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OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

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MEMORANDUM

SUBJECT: Environmental Concerns of Polymers *M. Zeeman*
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As per your request, this is the current status of the environmental concerns of polymers (MW > 1000). Vince Nabholz, EEB, prepared this response.

ENVIRONMENTAL CONCERNS OF POLYMERS

All polymers are divided into four classes depending on the type of electronic charge of the polymer: nonionic (neutral); anionic (negative charge); cationic (positive charge); and amphoteric (mixture of positive and negative charges on same molecule) polymers.

I. POLYMERS WITH MW < 1000.

Polymers with MW < 1000 and some water solubility may be of concern because of their potential to act like polymers whose MW > 1000 and of their potential to be absorbed through biological membranes and cause systemic effects.

A. Polynonionic (neutral) polymers.

Small neutral polymers are generally assessed based on the type of functional group, e.g, aniline, phenol, alcohol, epoxide, etc. Polynonionic polymers are evaluated on the basis of their octanol/water partition coefficients (K_{ow} or P), melting point (mp), water solubility (SH_2O), and predicted toxicity to aquatic

organisms using structure activity relationships (SAR, e.g., quantitative structure activity relationships [QSAR]) just as you would assess a monomer with the same functional group. For example, polyphenols are assessed as you would assess a phenolic monomer using the phenol SARs (Clements 1988).

B. Polyanionic (negatively charged) polymers.

Small polyanionic polymers are assessed by using the nearest analog method. The chemical structure of the anionic group(s), e.g., carboxylic acid, phosphoric acid, sulfonic acid, is compared to analogous larger polymers with significant amounts of low molecular weight (LMW) components or polyanionic monomers (e.g., EDTA) for which there is environmental test data. In general, the concerns for these small polymers are the same as for the large polymers whose MW > 1000 with the additional concern for the potential absorption and subsequent systemic toxicity.

C. Polycationic (positive charged) polymers.

Polycationic polymers are assessed by using either the SARs for polycationic polymers (Clements 1988), the aliphatic amine SARs, the SARs for quaternary ammonium surfactants (Clements 1988), or the generic review of small quaternary ammonium (non-surfactant) compounds.

D. Polyamphoteric (polymers containing cationic and anionic charges within the same molecule) polymers.

Small polyamphoteric polymers with equal numbers of cationic charges and anionic charges, or with greater cations than anions are treated as a polycationic compound. The toxicity of the polycationic portion of the compound is reduced based on the number of anionic charges. When there are greater numbers of anions than cations, the compound is treated as a polyanionic polymer.

II. POLYMERS WITH MW > 1000.

Hazardous polymers with MW > 1000 are expected to be water soluble (or self-dispersing), are not expected to be absorbed through biological membranes, and are expected to assert their toxicity by affecting the outer membranes of aquatic organisms or the near environment of the organism (e.g., over-chelation of nutrient elements). Insoluble polymers are not expected to be toxic unless they are ground up into fine particles. The toxicity of finely ground particles is due to indirect (physical) toxicity (e.g., the clogging of respiratory organs such as gills) and only occurs at high concentrations, i.e., acute toxicity

values of greater than 1000.0 mg/L and chronic toxicity values of greater than 50.0 mg/L. The toxicity of finely ground insoluble polymers does not depend upon the chemical structure of the polymer.

A. Nonionic (neutral) polymers.

Polynonionic polymers which have MW > 1000 are of low concern.

B. Anionic (negatively charged) polymers.

Polyanionic polymers which have MW > 1000 and which are water soluble (miscible or self-dispersing) are of concern for aquatic toxicity. Polyanionic polymers are divided into three subclasses: poly(carboxylic acids), poly(aromatic sulfonates), and poly(aliphatic sulfonates).

1. Poly(carboxylic acids) are of concern only for their toxicity to green algae. Toxicity to algae as defined by the 96-h EC50 for growth inhibition, is moderate with toxicity values ranging from 1 to 100 mg/L (ppm). It appears that the mode of toxic action of these poly(carboxylic acids) is over-chelation of nutrient elements needed by algae for growth. When enough calcium (as divalent cation) is added to a polymer to satisfy its anionic charges, toxicity to algae is mitigated. It is unknown if calcium (as calcium carbonate in water with hardness of 100 to 150 mg/L as CaCO₃) added to algal growth medium will also mitigate toxicity to an equal degree.

