Mechanistic Insight for the *N*-Nitrosodimethylamine (NDMA) Formation Potential of Amine-based Water Treatment Polymers

Sang-Hyuck Park[a], Shuting Wei[b], Boris Mizaikoff[b], Amelia E. Taylor[c], Mustafa Aral[a], and Ching-Hua Huang[a]

[a] School of Civil & Environmental Engineering, GT

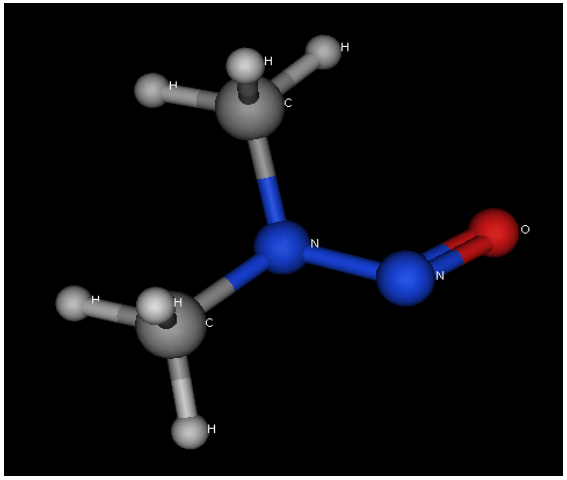
[b] School of Chemistry & Biochemistry, GT

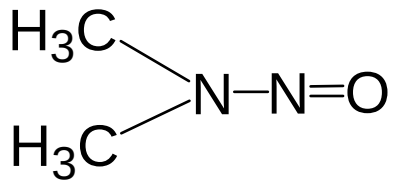
[c] Polychemie Inc., a subsidiary of SNF

March 29, 2007

Georgia Institute of Technology

Introduction - NDMA





***N*-nitrosodimethylamine (NDMA)**

- **An emerging disinfection by-product (DBP) generated during chlorine-based disinfection**
- **Formation mechanism can be explained by UDMH oxidation-based pathway or specialized nitrosation pathway rather than traditional nitrosation pathway**

(Mitch & Sedlak, 2002; Choi & Valentine, 2002, 2003; Schreiber & Mitch 2005, 2006)

Introduction - NDMA

- **Reasonably anticipated to be a human carcinogen**
  (National Toxicology Program in DHHS, 2004)
- **More toxic and challenging to detect than traditional DBPs**

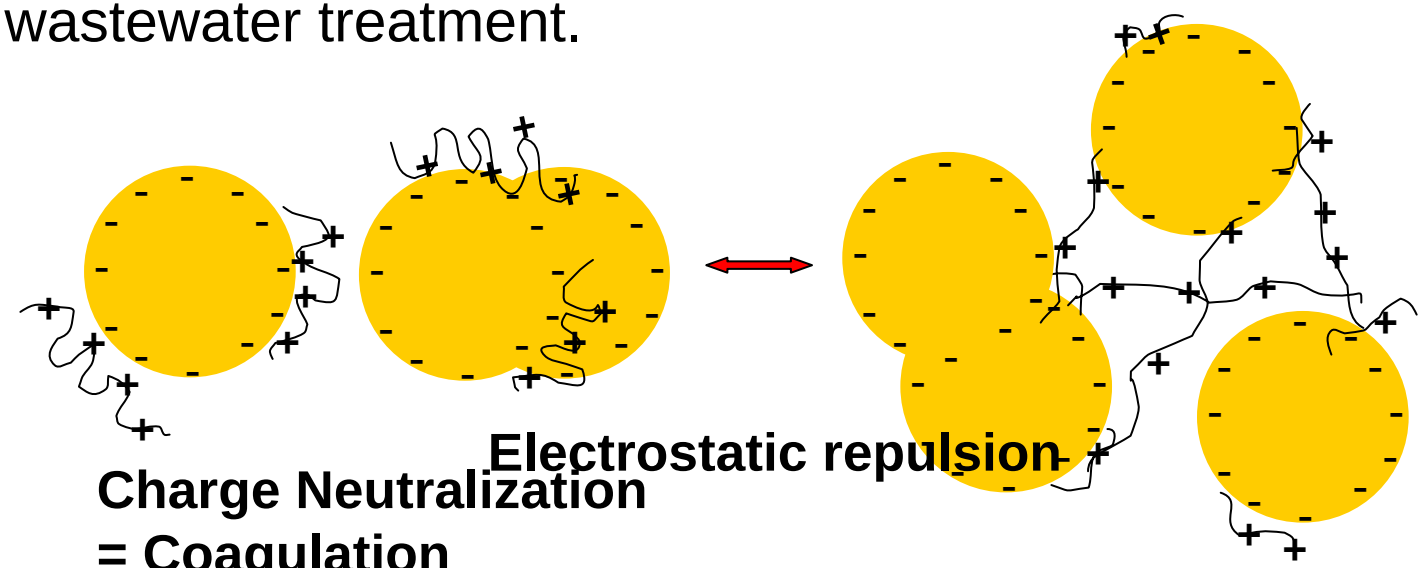
EPA DBP regulations	MCL (µg/L)
Total THMs	80
5 Haloacetic acids	60
Bromate	10
Chlorite	1000

NDMA advisory guidelines	Conc. (µg/L)
10^{-6} Cancer Risk Level (EPA)	0.0007
Notification Level (CA)	0.010
Public Health Goal (CA)*draft	0.003
MAC (Ontario, Canada)	0.009

- **Listed in UCMR 2 (Unregulated Contaminant Monitoring Regulation) for drinking water systems (US EPA, 2005)**

Introduction - Water Treatment Polymers

• Used to help separate particles from water in coagulation, flocculation and sludge dewatering in drinking water and wastewater treatment.



