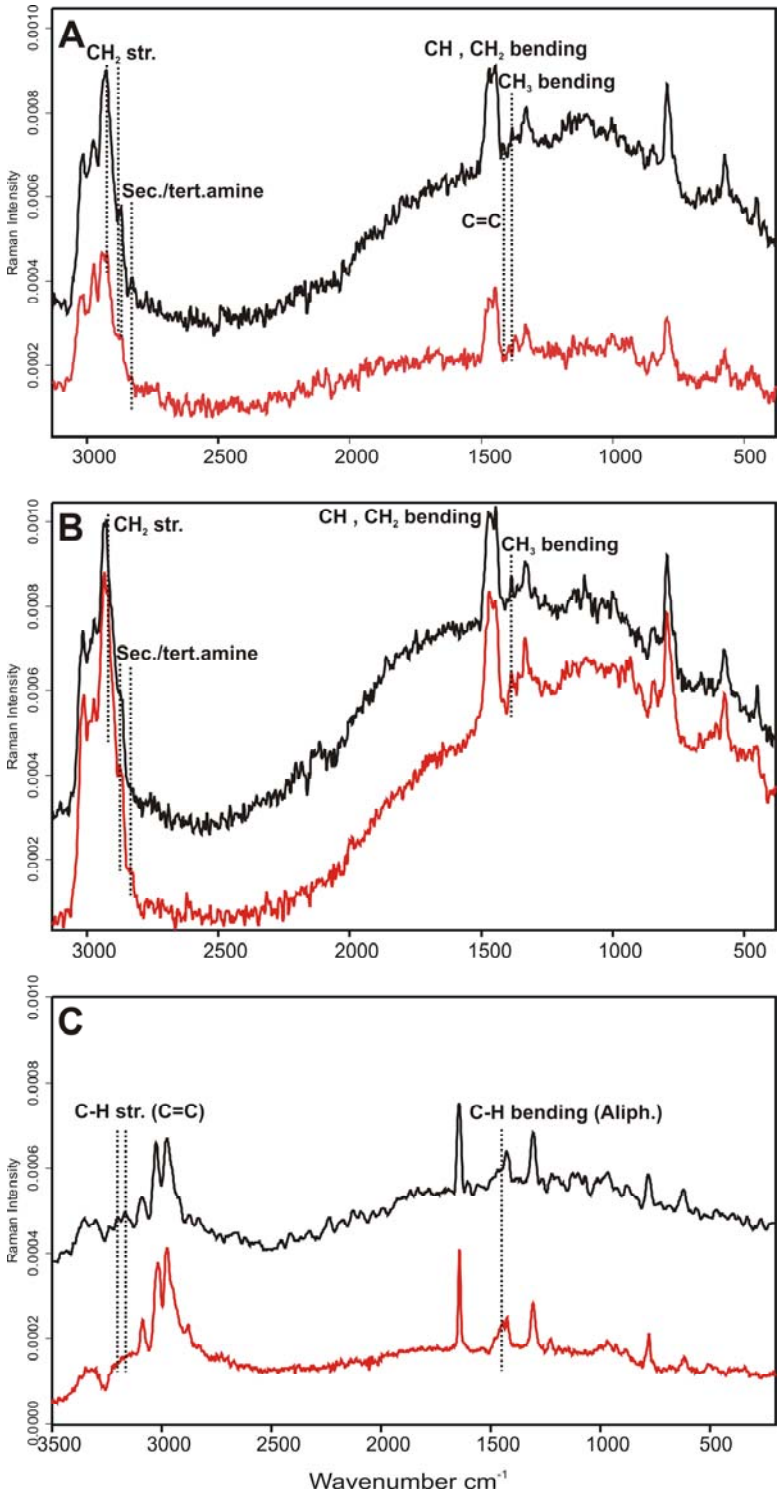


Figure 4. 15 (A): Raman spectra of lowest MW polyDADMAC before [black] and after [red] monochloramination. (B): Raman spectra of highest MW polyDADMAC before [black] and after [red] monochloramination. (C): Raman spectra of DADMAC monomer before [black] and after [red] monochloramination