a. Structural requirements. Poly(acrylic acid) is moderately toxic to green algae and appears to be the most potent form of poly(carboxylic acid) in its ability to chelate nutrient elements. It's chemical structure is --[CC(COOH)]-- where you have a carboxylic acid on every other (or alternating) carbon(s) in the polymer backbone. The carboxylic acids are paired and equal distance from the polymer backbone. Test data for poly(maleic acid) indicated low toxicity to algae, i.e., 96-h EC50 = 560.0 mg/L, and, thus, a weak ability to chelate nutrient elements. In this polymer, there is a carboxylic acid on every carbon of the polymer backbone, i.e., --[C(COOH)C(COOH)]--. Additional PMN test data have suggested that (1) when the carboxylic acids are further separated, e.g., a carboxylic acid on every fifth carbon of the polymer backbone, or (2) when the carboxylic acids are different distances from the polymer backbone, the polymer's ability to chelate nutrient elements is reduced. The test data to support these last two conclusions are weak. In summary, the most potent structure for poly(carboxylic acid) polymers is paired acids which are equal distant from the polymer backbone and which have one acid on alternating carbons.

b. Mitigation of toxicity. The toxicity of poly(acrylic acid) polymers has been shown to be mitigated 13 times by the addition of one equivalent of Ca to the polymer before testing. PMN test data have indicated that the 96-h EC50 increased from 37.4 mg/L to 500.0 mg/L if you chelate the polymer with divalent ions before exposure to algae. This indirect toxicity to algae via over-chelation of nutrient elements may be an laboratory artifact because (1) many poly(carboxylic acid) polymers are used as scale inhibitors and are released to the natural environment chelated with Ca and Mg, (2) these polymers are initially tested as the Na or K salt, and (3) the OTS Environmental Test Guideline recommends a growth medium which has a hardness of only about 15.0 mg/L as CaCO₃. This represents very soft water and the average hardness of freshwater in the United States is about 120.0 mg/L. In those cases where the polymer is not used as a scale inhibitor and is released to the environment as the Na or K salt, the hardness of the receiving waters (i.e., 120.0 to 150.0 mg/L) may cause a substantial mitigation of the toxicity relative to the toxicity observed in the standard algal toxicity test. However, there are not sufficient test data to demonstrate the amount of mitigation due to moderately hard growth medium.

c. Testing scheme. (1) Polymers used as scale inhibitors and released to the environment chelated with calcium and magnesium ions should be tested three times with freshwater green algae: (a) test chemical as is, (b) test chemical with an equivalent of Ca⁺⁺ added to the stock solution, and (c) test chemical as is but tested with modified algal test/growth medium. Calcium alone or Ca and Mg is added to attain a measured hardness of about 150.0 mg/L as CaCO₃. If Ca and Mg are added together, then add Ca and Mg in the ratio of 2 Ca to every Mg. Test results from the test with an equivalent of Ca added to the polymers will be used to assess releases from use. Test results with the polymer as the Na or K salt will be used to assess releases from manufacturing and processing. All stock solutions should be adjusted to pH 7 before testing because PMN test data have shown that, if the polymer is tested as the acid or with excess acid, the toxicity from the acid was greater than the toxicity of the polymer via over-chelation. (2) Polymers not used as scale inhibitors and are released to the environment as produced (generally as the Na and K salts) should be tested twice with green algae: (a) the polymer as is, and (b) the polymer with modified algal test/growth medium.

2. Poly(aromatic sulfonates). a. Polymers showing toxicity. Poly(aromatic sulfonate) polymers with MW greater than 1000 may be of moderate concern for acute toxicity towards fish and green algae. Polymers in this class have the following characteristic monomers: sulfonated phenols, sulfonated cresols, sulfonated diphenolsulfones, sulfonated diphenyloxides, and sulfonated diphenylsulfones. This concern is based on two facts.

The first is test data for 8 PMN polymers which indicated acute toxicity values of about 5.0 mg/L for fish (as a 96-h LC50) and 20.0 mg/L for algae (as a 96-h EC50). This evidence is weak because while these polymers have average number MWs equal to or greater than 1000, they has substantial amounts of low molecular weight (LMW) components: > 10% < 500 and > 25% < 1000. The observed toxicity could have been due to the LMW components. However, the second fact is that the Agency has recently received data for a PMN polymer which had a MW = 12,200, <0.1% <500, and <0.1% <1000, contained a carboxylic acid substituted diphenolsulfone, and was moderately toxic to aquatic organisms, i.e., fish 96-h LC50 = 72.0 mg/L, daphnid 48-h LC50 = 86.0 mg/L, and green algal 96-h EC50 = 40.0 mg/L (hardness [H] of medium = 18.0 mg/L as CaCO₃). This polymer was tested three additional times with harder growth medium. There was no significant mitigation of the toxicity, i.e., H = 46 mg/L, EC50 = 24.0 mg/L, H = 152 mg/L, EC50 = 20 mg/L, and H = 160 mg/L, EC50 = 47.0 mg/L. The only common monomer between these two sets of polymers was the acid substituted diphenolsulfone.

b. Polymers showing low toxicity. Poly(aromatic sulfonate) polymers which have been shown to have low toxicity (i.e., acute toxicity values greater than 100.0 mg/L) or are highly suspected of having low toxicity are composed of the following monomers: benzene sulfonates and sulfonated naphthalene.

