P2 Assessment of Polymers

A Discussion of
Physical-Chemical Properties,
Environmental Fate,
Aquatic Toxicity,
and Non-Cancer Human Health Effects
of Polymers

Vince Nabholz, U.S. EPA

P2 Assessment of Polymers

- **Definition of polymer for P2 assessment purposes**
  - **A polymer is a chemical made up of covalently linked repeating units, generally with MWn >1,000**
    - **< 25% < 1000**
    - **< 10% < 500**

- **(Q)SAR assessment of polymers may not be possible with some Sustainable Futures models and methods due to:**
  - **Limited data sets**
  - **Large molecular weight (>1,000)**
  - **The presence of multiple species (mixtures)**

P2 Assessment of Polymers

- **Polymer assessment based on combination of**
  - **QSAR prediction**
  - **SAR - Read-across methods**
  - **Professional judgment**
- **Primary reference (PDF Version included in hand outs)**
  - **Boethling, Robert S. and Nabholz, J. Vincent "Environmental Assessment of Polymers under the U.S. Toxic Substances Control Act", pp. 187-234, in Ecological Assessment of Polymers Strategies for Product Stewardship and Regulatory Programs, Hamilton, John D. and Sutcliffe, Roger (eds.), (1997) Van Nostrand Reinhold.**

Polymer Assessment Goals

- **Screening Level Assessment**
  - **Qualitative and/or Quantitative**

- **Looking for a snapshot of how the polymer will act (fate and toxicity)**
  - **Important to distinguishing between low concern, and NOT low concern**

Properties Affecting Polymer Assessment

- To assess polymer, you need to know:
  - MW_n and % of Low Molecular Weight (LMW) components (%<1000, %<500)
    - LMW components may need to be assessed separately
  - Polymer Composition (Monomers)
  - Polymer Charge
    - Neutral, Anionic, Cationic, Amphoteric
  - Structural Features
    - Reactive Functional Groups (RFGs)
    - Particle Size and Inhalability

Molecular Weight (MW) and Low Molecular Weight (LMW) Components

Three Categories of Polymers Identified

- Category 1: MW_n <1,000
  - May be assessed as a "discrete" chemical (with representative structure)
- Category 2: MW_n >1,000; ≥25% with MW <1,000 and ≥10% with MW <500
  - Assess polymer and LMW materials (SAR modeling with representative structure)
- Category 3: MW_n >1,000; <25% with MW <1,000 and <10% with MW <500
  - Assess polymer using nearest analog approach or by estimation

* Human health concerns for polymers of MWn >10,000 are discussed in the human health section

Polymer Charge

- Nonionic, Anionic, Cationic, Amphoteric
  - Charge affects many aspects of the assessment
    - Physical properties
    - Fate
    - ecotoxicity
    - Human toxicity

Cationic Polymers

- Carbon-based polymer backbone
- Silicone-based backbone
- Natural-based backbone: chitin (glucosamine), tannin, starch

Anionic Polymers

- **Poly(aromatic acids): bisphenolsulfones, cresols, phenol, biphenylsulfones, biphenylethers, naphthalene, benzene**

- **Poly(aliphatic acids)**

Example: Dividing up Dyes

- Nonionic
- Cationic
  - delocalized charge, localized charge +1, +2, +3, +4, etc; then, triphenylmethanes, acridines, phenothiazines, thiazoliums, azo, anthraquinones, phthalocyanines
- Anionic:
  - number of acids 1,2,3,4, etc; then, aminoanilines, anthraquinone, anilines, phenols, benzothiazoles, FWAs, chelated: Cu, Cr, Co, Fe.
- Amphoteric

Example: Dividing up Surfactants via Hydrophile

- Nonionic
  - ethoxylates; polyalcohols; alpha,omega-dialkyl-ethoxylates; TWEENs
- Cationic
  - N, P, S, number of dominant alkyls, ETHOMEENs, N-ethoxylates, quanidines
- Anionic
  - type of acid, ethoxylated
- Amphoteric

Structural Features

- Reactive Functional Groups (RFGs)
  - Examples include, but are not limited to: acrylates/methacrylates, epoxides, phenols, sulphonates, Isocyanates, etc.
- Physical Features
  - Inhalability/particle size
  - Swellability
  - Fibrous properties
- Primarily affects mammalian toxicity

Physical Properties Assessment

- Based primarily on size of polymer
- Charge and structural features also play a role
- Most polymers will fit a general trend
  - See Interpretive Assistance Document for Polymers provided in hand-out material

Physical Properties (cont.)

- Vapor pressure – generally very low ($<10^{-8}$ mm Hg)
- Henry's Law constant – generally very low ($<10^{-8}$ mm Hg)
- Water solubility
  - Neutral – usually insoluble
  - Ionic – may be dispersible

Physical Properties (cont.)