Charge Neutralization
= Coagulation

Electrostatic repulsion

Intermolecular Bridging
= Flocculation

e.g. Coagulants: polyDADMAC, polyamine,
Flocculants: Mannich polymer, cationic polyacrylamide

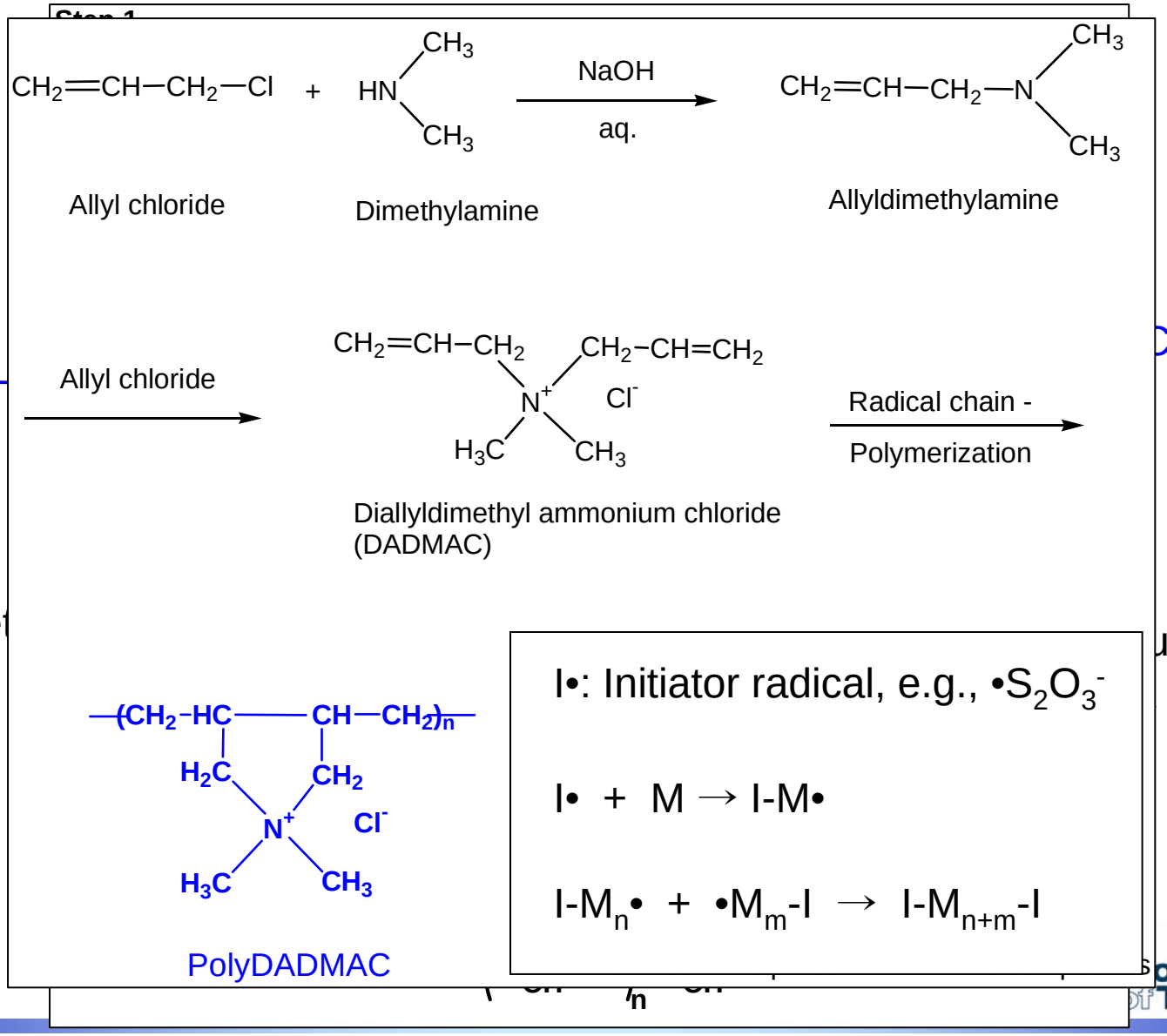
Research Statement

- Amine-based water treatment polymers have recently been suggested as NDMA precursors because they contain dimethylamine-based functional groups in their structures

Research Objectives

- To understand mechanistically how NDMA may form from amine-based water treatment polymers during disinfection processes.
- To develop means to reduce NDMA formation potential of amine-based water treatment polymers

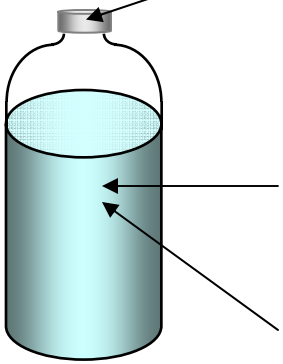
Materials and Methods



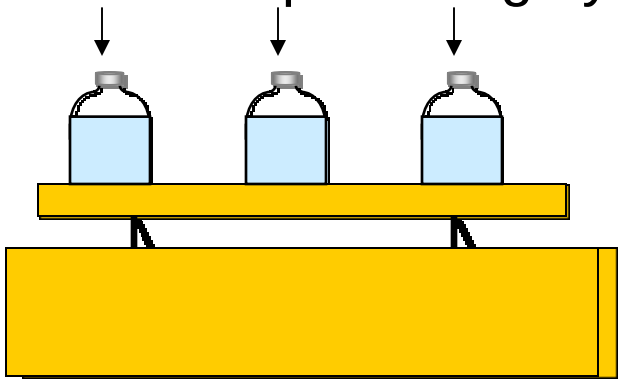
Poly(dimet ... um chloride):

Materials and Methods (continued)

Experimental set-up



- Buffers for pH control : pH 7.5 and pH 5 – 9
  (pH 5: acetate, pH 6: bicarbonate,
  pH 7-8: phosphate, and pH 9: borate)
- Polymers and intermediate compounds:
  0.5-10 mg/L as active
- Preformed monochloramine: 4 - 10 mg as Cl_2/L
- Reaction quenching by ascorbic acid