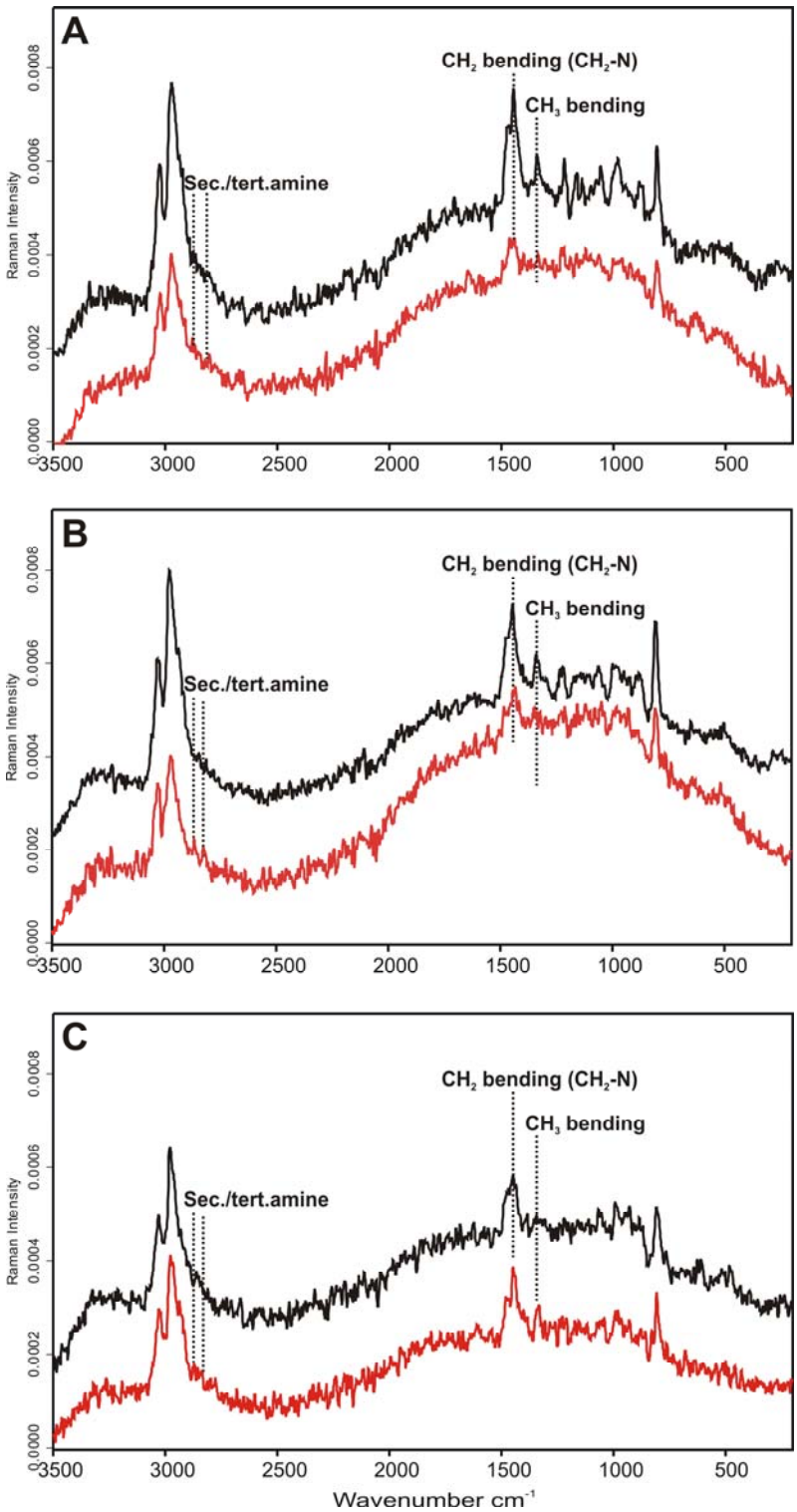


Figure 4. 16 (A): Raman spectra of lowest MW polyamine before [black] and after [red] monochloramination. (B): Raman spectra of lower MW polyamine before [black] and after [red] monochloramination. (C): Raman spectra of highest MW polyamine before [black] and after [red] monochloramination.