- Soluble
- Dispersible
- Micro emulsions / Macro emulsions
- Dispersed solid particles
- Gels
- Micro micelles / Macro micelles
    - Surfactants

Environmental Fate

- Environmental Fate Assessment
  - based on size, charge, and polymer make up (monomers and end groups)
- The goal is to establish how the chemical will behave in the environment
  - Partitioning – where it will go?
  - Persistence – how long it will last?
- Screening Level Assessment

Environmental Fate - Partitioning

- POTW Removal
  - POTW removal is based on MW_n and charge
  - Cationic, Amphoteric, Nonionic, and Insoluble and Non-dispersible Anionic
    - Ranges from 50% at MW_n of <500 – 90% at MW_n of >1,000
  - Soluble or Dispersible Anionic
    - Ranges from 0% at MW_n of <5,000 – 90% at MW_n of >50,000

Environmental Fate - Partitioning

- **Soil Mobility**
  - Polymers tend to have poor mobility in soil
- **Volatilization from water**
  - Polymers tend to be insoluble in water, but do not volatilize from water
- **Bioconcentration Factor (BCF)**
  - MWn <1,000, use EPI Suite
  - MWn >1,000, Low BCF Concern (100 can be used for modeling purposes)

Environmental Fate - Partitioning

- Overall Partitioning Picture
  - Generally polymers will partition to
    - Soil, suspended particles, sediments, and sludge
  - Soluble and/or dispersible polymers may remain partially in water
  - Partitioning to air only as particulate (dust), not usually significant

Environmental Fate - Degradation

- Hydrolysis
  - Hydrolysis of susceptible groups solubility dependant
  - Not usually a major removal route
- Air oxidation
  - Poor partitioning to air
  - Presence of polymer as particle in air reduces potential removal rate
  - Not a major route of removal

Environmental Fate - Degradation

- Spontaneous Degradation
  - This will be polymer specific
  - In most cases it will be a known property
- Polymerization
- Biodegradation
  - In most cases polymers will be resistant to biodegradation
    - Due to size and hydrophobicity
  - Exceptions are usually polymers designed for rapid biodegradation

Environmental Fate - Overall Picture

- General Trends
  - Polymers will tend to partition to
    - Soil, suspended particles, sediments, and sludge
  - High persistence concern
  - Low concern for bioconcentration (BCF)
- Exceptions will exist
  - High solubility
  - Polymers designed for degradation
  - Polymers with low MW_n
  - Insoluble polymers in a solvent

Aquatic Toxicity

- **Assessment method varies**
  - **Main grouping is based on polymer charge (Neutral, Anionic, Cationic, and Amphoteric)**
- **Insoluble or non-dispersible polymers generally have low aquatic toxicity hazard concern (regardless of charge)**
  - **Not soluble or bioavailable**
  - **Exceptions may include finely divided particles**
- **For polymer with MW_n of <1,000 (category 1) or those with significant amounts of LMW components (category 2), ECOSAR may be used**

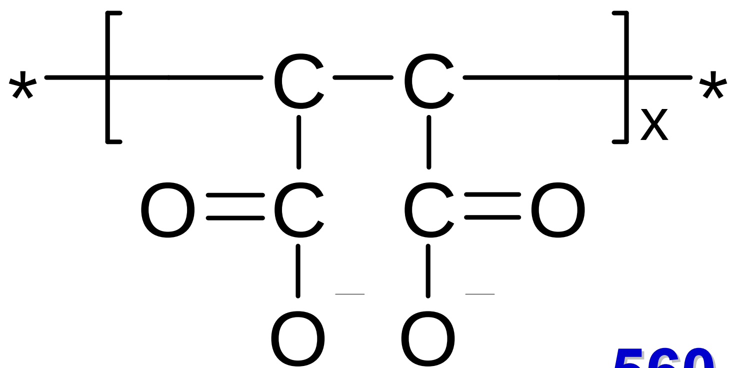
Aquatic Toxicity - Neutral Polymers

- Nonionic polymers tend toward low hazard concern
- Exception is neutral polymers that are blocked for use as a surfactant or dispersant, these may exhibit toxicity
  - Use nearest analog approach
  - Or SAR