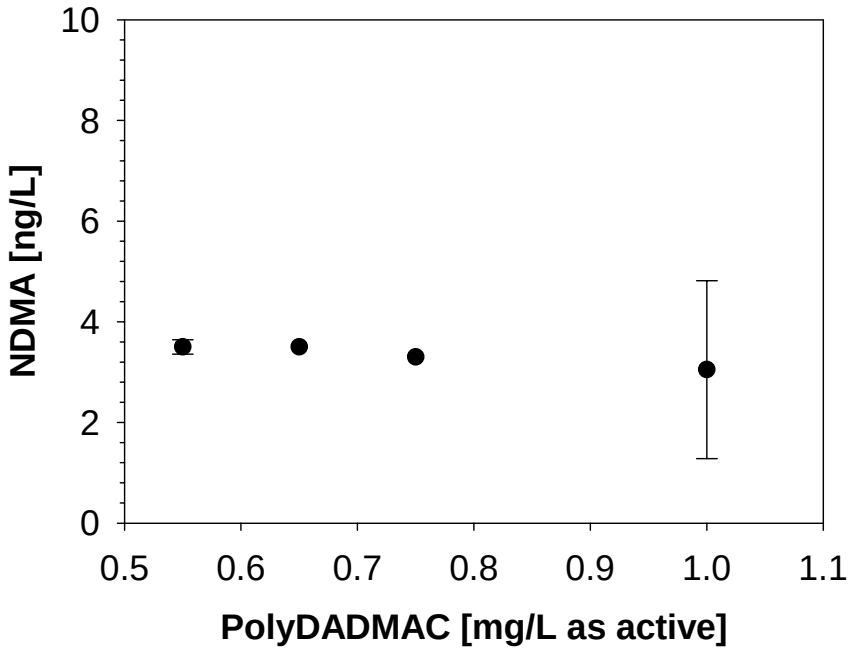
- Reaction for 24 hrs
  or other given times

Materials and Methods (continued)

Analytical Methods

- **NDMA:** Solid Phase Extraction (SPE) → GC/MS
- **DMA:** Derivatization →Liquid Liquid Extraction (LLE) → GC/MS
- **Polymer intermediate compounds:** LC/MS
- **Free chlorine and monochloramine:** DPD-FAS titration
- **Polymer structure analysis:** FT-IR and Raman spectroscopy

Results (1): NDMA formation potential tests in conditions similar to water treatment plants



Test conditions:

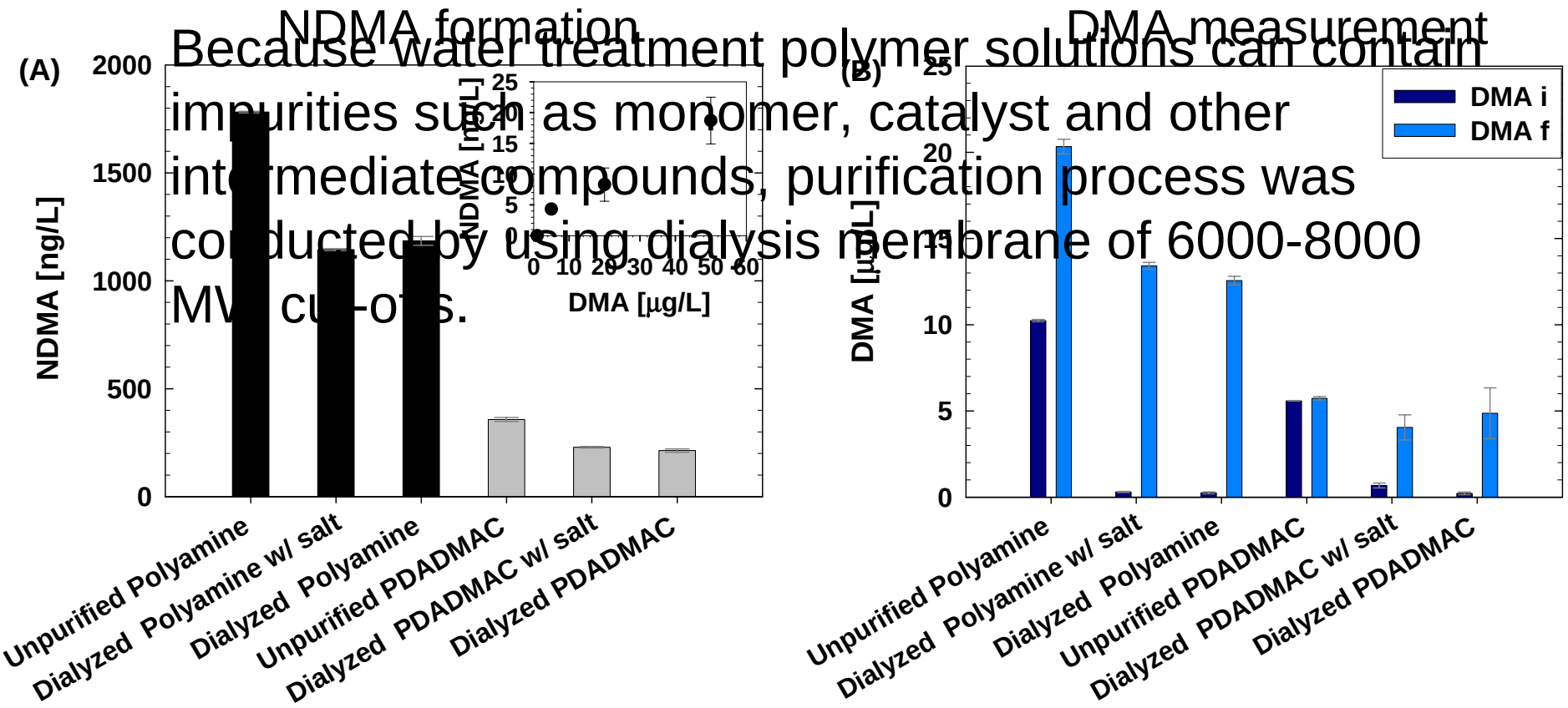
- Coagulation: raw waters with 19-37 ppm alum and varying amount of polyDADMAC
- Monochloramine: 4 mg as Cl_2/L
- Chloramination time: 2 hrs
- pH 7.9 and 23 °C

Mechanistic Study Outline

- Effect of polymer purification
- Effect of pH
- Polymer structure change analysis during chloramination (FT-IR & Raman)
- Effect of molecular weight of polymers
- Polymer intermediate compounds
- Comparison of NDMA formation potential of polyamine and polyDADMAC

