P2 Assessment of Polymers

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

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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

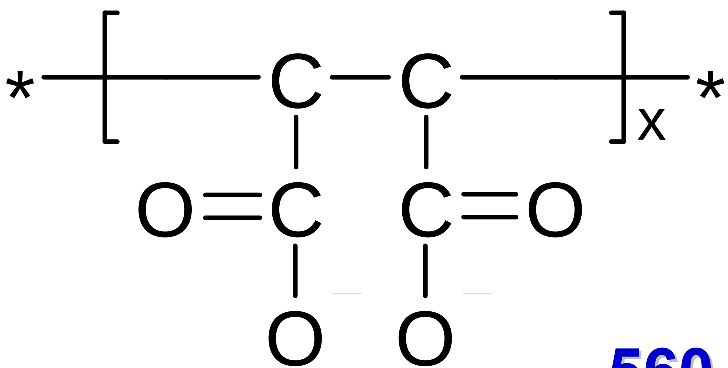
- Nonionic polymers tend toward low hazard concern
- Exception is neutral polymers that are blocked for use as a surfactant or dispersant, these may exhibit toxicity
  - Use nearest analog approach
  - Or SAR

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

SAR POLYMERS

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



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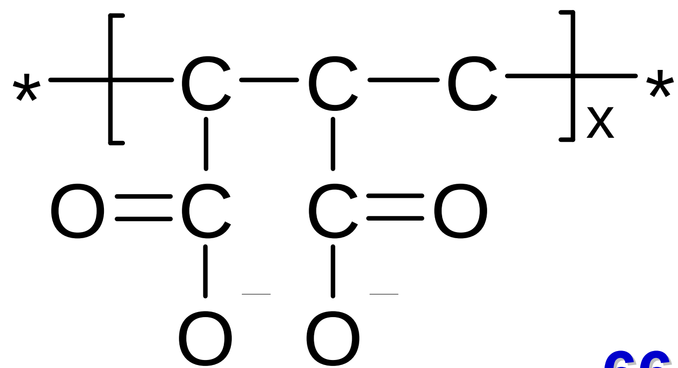

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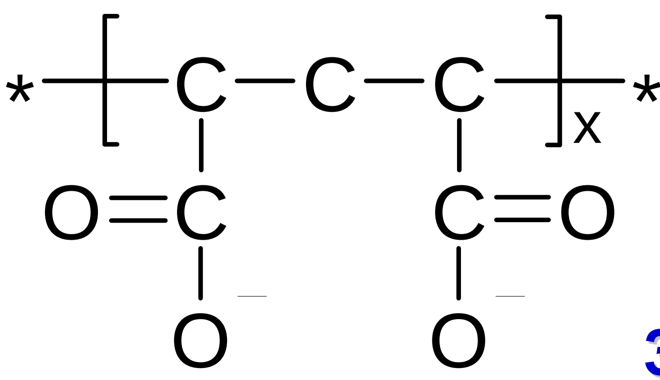

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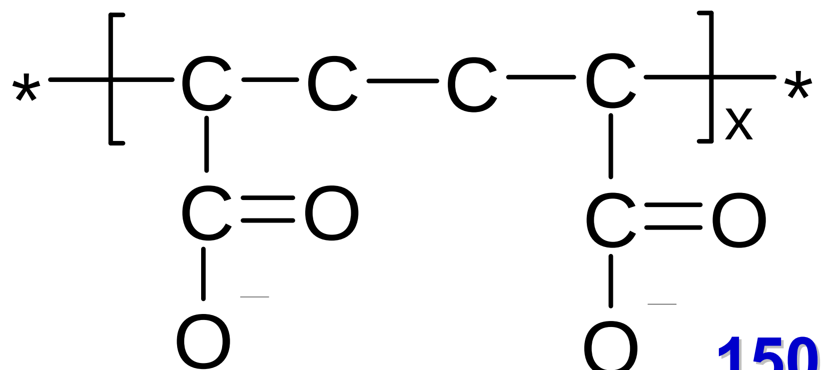