3. Poly(aliphatic sulfonates). There are not enough test data for these polymers to draw any firm conclusions about their toxicity. However, it is suspected that if these polymers show toxicity to aquatic organisms it will be to algae as was observed for the poly(carboxylic acid) polymers.

c. Polycationic (positively charged) polymers.

Polycationic polymers include polyamines (primary amines, secondary amines, and tertiary amines); quaternary amines; polysulfoniums; and polyphosphoniums. Polymers of concern have MWs >1000 and are water soluble (miscible or self-dispersing). Polymers based on polyglucosamines (i.e., chitosan) are much less toxic than predicted and are no longer of concern.

1. Toxicity. Aquatic toxicity in clean water (i.e., total organic carbon [TOC] < 2 mg/L) increases exponentially with increasing cationic charge density, i.e., protonated and/or quaternarized-N, S or P. An SAR for polycationic polymers has been published by Clements (1988). Charge density is measured as per cent amine-N for nitrogen-based polymers; equivalent weight of N, S, or P; or # cations/1000 MW. Toxicity to aquatic organisms increases exponentially until about 2.5 cations/1000 MW (or 3.5% amine-nitrogen or an equivalent weight = 400), thereafter, toxicity becomes asymptotic. Acute toxicity values

to fish and daphnids (i.e., aquatic invertebrates) are > 100 mg/L [i.e., low concern] at < 0.2 cations/1000 MW (or equivalent weight >5000 or <0.3% amine-nitrogen); 100 to 1 mg/L [i.e., moderate concern] at charge densities of >0.2 to 1.6 cations/1000 MW (or equivalent weights between 5000 and 625, or percent amine-nitrogen between 0.3 and 2.2); and < 1 mg/L [i.e., high concern] at > 1.6 cations/1000 MW (or equivalent weights < 625 or percent amine-nitrogen > 2.3). Green algae are about 6 times more sensitive than fish (i.e., algal 96-h EC50 versus fish 96-h LC50). The mode of toxic action for these polymers is surface active (i.e., they react with biological membranes), however, when MW falls below 1000, some systemic toxicity may also occur.

2. Mitigation of toxicity. The aquatic toxicity of these polymers with MW > 1000, < 10% <500, and < 25% <1000 is highly mitigated by the presence of dissolved organic carbon (DOC) in water. For polymers with charge densities => 2.4 cations/1000 MW (or equivalent weight < 400 or > 3.3% amine-nitrogen), the acute toxicity to fish is reduced about 94 times when the measured TOC in water is 10 mg/L as the result of adding humic acid to dilution water (i.e., TOC = 10 mg/L is equivalent to 27.6 mg/L humic acid, sodium salt; CASRN [1415-93-6]; Aldrich H1,675-2; Merck Index 10,4649). This mitigation factor of 94 is based on the results of testing 8 polymers.

The toxicity of polymers with MW > 1000 and significant amounts of LMW material, i.e., > 10% < 500 and > 25% < 1000 is mitigated less by dissolved organic matter in the water column. Two polymers with significant amounts of LMW material (i.e., one with MW = 1000, 23.3% <500, and 32.3% <1000; and another with MW = 1030, 12% <500, and 38% <1000) had mitigation factors of only 26 and 21, respectively.

The aquatic toxicity of polymers with charge densities => 2.4 cations/1000 MW (or equivalent weights <400 or >3.3% amine-nitrogen) are now of low concern for aquatic organisms living in the water column of the aquatic environment because of the predicted low risk.

There is one known exception to the mitigation/low bioavailability scenario for these polymers. When these polymers are formulated with excess acid, e.g., 20% excess acid more than you need to protonate all of the amines in a polymer; and the product pH is about 2, these polymers will fail to flocculate DOC in the water column and DOC does not appear to mitigate the acute toxicity to fish.

3. Partitioning to sediments. Many polycationic polymers are designed to react with DOC in the water column to form an insoluble flocculent. This flocculent eventually settles on sediments and accumulates in sediment. Sediment toxicity testing

with species which ingest sediment has shown that polycationic polymers with charge densities of \Rightarrow 3.0 cations/1000 MW (or \Rightarrow 3.0 cations/1000 MW or an equivalent weight \leq 333.0) are not bioavailable to cause any toxicity and are thus of low concern in sediments (Rogers and Witt (1989)).