Results (2): Effect of Purification

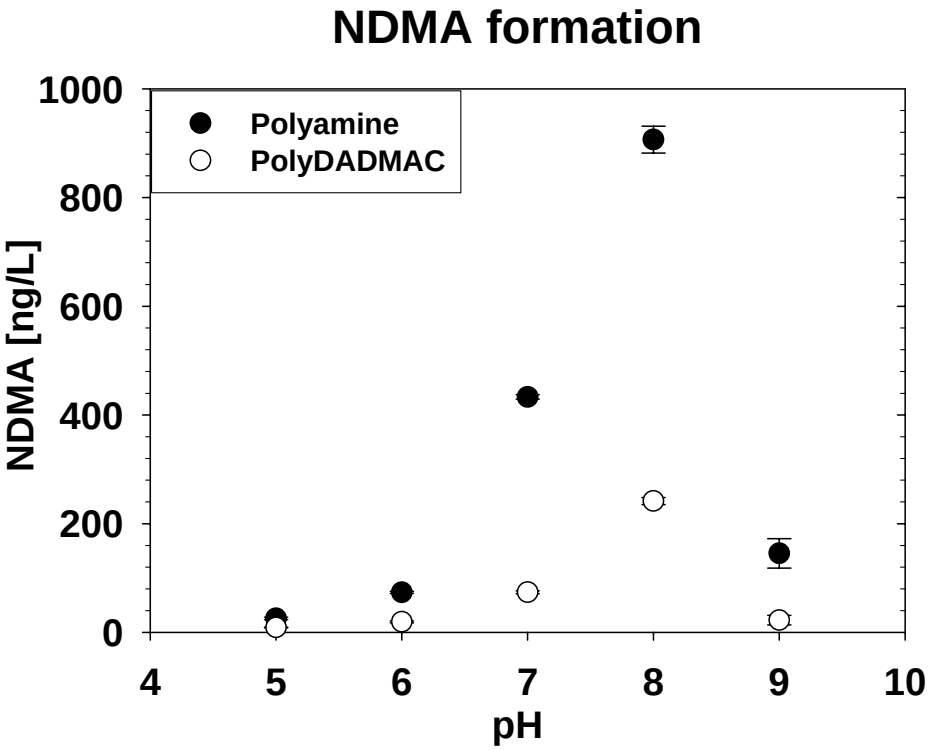
Because water treatment polymer solutions can contain impurities such as monomer, catalyst and other intermediate compounds, purification process was conducted by using dialysis membrane of 6000-8000 MW cut-offs.

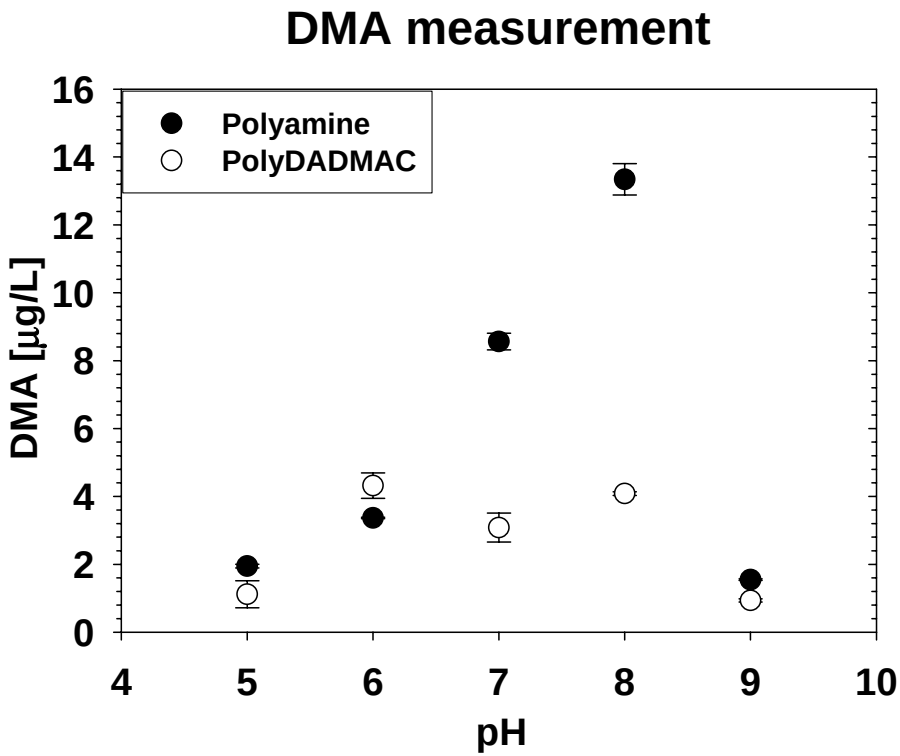


Reaction conditions:

- Polymer: 10 mg/L as active ingredient
- Monochloramine: 10 mg as Cl_2/L
- Reaction time: 24 hrs at pH 7.5, 23°C

Results (3): Effect of pH





Reaction conditions

- Polymer: 10 mg/L of purified polymers as active ingredient
- Monochloramine: 10 mg as Cl_2/L
- Reaction time: 24 hrs at pH 5 – 9, 23°C

Results (4)