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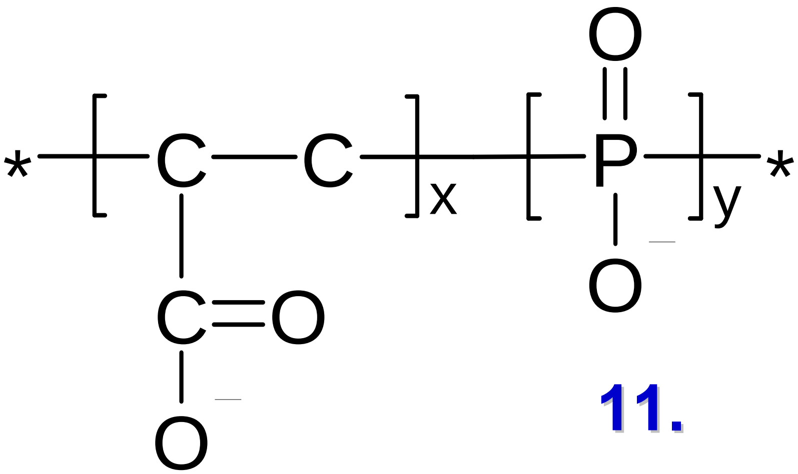
SAR POLYMERS

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



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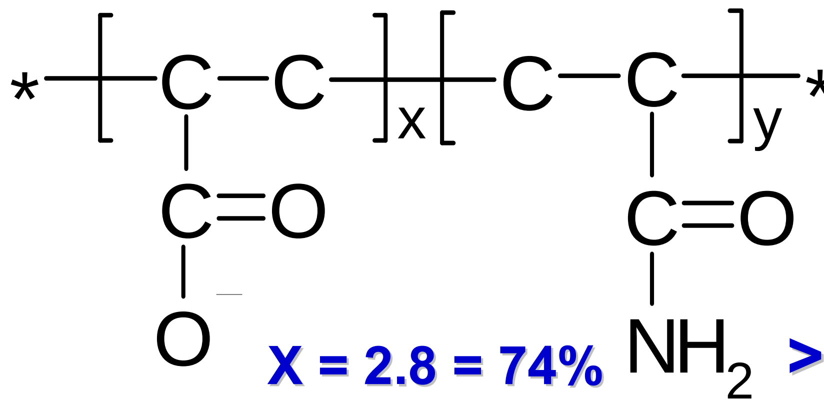
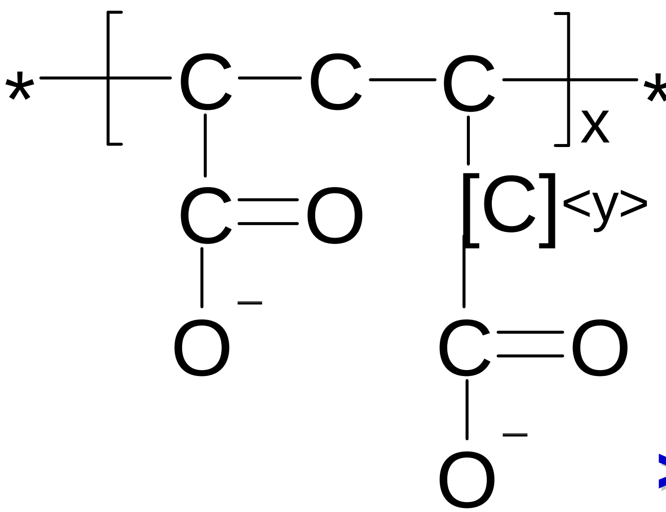


x = 2.8 = 74%
y = 1.0 = 26%

>100.