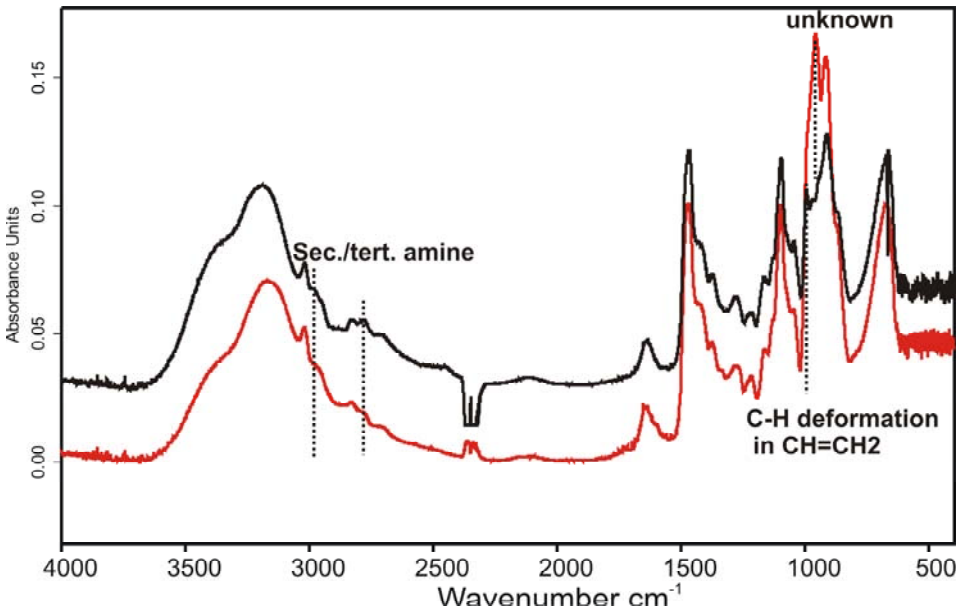


Figure 4. 17 IR spectra of lowest MW polyamine before [black] and after [red] monochloramination.

5 Summary of Results

General Screening of NDMA Formation Potential of SNF Polymers: Four types of water treatment polymers (cationic polyacrylamide (cationic PAM), aminomethylated polyacrylamide (Mannich), poly-diallyldimethylammonium chloride (polyDADMAC) and polyamine) were evaluated in aqueous solutions at circumneutral pH and room temperature to form *N*-nitrosodimethylamine (NDMA) upon exposure to nitrite, free chlorine, monochloramine or chlorine dioxide. High dosages of polymer and oxidant and long reaction times were employed in order to assess the maximum potential to form NDMA. In general, the NDMA formation potential followed the trend of Mannich >> polyamine > polyDADMAC > cationic PAM. The concentration of the well-known NDMA precursor dimethylamine in the polymer samples (without exposure to oxidant) also followed the similar trend above. Among the four oxidants, reactions with monochloramine resulted in the highest level of NDMA while reactions with chlorine dioxide results in the lowest level of NDMA.

Mechanism of NDMA Formation from Polyamine and PolyDADMAC: Reaction of polyamine and polyDADMAC with monochloramine can result in polymer degradation and release of DMA, evident by the increase in DMA concentration after monochloramination in many cases. The NDMA formation potential of the polymers depends strongly on released DMA from polymer degradation rather than on the initial residual DMA in the polymers. The results of pH effect also support the importance of polymer degradation and DMA release on the overall NDMA formation potential, in which at pH values where higher NDMA formation was observed, more DMA release was also found. Furthermore, the results show that degradation of polymer and formation of NDMA are both most significant at circumneutral pH range (near pH 8) that is commonly encountered in water and wastewater treatment plants. Kinetic studies indicate that NDMA formation from the polymers has slow kinetics and the reactions can continue for many days to yield more and continue to release NDMA.

Polyamine is more easily degraded during monochloramination and exhibits greater NDMA formation potential than polyDADMAC. From examining the effect of polymer purification, the effect of polymer molecular weight, and reactions involving model polymer intermediate compounds, the results combined point to the conclusions that tertiary amine chain ends of polyamines play a major role in polyamine's NDMA formation potential. In contrast, degradation of quaternary ammonium groups and residual DMA-containing intermediates such as allyldimethylamine are the significant factors in polyDADMAC's NDMA formation potential. The higher NDMA formation potential of polyamine compared to polyDADMAC is due to: (i) the presence of tertiary amine rather than quaternary ammonium end groups that are more reactive to monochloramine and more easily degraded to yield DMA; (ii) a higher fraction of DMA moieties per mass basis in the case of polyamine; and, (iii) the greater flexibility of polyamine chains that may allow better interaction with monochloramine oxidant in solutions.

NDMA Formation from SNF Polymers under Relevant Water Treatment Conditions: In most experiments that were conducted under conditions representative of real water treatment plants (in contrast to the mechanistic studies in which reactions were conducted at conditions that maximize NDMA formation), coagulation with Alum and either polyamine or polyDADMAC

yielded NDMA at levels lower than the current notification levels in CA (i.e., 10 ng/L) and Canada (i.e., 9 ng/L). This was true even when the employed polymer concentration was 2 to 3 times higher than what's typical at drinking water treatment facilities. Overall, the results indicate that SNF's polyamines and polyDADMACs, when employed under typical conditions at drinking water treatment plants, are unlikely to cause NDMA formation that exceeds the level of current concern.