Polymer Structure Analysis by FT-IR and Raman Spectroscopy

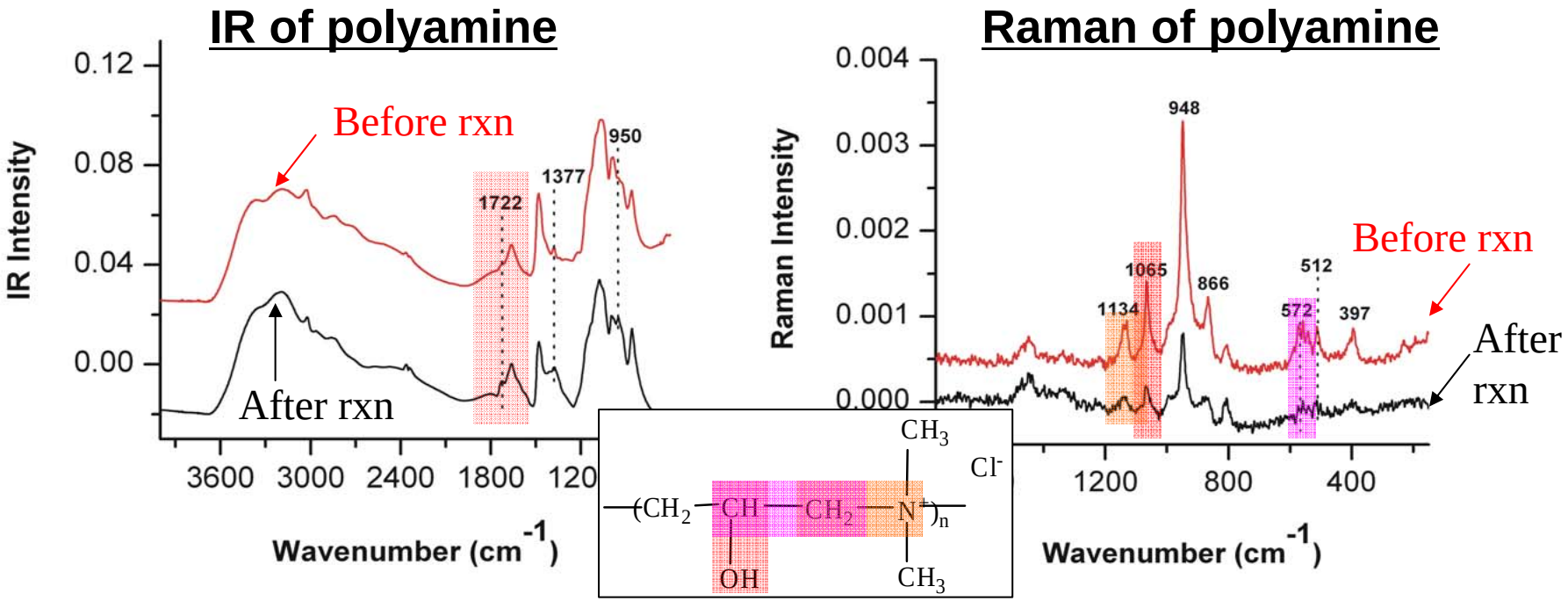
High concentration set-up for polymer structure analysis:

1 g/L polymer + 200 mg/L MCA for 24 hrs at pH 7.5

NDMA analysis

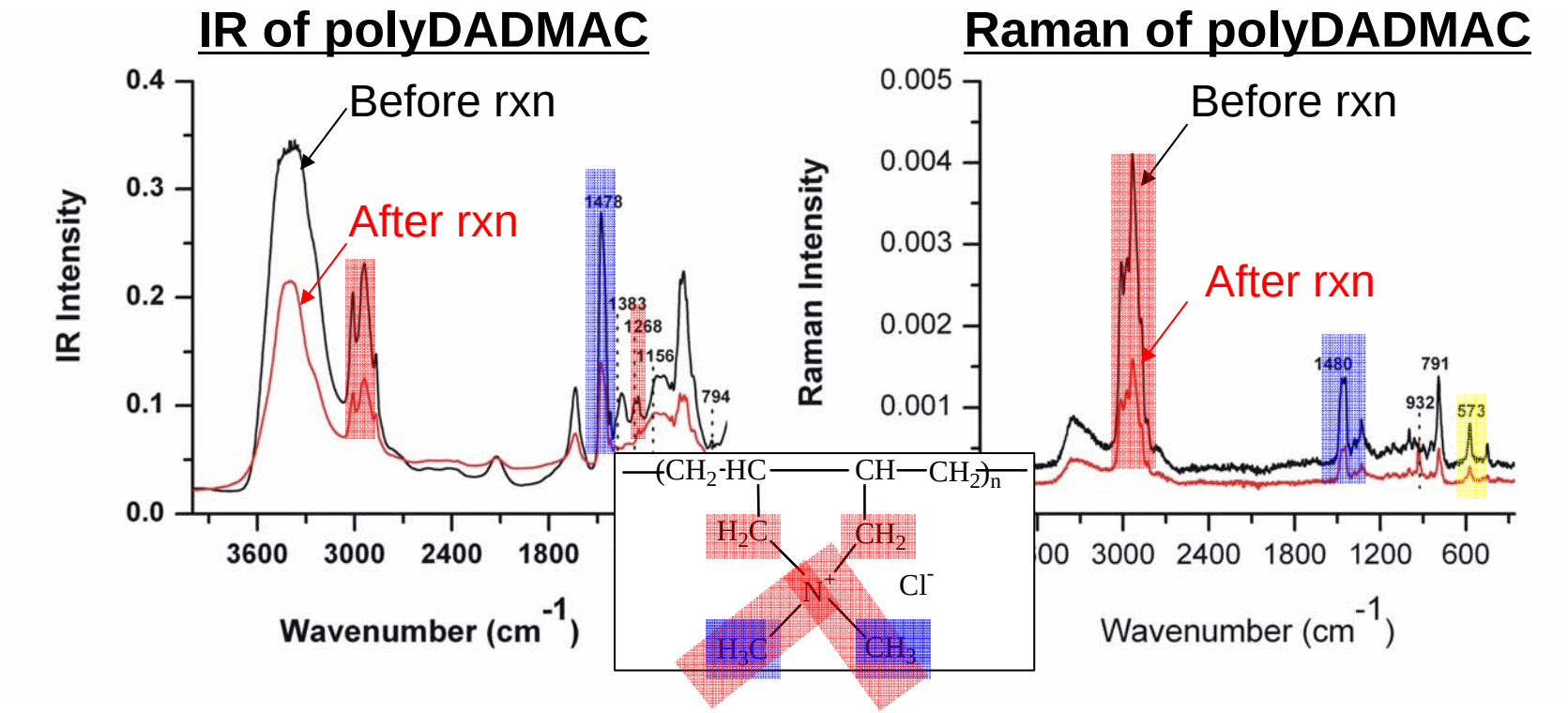
- Drying and other pretreatment for IR and Raman analysis
- Observation of polymer structure change before and after reactions by IR and Raman

Results (4) (Continued)