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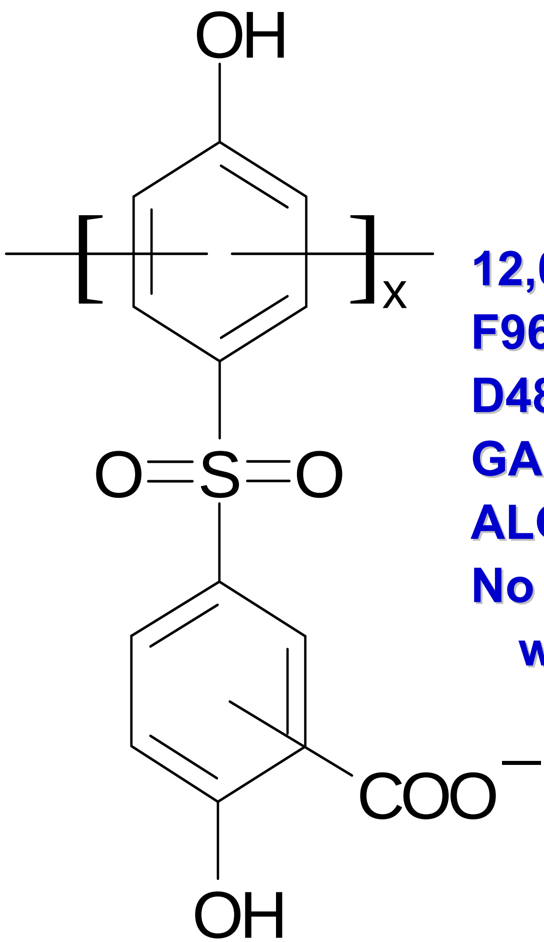
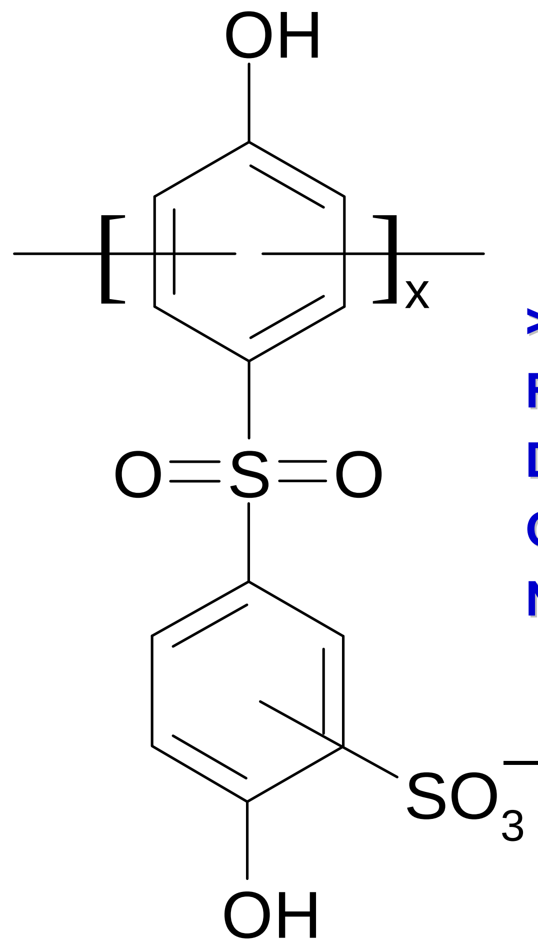
Polyanionic Polymers
Poly (Aromatic Sulfonates)

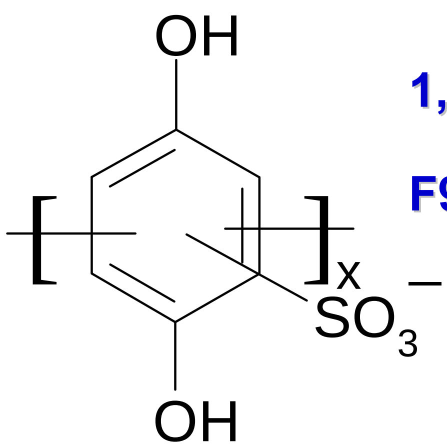


12,000 / 0 / 0
F96 = 70. mg/L
D48 = 90.
GA96 = 40.
ALGALICIDAL
No Mitigation with Ca^{2+}



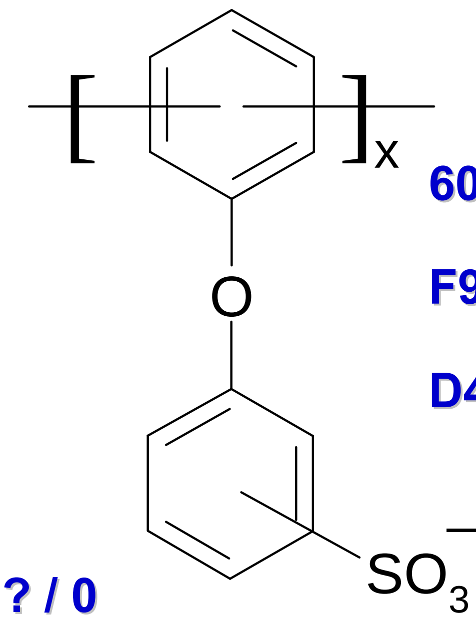
> 1,000 / 40 / 15
F96 = 5. mg/L
D48 = 145.
GA96 = 20.
No Mitigation with Mg^{2+}

Polyanionic Polymers
Poly (Aromatic Sulfonates)



1,000 / ? / ?