4. Selection of humic acid for mitigation testing. Humic acid was selected as the representative dissolved organic carbon (DOC) based on research done by Cary et al (1987). Cary et al measured the mitigation of 4 suspended solids and five dissolved organic carbon (DOC) compounds on the acute toxicity of four cationic polyelectrolytes to freshwater fish and aquatic invertebrates. Humic acid was about average in its ability to mitigate toxicity. Analysis of Table 4 in Cary et al indicated that the mitigation factors (MF) for humic acid were closest to the mean MF for all of the DOCs tested. The mean MF factor was calculated for each of the polymer/species combinations. The MF of each DOC was compared to the mean MF and the absolute value of the difference was averaged for that DOC. Humic acid had the lowest average difference or, in other words, the MFs for humic acid were closest to the mean MF for each polymer/species combination, i.e., lignin > tannic acid > fulvic acid > lignosite > humic acid. In addition, humic acid is easily available from chemical supply companies.

5. Selection of 10 mg TOC/L to set the mitigation factor.

Ten mg TOC/L has been used in Agency hazard and risk assessments for three reasons: (a) concentrations of humic acid in natural waters are rarely measured, (b) the average measured amount of TOC in natural freshwater of the US is about 6.79 mg TOC/L (Lynch 1987), and (c) 10 mg TOC/L is a round number close to 7 which errs on the side of safety. Lynch (1987) analyzed the EPA Office of Water's STORET Data Base for measured amounts of TOC in US waters. Lynch found 67,994 measurements of TOC taken from 1977 through 1987 from all over the US (i.e., 19 of 23 major river basins in the US). These TOC measurements were lognormally distributed and skewed toward the larger amounts of TOC. The geometric mean of these data was 6.79 mg TOC/L. Since the Agency does generic risk assessments for most chemicals, at least the first time they are assessed, it was decided to use the average amount of TOC in natural waters as the benchmark amount of dissolved organic carbon.

6. Testing Scheme. a. The base set of environmental toxicity tests are done in clean dilution water. The base set of environmental toxicity tests include: (1) the fish acute toxicity test, the daphnid acute toxicity test, and the green algal toxicity test. All of the above tests will be done with the static method and will be based on nominal concentrations corrected to 100% active ingredients. Clean dilution water is defined as water with < 2 mg TOC/L.

b. The fish acute toxicity test will be done at least two more times with different concentrations of humic acid (HA) dissolved in the dilution water (CFR §795.115): the first test will be done with 20 mg HA/L dissolved in the dilution water. If the humic acid and the cationic chemical forms a flocculent, precipitate, or a viscous mixture which significantly interferes with the behavior of the fish or causes physical toxicity (e.g., clogging of gills), then the concentration of humic acid will be reduced (e.g., to 15 mg HA/L) until physical toxicity is not significant; the second test will be done with a humic acid concentration which is lower than the first, e.g., if the first test is done with 20 mg/L humic acid then the second test will be done with 10 mg HA/L.

c. Total Organic Carbon (TOC) determinations need to be done for the clean dilution water and for each concentration of humic acid; three TOC determinations for the clean dilution water and three determinations for each humic acid control.

d. If humic acid reduces the toxicity significantly, i.e., toxicity is substantially reduced in the presence of 10 mg TOC/L and the risk to water column organisms has been eliminated, then the only further testing will be sediment toxicity testing.

e. Sediment toxicity testing may include (1) tadpoles gavaged with contaminated sediment for 30 days (CFR §795.145), (2) tadpoles exposed to contaminated sediments in same tank for 30 days (CFR §795.145), or (3) adult daphnids exposed to contaminated sediments in same tank for 30 days (CFR §795.135).

f. If humic acid does not reduce toxicity, and there is still a significant risk to water column organisms in the presence of 10 mg TOC/L, then chronic toxicity testing for fish and aquatic invertebrates will be required.

g. The chronic toxicity test for fish (CFR §797.1600) is the fish early life stage toxicity test using clean dilution water, the flow-through method and nominal concentrations based on 100% ai. The chronic toxicity test for aquatic invertebrates (CFR §797.1350) is the daphnid partial life cycle toxicity test using clean dilution water, flow-through method, and nominal concentrations based on 100% ai.

D. Polyamphoteric (polymers containing cationic and anionic charges within the same molecule) polymers.

Polyamphoteric polymers with equal numbers of cationic charges and anionic charges or with greater cations than anions are treated as a polycationic polymer. The toxicity of the polycationic polymer portion of the polymer is reduced based on the number of anionic charges. When there are greater numbers of anions than cations, the polymer is treated as a polyanionic polymer.

III. REFERENCES.

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