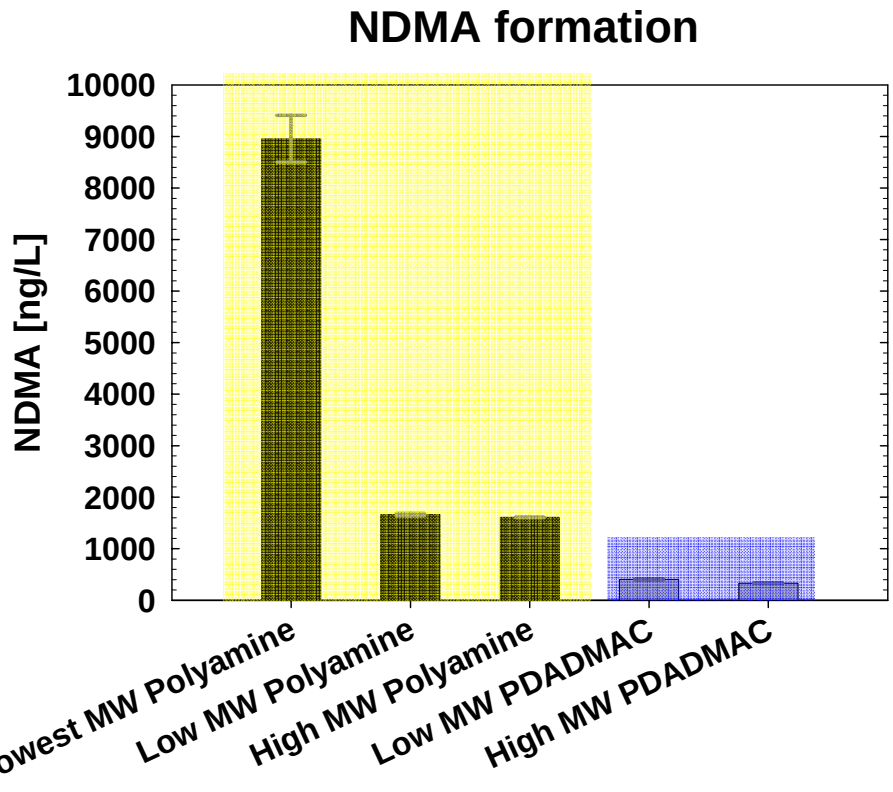
- *Oxidation of CH-OH group*: occurrence of C=O band (1722 cm^{-1}) in IR; decrease of C-O stretching (1065 cm^{-1}) in Raman.
- *Cleavage of CH_2-N bond*: decrease of C-N stretching (1134 cm^{-1}) in Raman.
- *Polymer chain change*: decrease of 572/512 cm^{-1} (CH/CH_2 rocking) in Raman.

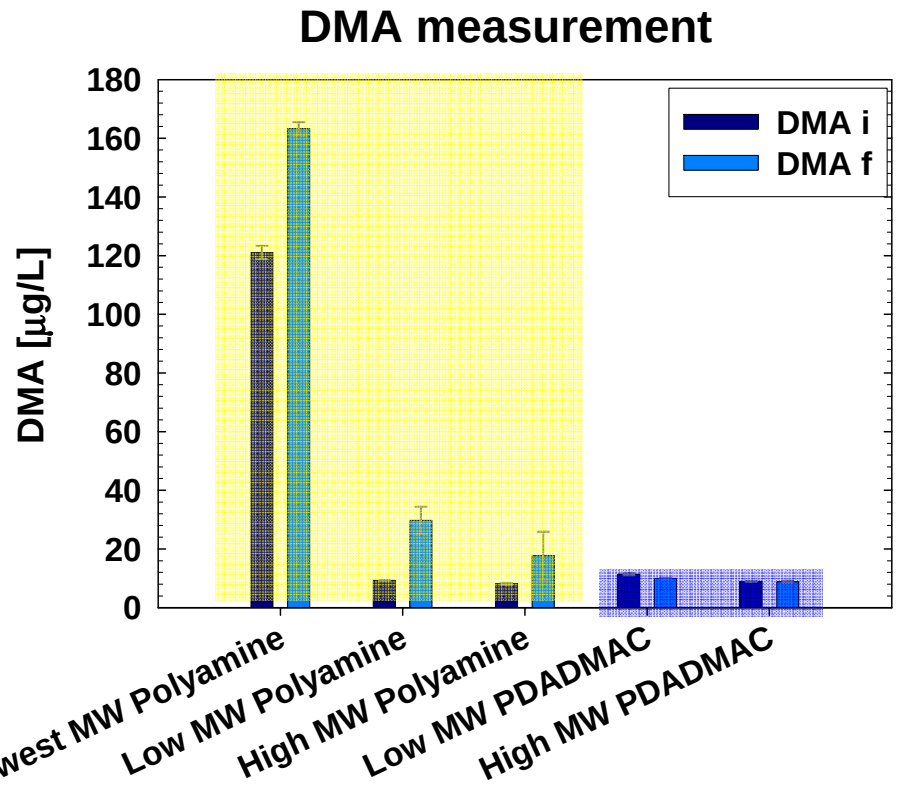
Results (4) (Continued)



- *Cleavage of $N(CH_3)_2$ group*: decrease of CH_3 deformation (1478 cm^{-1}), CH_3-N stretching (1268 cm^{-1}) and CH_2-N stretching (794 cm^{-1}) in IR; decrease of CH_3 asymmetric deformation (1480 cm^{-1}) in Raman.