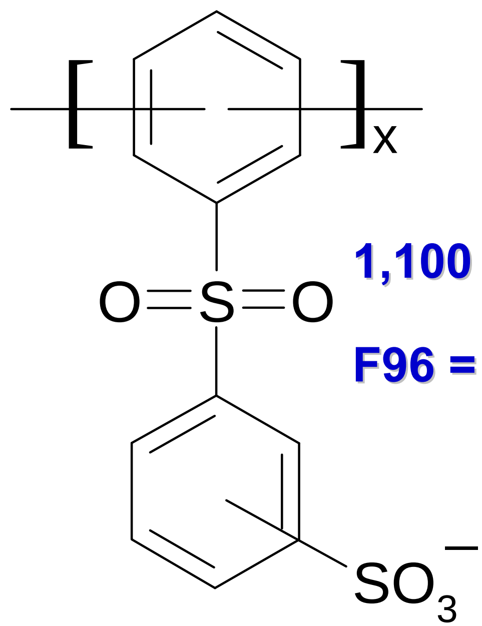
F96 = 2. mg/L



600 / 90 / 40

F96 = 30. mg/L

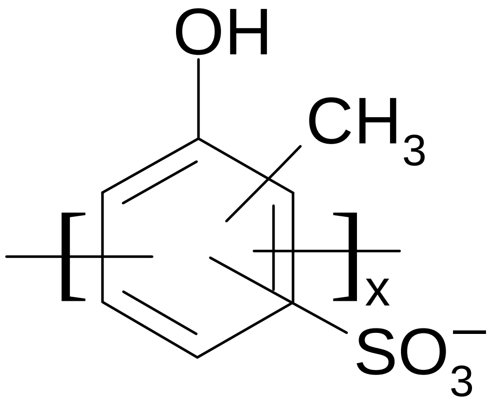
D48 = 120.



1,100 / ? / 0

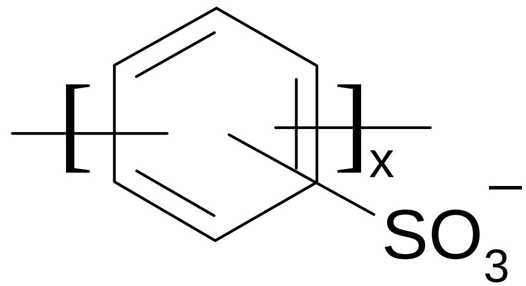
F96 = 3. mg/L

Polyanionic Polymers
Poly (Aromatic Sulfonates)



12,000 / ? / ?

F96 = 3. mg/L

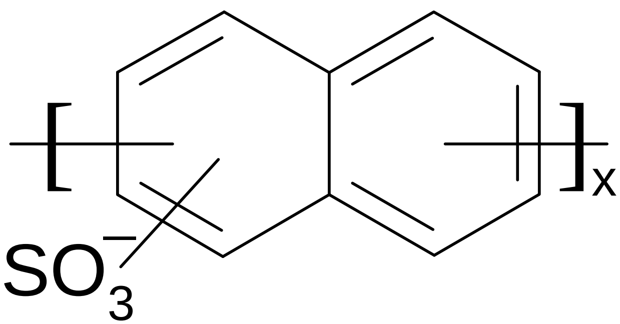


3,000 / 30 / 1

F96 = 600. mg/L

D48 = 900.

GA = 800.