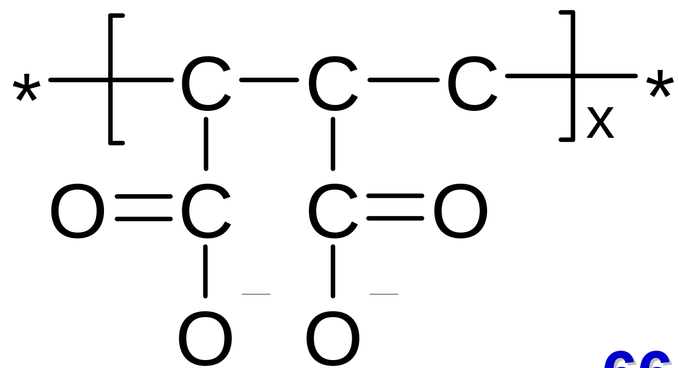
Aquatic Toxicity - Anionic Polymers

- **Polyanionic polymers that are soluble or dispersible may exhibit ecotoxicity**
- **Two main classes**
  - **Poly(armomatic acids)**
  - **Poly(aliphatic acids)**
- **Nearest analog approach**
  - **Tables with many analogs are collected in the “Environmental Assessment of Polymers under the U.S. Toxic Substances Control Act” chapter**

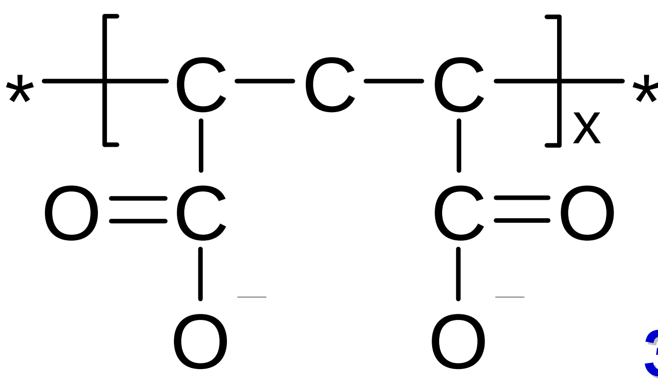
Polyanionic Polymers
Poly (Carboxylic Acids)
Structure and Green Algal 96-h EC50 (mg/L)



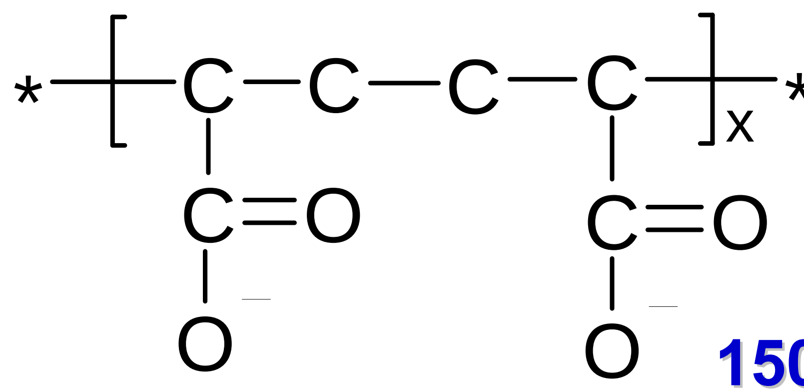
560.



66.

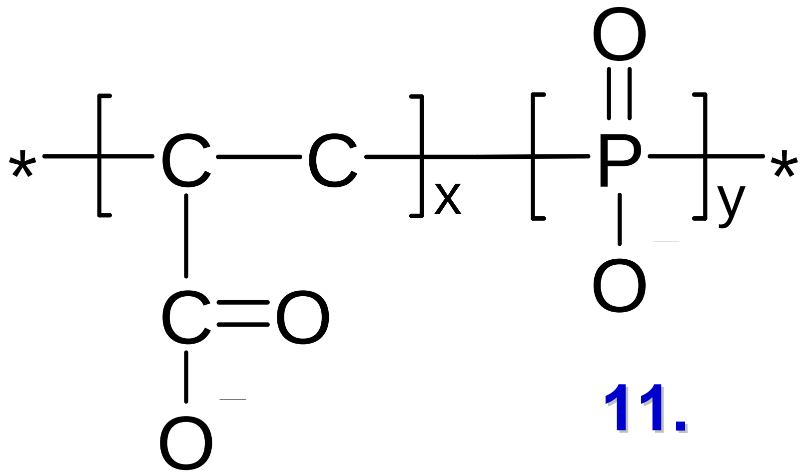


3.

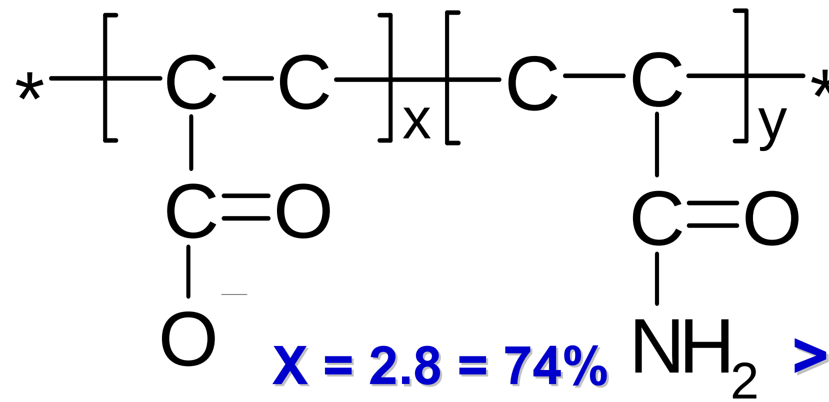


150.