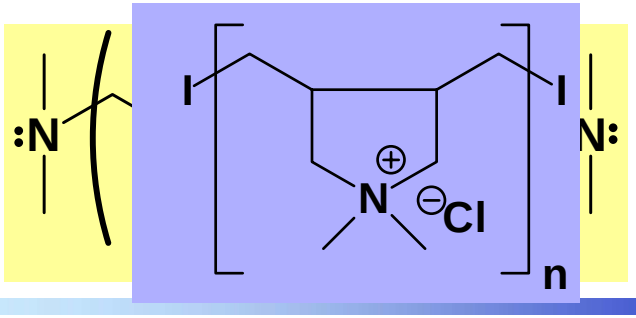
Results (5): Effect of Molecular Weight



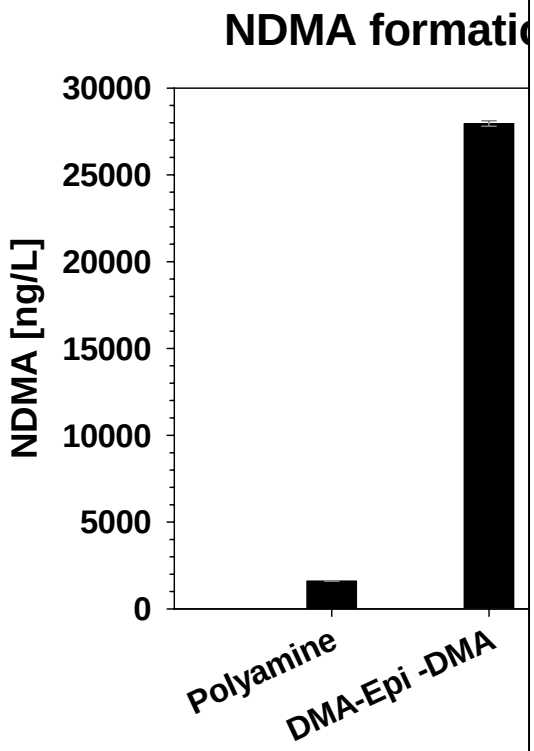


Reaction conditions

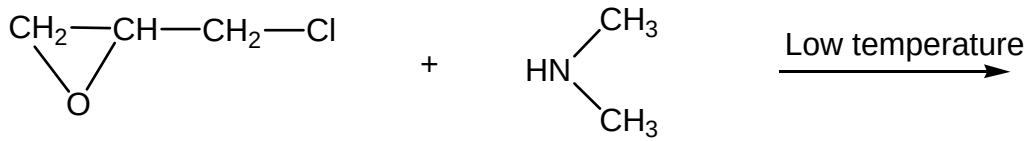
- Polymer: 10 mg/L as active ingredient
- Monochloramine: 10 mg as Cl_2/L
- Reaction time: 24 hrs at pH 7.5, 23°C



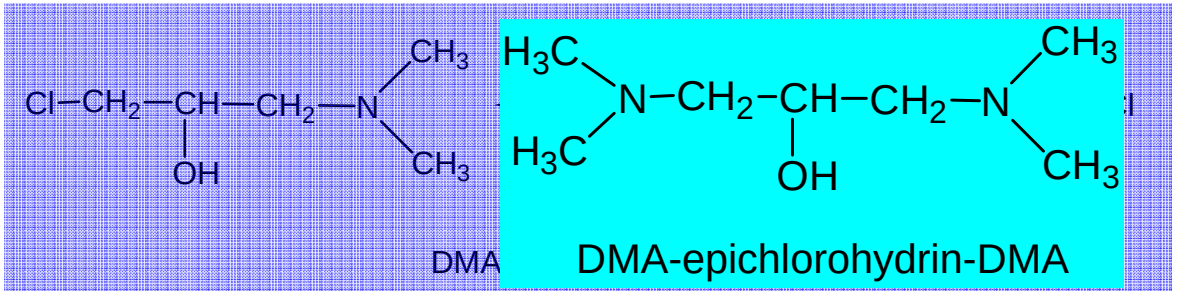
Results (6): Polyamine Intermediate Compound