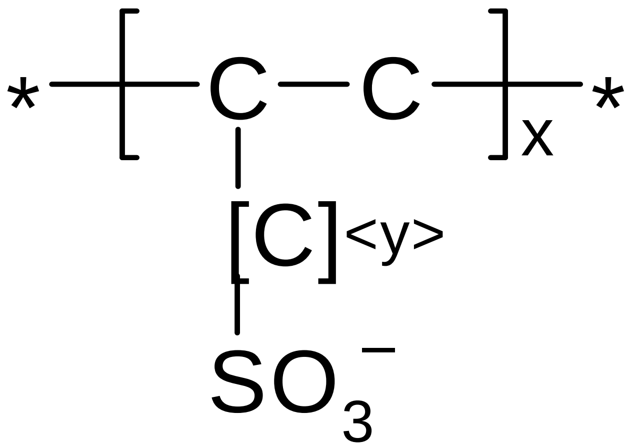
8,000 / ? / ?

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

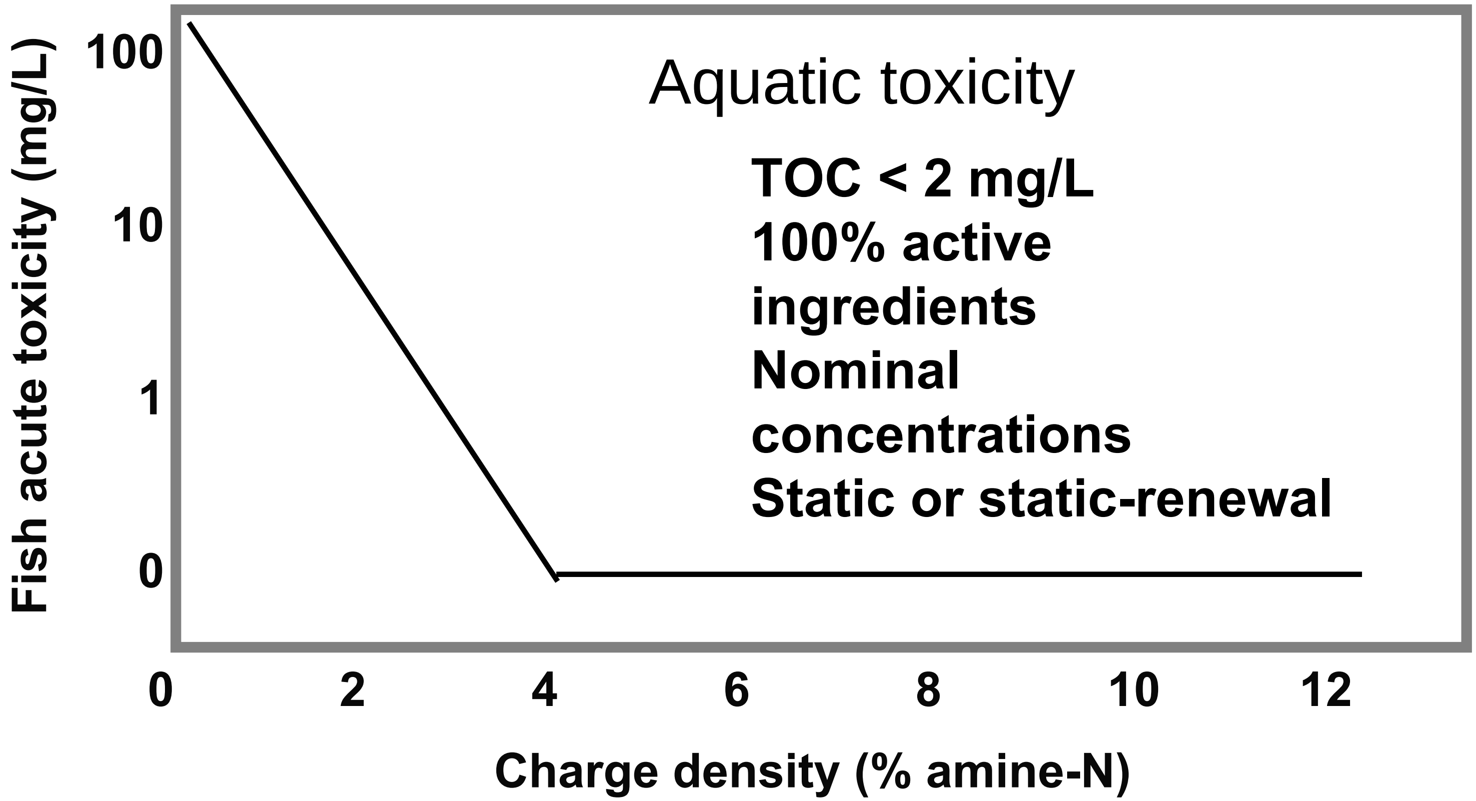
Aquatic Toxicity - Cationic and Amphoteric Polymers (cont.)