Polyanionic Polymers
Poly (Carboxylic Acids)
Structure and Green Algal 96-h EC50 (mg/L)

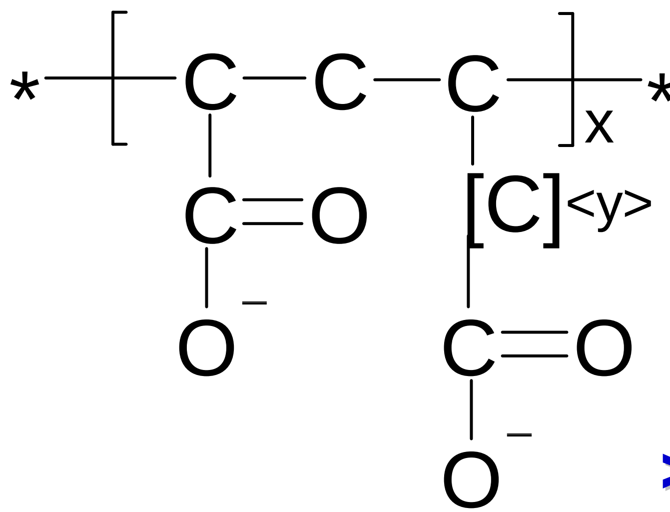


11.



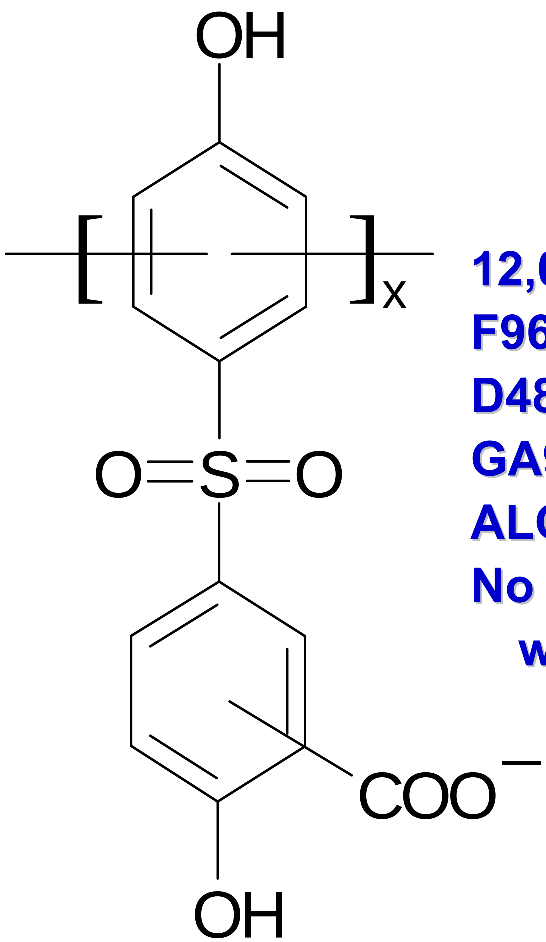
X = 2.8 = 74%
y = 1.0 = 26%

>100.

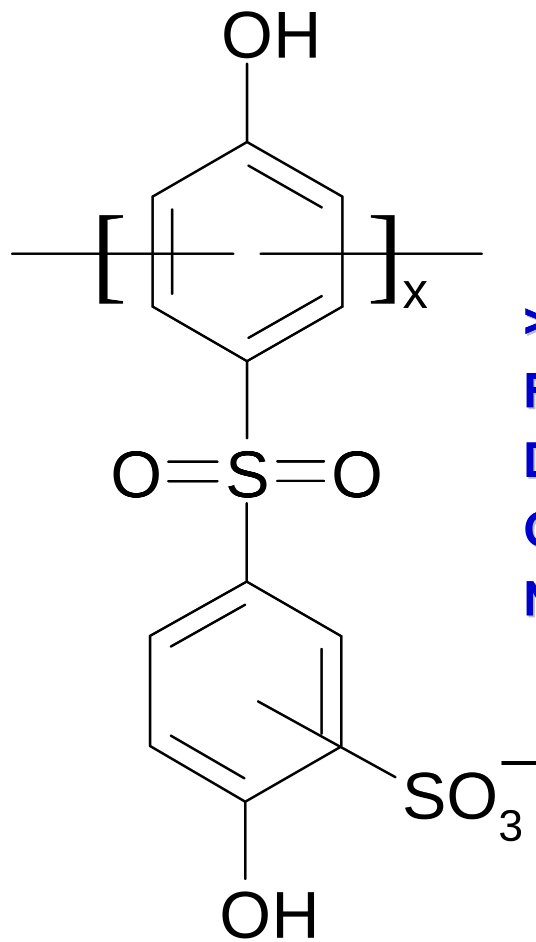


>100.