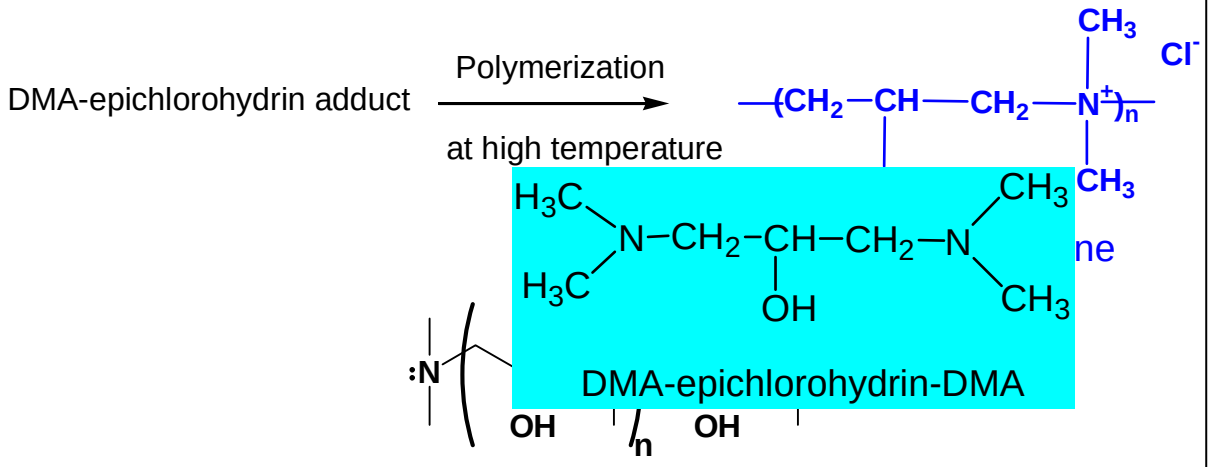
Step 1



Epichlorohydrin + Dimethylamine



Step 2

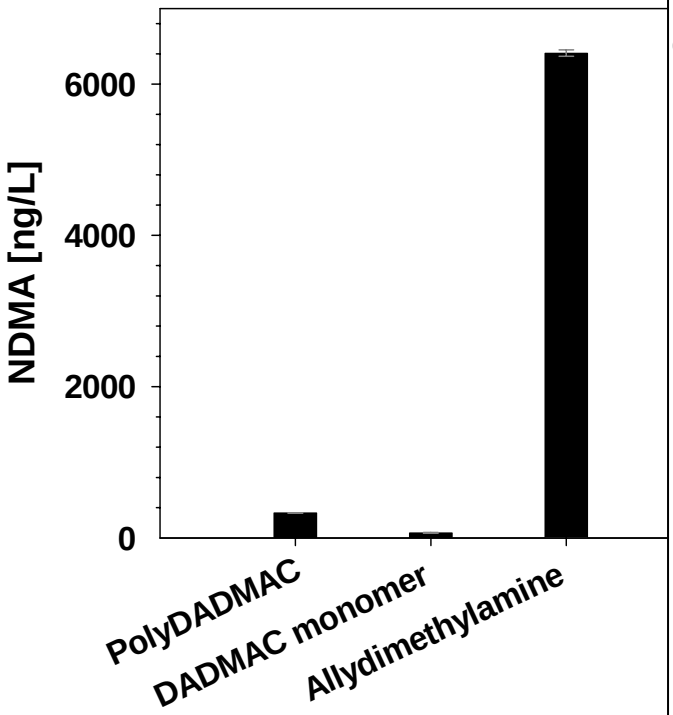


Reaction conditi

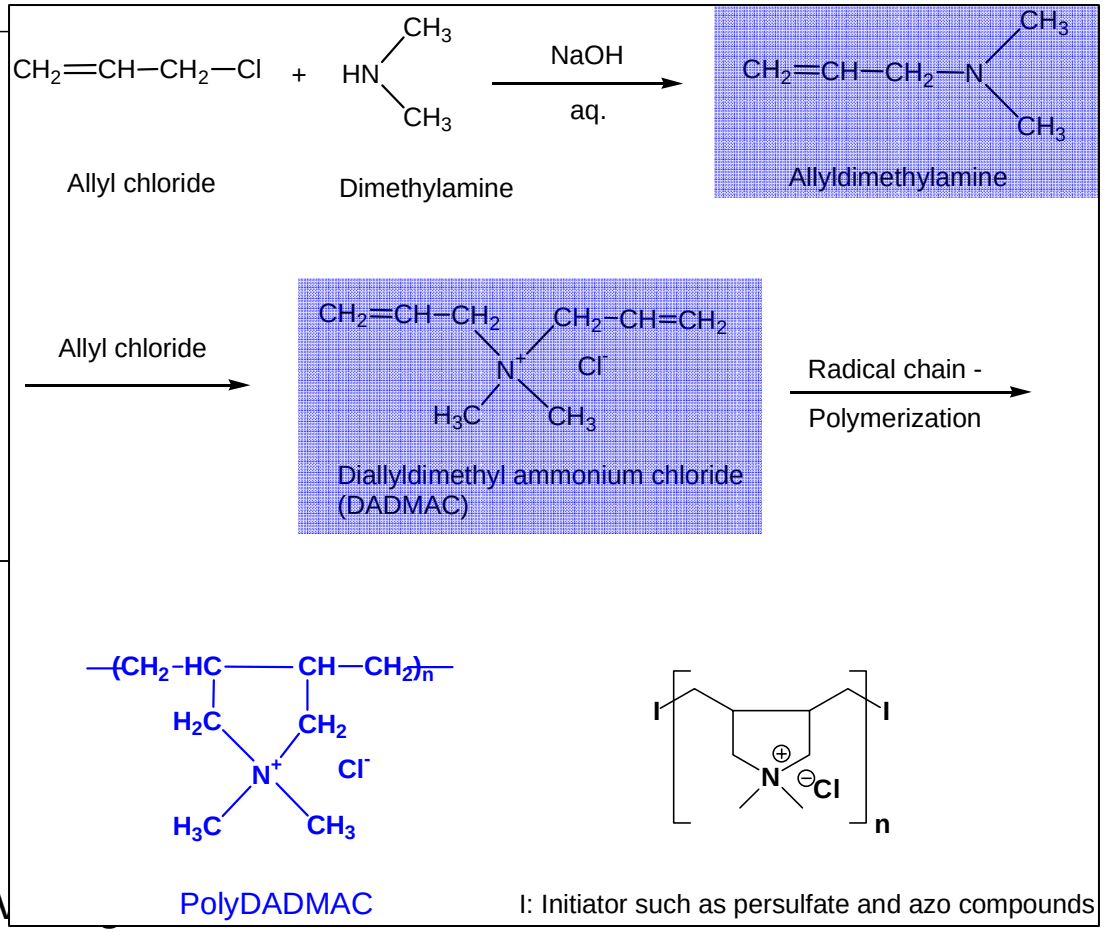
- Polymer: 10 mg/L
- Intermediate com
- Monochloramine:
- Reaction time: 24

Results (7): PolyDADMAC Intermediate Compounds

NDMA formation



DMA measurement



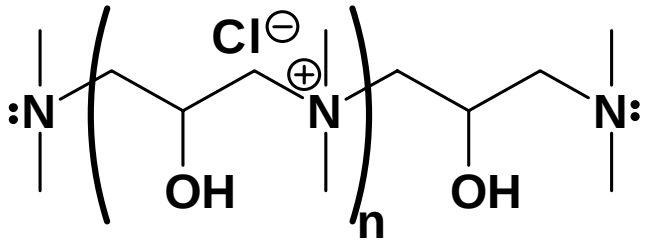
Reaction conditions

- Polymer: 10 mg/L as activ
- Intermediate compound: 10 mg/L
- Monochloramine: 10 mg as Cl_2/L
- Reaction time: 24 hrs at pH 7.5, 23°C

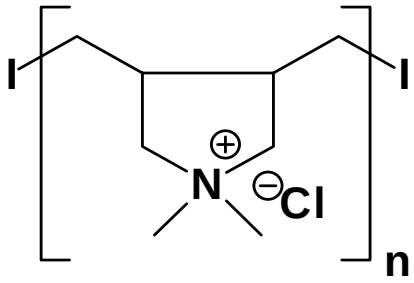
Georgia Institute of Technology

Why does polyamine produce more NDMA than polyDADMAC?

1. Polyamine has tertiary amine at the end of polymer chain.



Polyamine



PolyDADMAC

2. Repeating unit of polyamine has higher NDMA formation potential than that of polyDADMAC.

3. Polyamine has less rigid polymer chain than polyDADMAC so that polyamine is more flexible and moves more freely in aqueous solution. This may give more chance to react with monochloramine.

Conclusions

- This study was conducted under conditions that maximize NDMA formation in order to gain insights for the mechanisms in which amine-based polymers can act as NDMA precursors.
- Preliminary results show that the NDMA formation potential of the polymers under conditions in line with those in typical water treatment plants was lower than the current advisory levels.
- The mechanistic study, however, provide useful results that can be the basis for designing polymers of minimized NDMA formation potential:

  1) Polymer purification reduces NDMA formation potential for polyamine and polyDADMAC, while does not eliminate the polymers' NDMA formation potential.

Conclusions (continued)

2) Direct reaction of polyamine and polyDADMAC with monochloramine can result in polymer degradation in several functional groups and release of DMA. NDMA formation potential is closely related to these two phenomena.

3) Polymer chain end plays the major role in polyamine's NDMA formation potential, while degradation of quaternary ammonium group and residual DMA-containing intermediate are the significant factors in PolyDADMAC's NDMA formation potential.

Acknowledgments

Financial Support: SNF Holding Company

People: Shuting Wei (GT)
Dr. Boris Mizaikoff (GT)
Dr. Mustafa Aral (GT)
Dr. Amelia Taylor (SNF)
Dr. Cédrick Favero (SNF)
Dennis Marroni (SNF)