- 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**

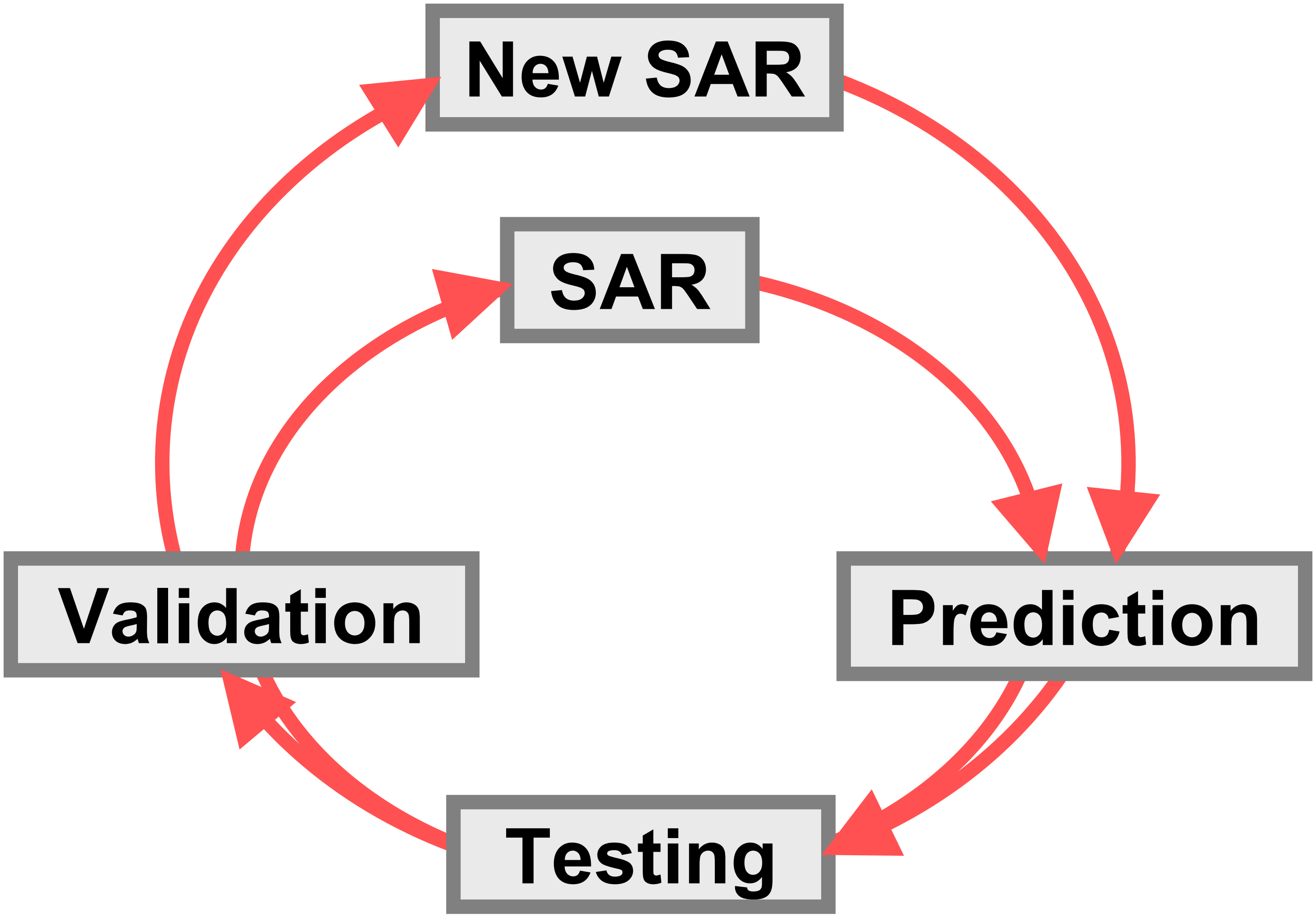
Non-Cancer Human Health Concerns

- 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

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  - 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