Polyanionic Polymers
Poly (Aromatic Sulfonates)

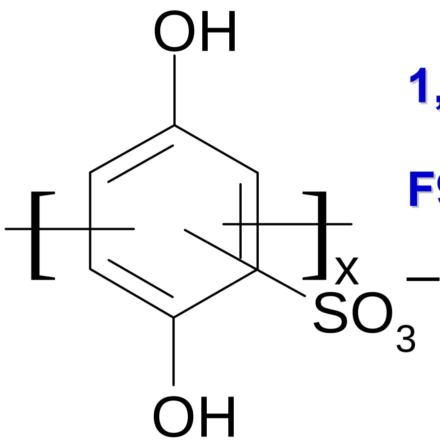


12,000 / 0 / 0
F96 = 70. mg/L
D48 = 90.
GA96 = 40.
ALGALICIDAL
No Mitigation with Ca^{2+}



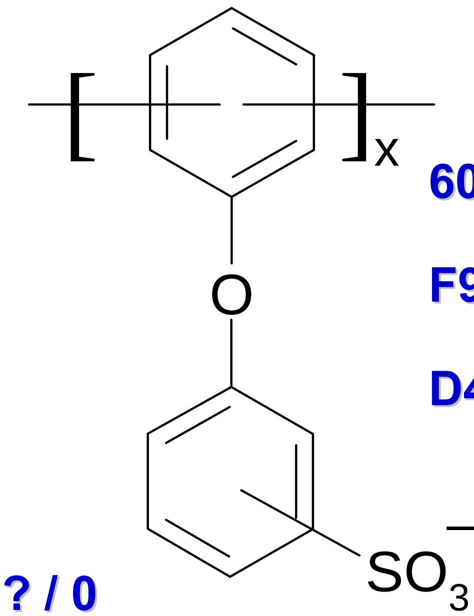
> 1,000 / 40 / 15
F96 = 5. mg/L
D48 = 145.
GA96 = 20.
No Mitigation with Mg^{2+}

Polyanionic Polymers
Poly (Aromatic Sulfonates)



1,000 / ? / ?

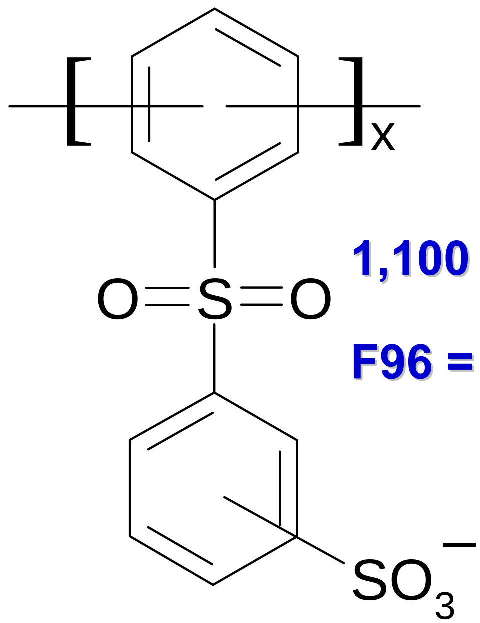
F96 = 2. mg/L



600 / 90 / 40

F96 = 30. mg/L

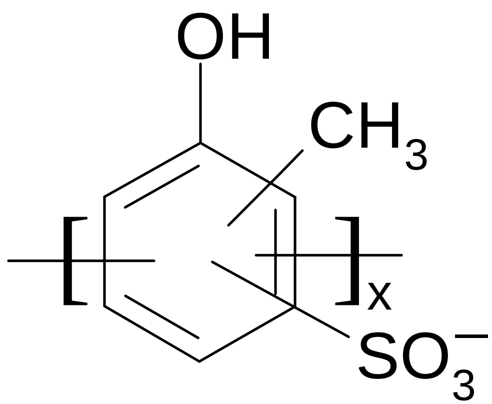
D48 = 120.