The temperature and pH effect is likely to attribute to the degradation of cationic PAM. PolyDADMAC and polyamine are stable when the solution temperature ranges from 22 ^{o}C to 62 ^{o}C. With pH increase of the polymer solutions, the structure of polyDADMAC and polyamine changes. The observation of NDMA as a reaction product of polyDADMAC and polyamine reaction with monochloramine involves the breakdown of the quaternary ammonium groups. The quaternary ammonium groups in the polymer are expected to be bound primarily in the cyclic structure (polyDADMAC) or polymer backbone (polyamine). The pH effect for polyDADMAC and polyamine is likely to contribute to the breakage of CH2-N bonds by Hofmann elimination to form a tertiary amine. However, it is possible that the non-cyclic amines or tertiary amine are present. These sites are less stable and easy to be attack by chlorine, which would result in the release of dimethylamine. The slow decomposition rate of the quaternary ammonium side chain of cationic PAM may explain why there is much less NDMA produced from PAM compared to polyDADMAC and polyamine. The reason that polyamine produce more NDMA than polyDADMAC involves the fact that the aliphatic straight chain structure of polyamine is more flexible than the ring structure of polyDADMAC. The experimental results on the polymer samples with different molecular weights indicate that the polymer with the lowest molecular weight is more active than the polymer with the highest molecular weight. Differences in the mobility and the number of active end groups (e.g. tertiary amine groups) could contribute to the different reactivities of the polymers.

This study was conducted using higher dosages of polymers and monochloramine and longer reaction times than those of typical water treatment conditions for the purpose of gaining mechanistic insight of NDMA formation from water treatment polymers. Considering that NDMA formation is quite dependent upon the amount of precursors and that chloramination typically occurs after coagulation, sedimentation and filtration and thus the residual polymer concentration in water is expected to be very low, whether the polymers contribute significantly to the overall NDMA formation at actual water and wastewater treatment systems is still left to be determined by additional tests.

Strategies to Minimize NDMA Formation Potential of SNF Polymers: Purification of polymers decreases NDMA formation potential to some extent by removing residual DMA and low MW oligomers that are potent NDMA precursors from the solution. However, it does not eliminate NDMA formation potential of the polymers since degradation of polymers to release DMA still occurs when exposed to monochloramine. Capping the tertiary amine chain ends of polyamine with quaternary ammonium functional groups [QUAT 188] effectively reduced the NDMA formation potential of polyamine to the level of polyDADMAC. In contrast, manufacturing polyDADMAC in mild conditions and chain end capping was not very effective

in reducing polyDADMAC's NDMA formation potential. Addition of salt to the solution also reduced the NDMA formation potential of both polyamine and polyDADMAC. The reduction in NDMA formation is increased with higher salt concentration.

From the mechanistic insight of NDMA formation obtained from this study, it can be recommended that: (i) if there are several choices of polymers for the desired water treatment, the introduction of other comonomers into the polymer structure in order to reduce DMA moieties without deteriorating its original function can be one alternative; and, (ii) the polymer degradation mechanism at the molecular level can be done by establishing a theoretical model for the polymer system with molecular dynamic simulation. Some suggestions for such modeling studies are as follows:

- Understanding the polymer-polymer interaction by putting more polymer units in the box. The coagulation or dispersion of polymer chain could be observed.
- NH2Cl can be included in the modeling system to see the electrostatic interaction between polymers and NH2Cl. It will get a more clear idea of the mechanism at reaction level.
- Experiments for polymers with different MW to understand the NDMA analysis results: NDMA amount: lowest MW>lower MW> highest MW.
- Experiments for polymers in different concentration. This would require more computational time to build and calculate large system. In order to get the system close to water plant dose, a very large water box needs to be created.
- NDMA formation potential test as in this study can be added as a part of toxicity and stability test after a new polymer is made up.

6 Future Studies

During a project meeting on April 22, 2007 the *MESL* research group recommended the following studies as an extension of the current study which will be completed during June 2007.

- **Study of Breakdown Mechanisms:**
  - Linking polymer breakdown potential with breakdown mechanisms;
  - Structural modification of polymers to reduce breakdown potential;
  - Polymers by different manufacturers;
  - Other types of polymers; and,
  - Other nitrosamines of concern (6 in EPA UCMR2 program).

- **Study of Polymer Behavior at Treatment Plants:**
  - Scalability of our results;
  - Tracing polymer and DMA release through treatment processes (bench-scale & pilot-scale);
  - Impact of source water conditions on polymer breakdown potential and NDMA formation (bench-scale & pilot-scale – site specific analysis);
  - Risk based analysis of site specific health effects studies (site specific analysis); and,
  - Interaction of polymers with membranes and potential for forming precursors.

- **Predictive Tools:**
  - Raman Specs. library can be set up for SNF use in their laboratories;
  - Molecular modeling for polymers' properties and reactions under water treatment-relevant conditions; and,
  - Molecular modeling as predictive tool for rational polymer modification and design.

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