1,100 / ? / 0

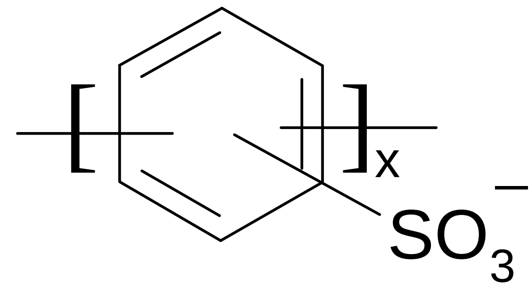
F96 = 3. mg/L

Polyanionic Polymers
Poly (Aromatic Sulfonates)



12,000 / ? / ?

F96 = 3. mg/L

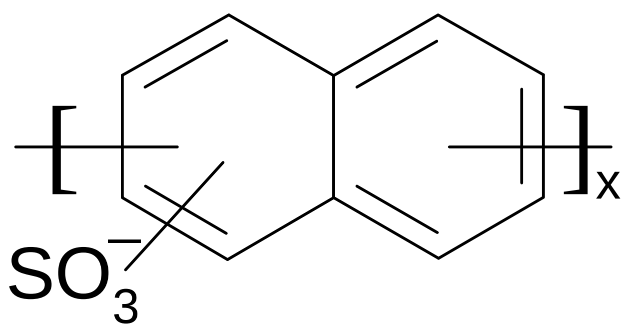


3,000 / 30 / 1

F96 = 600. mg/L

D48 = 900.

GA = 800.



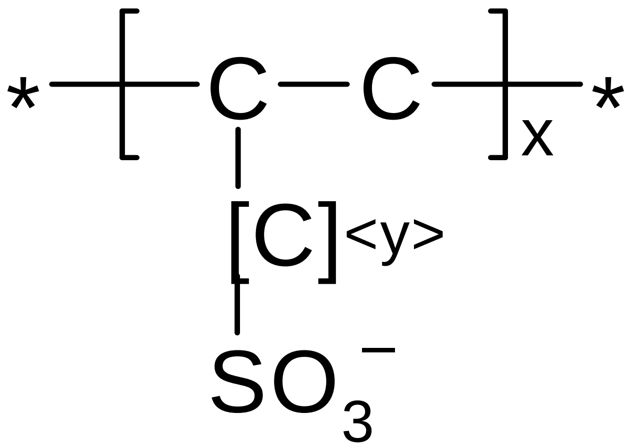
8,000 / ? / ?

F96 = 150. mg/L

D48 = 500.

GA96 = 300.

Polyanionic Polymers
Poly (Aliphatic Sulfonates)



3,000 / 30 / 10

F96 > 500. mg/L

D48 = 800.

GA96 = 800.

Aquatic Toxicity - Cationic and Amphoteric Polymers

- Cationic polymers that have a net positive charge or that may become positive may pose a hazard concern for ecotoxicity
  - Cationic atoms of concern include (but are not limited to): Nitrogen, phosphorus, and sulfur
    - Nitrogen is the cationic group in 99% of cases
  - Nitrogens in or on an aromatic ring, amides, nitriles, nitro groups, and carbo diimides are not considered

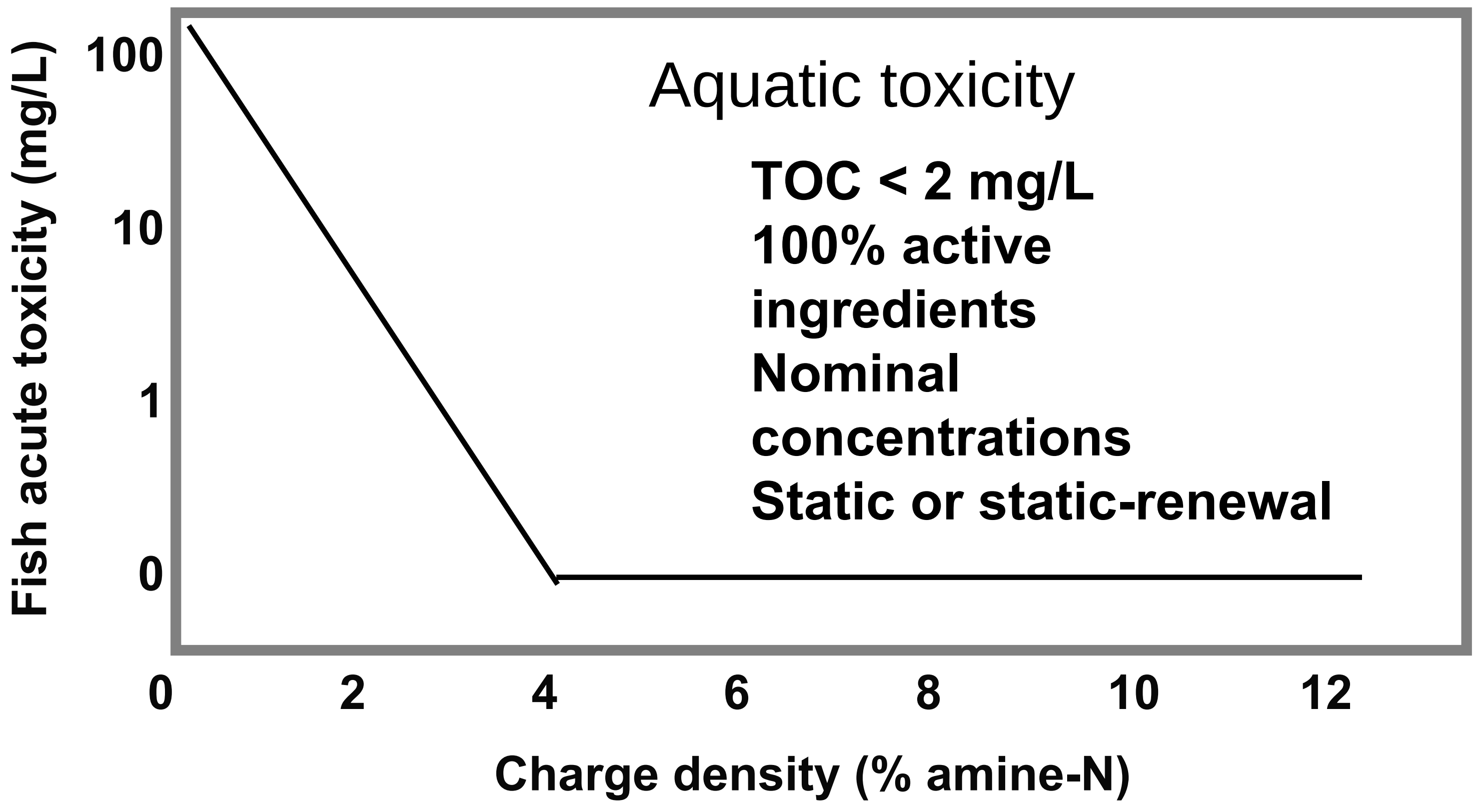
Aquatic Toxicity - Cationic and Amphoteric Polymers (cont.)

- Factors in ecotoxicity estimation
  - Percentage of amine nitrogen (%A-N) or other cation by weight
    - Nitrogens in or on an aromatic ring, amides, nitriles, nitro groups, and carbo diimides are not considered
  - Amphoteric polymers
    - %A-N is adjusted based on cation-to-anion ratio (CAR)
  - Backbone
    - SARs available for carbon based, silicon based, and naturally occurring polymer backbones

Aquatic Toxicity - Cationic and Amphoteric Polymers (cont.)

- **Toxicity may be mitigated by water hardness**
  - **Mitigation Factor (MF) equations included, also based on %A-N**
- **Toxicity is estimated by:**
  - **Choosing correct SAR for backbone**
  - **Calculating %A-N**
  - **Calculating base toxicity**
  - **Calculating MF**
  - **Adjusting toxicity based on MF to give final endpoint**

Polycationic Polymers
Polyamine Polymers



Applying Mitigation Factors

- **Cationic and Amphoteric Polymers: Mitigation of Toxicity**
  - **Standard aquatic hazard testing media (OECD) usually has a low total organic content (TOC) which may result in artificially high toxicity of polycationic and amphoteric polymers in those media.**

Mitigation Factors

- To correct for TOC in actual surface water a mitigation factor (MF) has been calculated, based on testing in standard media
- The MF is dependent on the overall charge density (%A-N) for the polymer
- Several conditions and/or structural features have been shown to affect the mitigation factor
- See page 8 of Interpretive Assistance Document for Polymers which provides further detials

Non-Cancer Human Health Concerns

- **Traditional U.S. EPA Human Health Effects Assessment based on:**
  - **Nearest analog approach**
  - **OncoLogic**
  - **U.S. EPA Chemical Categories Report**
    http://www.epa.gov/oppt/newchems/pubs/chemcat.htm
  - **Structural Features**

Non-Cancer Human Health Concerns

- Traditional Health Assessment approach is relevant for polymers
  - Chemical Categories
  - Nearest analog approach
  - LMW components and residual monomer(s) may need to be considered
- Special considerations for polymers
  - Large inhalable polymers
  - OncoLogic is run differently

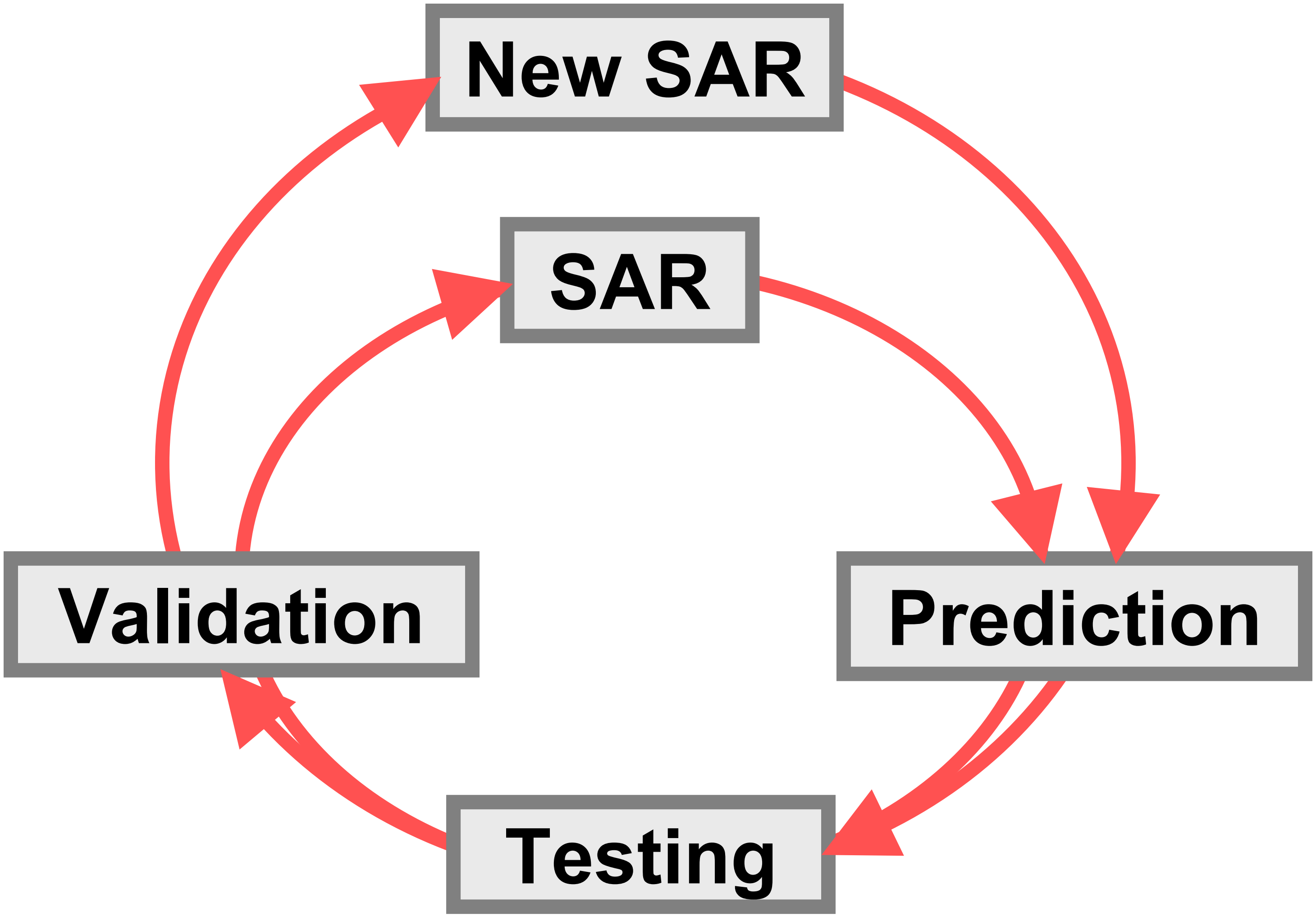
Non-Cancer Human Health Concerns

- **Large Inhalable Polymers**
  - **Polymers with MW_n of >10,000 are generally of concern only for lung effects**
- **There are three further distinctions**
  - **Soluble – Not generally a concern**
  - **Insoluble – Concern may exist**
  - **Swellable – Concern may exist**

Non-Cancer Human Health Concerns

- Cationic/Amphoteric Binding to Lungs
  - Binding to Lung Membrane
    - Charge
    - Reaction
    - Alkoxysilanes
- Waterproofing of lung membranes
  - Anti-stain aerosols
  - Anti-stain polymers
    - Polysilicones

SARs, QSAR Models, and Assessment Methods for Polymers Continually Updated as New Information is Available



References

- Boethling, Robert S. and Nabholz, J. Vincent "Environmental Assessment of Polymers under the U.S. Toxic Substances Control Act", pp. 187-234, in Ecological Assessment of Polymers Strategies for Product Stewardship and Regulatory Programs, Hamilton, John D. and Sutcliffe, Roger (eds.), (1997) Van Nostrand Reinhold.
  - Included on Sustainable Futures Workshop CD
- Interpretive Assistance Document for Polymers
  - Available on the EPA website:

    http://www.epa.gov/oppt/sf/meetings/train.htm#materials