

POLYCARBOXYLATES



THE SOAP AND DETERGENT ASSOCIATION

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INTRODUCTION

This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on polycarboxylates; and 2) conclusions drawn from a risk assessment of polycarboxylates in the United States. Although focused on conditions in the U.S., data from other parts of the world that are relevant to a U.S. assessment are included in the monograph. The monograph is written for a technical audience, but not necessarily one familiar with environmental risk assessment.

The monograph is formatted into five sections. The first section describes polycarboxylates, their chemical structure and U.S. consumption volumes. The second section describes the function of polycarboxylates in cleaning products. The third section describes their fate and exposure concentrations in the environment. The fourth section presents environmental effects information. The fifth section presents a comparison of exposure and effects concentrations in the framework of an environmental risk assessment.

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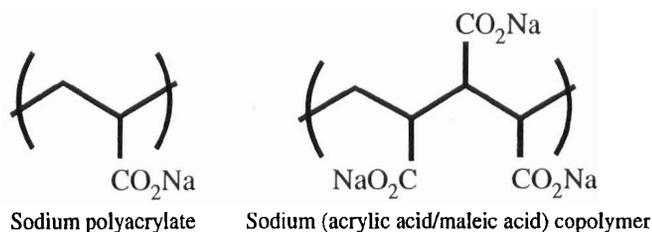
INGREDIENT IDENTIFICATION

Chemical Description

Polycarboxylates are anionic polymers with a carbon-carbon backbone and attached carboxyl functionality. Polycarboxylates are identified by the monomers used in their preparation and the molecular weights of the resultant polymers. The most commonly used polycarboxylates are sodium polyacrylate with average molecular weights (Mw) of 2,000-10,000, and sodium (acrylic acid/maleic acid) copolymers with average Mw of 20,000-70,000^a. These products are very water soluble and are typically supplied as 40-50% solutions (by weight), but dry powders are available. The Chemical Abstracts Services (CAS) has assigned numerous registry numbers to polycarboxylates, of which 9003-04-7 (2-propanoic acid, sodium salt, homopolymer) and 52255-49-9 (2-propanoic acid, polymer with 2,5-furandione, sodium salt) are representative examples.

U.S. Consumption

The total end use of low molecular weight polycarboxylates in the U.S. in 1993 was estimated to be 165 million pounds (MM lbs./yr.) on an actives basis, of which 58 MM lbs. were used in detergents and cleaners (Goin, Somogyi, Janshekar and Ishikawa, 1995). Other applications are as dispersants in water treatment; in pigment slurry production (clays, titanium dioxide, calcium carbonate); in water-soluble paints; and in textile and leather processing.



INGREDIENT FUNCTION

Polycarboxylates are added to cleaning products as production aids, performance enhancers, builder assists, antiredeposition agents, and for particle property improvement. These polymers can be used in home laundry detergents, automatic dishwashing detergents, industrial and institutional cleaning formulations, bar soaps and hard surface cleaners. Household powder laundry detergents are the major end use in the U.S. and can contain polycarboxylates in the range of 0.5-5%, depending on the formulation and intended function of the polymer.

^a Polymeric products contain molecules having many different chain lengths. Since a distribution of molecular weights (MW) exists in any sample of polymer, the experimental measurement of Mw can only give an average value. These reported values represent the weight-average molecular weight based on the distribution from each molecule's mass. For a more detailed discussion of polymer Mw distributions, see, for example, Billmeyer, Jr., 1962.

The key performance properties of polycarboxylates are as a dispersant for soils (for removal and prevention of soil redeposition), and in crystal growth inhibition to prevent incrustation of inorganic salts onto fabrics (especially in non-phosphate laundry detergent powders). If polycarboxylates are not present in a detergent (and particularly a non-phosphate powder), particulate soil cleaning efficiency may be diminished and graying or harshness of the washed fabrics may occur. Additionally, detergent processing could be adversely affected and particle integrity could be decreased.

ENVIRONMENTAL FATE AND EXPOSURE

Fate

The major source of the polycarboxylates likely to be released to surface waters is cleaning products used in the home. The other applications for low molecular weight polycarboxylates are highly unlikely to result in surface water discharge or release of the polymer to the aquatic environment. It is reasonable then to consider only polycarboxylates used in consumer cleaning products.

Therefore, the most probable route of environmental exposure is as a result of laundry detergent use and discharge of the wash water to municipal or on-site waste treatment systems. Use of other cleaning products would also lead to discharge to waste treatment systems and, in some cases, landfills as a result of wiping surfaces with cloths or paper towels.

Release of polycarboxylates to surface waters from pigment slurries is not as likely, since the polycarboxylate is strongly bound to the pigment. If discharges are made from water treatment applications, they would be more site specific but could include both direct discharges to natural waters as well as discharges to treatment facilities.

Biodegradation

Biodegradation of polycarboxylates is dependent on the molecular weight of the polymer, with increasing molecular weight resulting in decreasing degradation (Freeman, Paik, Swift, Wilczynski, Wolk and Yocum, 1996). In general, polycarboxylates used in cleaning applications are higher in molecular weight than the polymers found to degrade. A polyacrylate with a Mw of 4,500 is mineralized to only 15% at environmentally realistic test levels (1 mg/L) as measured by CO₂ evolution (Freeman and Bender, 1993). This degradation presumably arises from the lower molecular weight fraction of a polymer's molecular weight distribution. Biodegradation of a 70,000 Mw copolymer has been reported to be 6-20%, depending on the test conditions (Chiadani and Poltronieri, 1990) which, as in the case of the polyacrylate, arise from the low

molecular weight fraction of the polymer. Table 1 summarizes the biodegradation test data for both polycarboxylates.

Stability

Polycarboxylates are generally stable to both chemical degradation and photodegradation, and especially so under environmental conditions. Hypochlorite can cause degradation of some polycarboxylates depending on the method of their preparation. This degradation appears to be significant only under extreme conditions not found in typical applications, and follows a chain scission mechanism which only partly breaks down the polymer (Jones, 1993). Thus, the environmental impact of the degradation products should be very similar to the starting polymer.

Treatability

Polycarboxylates do not impact adversely on the operation of a sewage treatment plant (sludge sedimentation, treatment capacity, sludge dewatering, etc.) (Chiaudani *et al.*, 1990; Freeman *et al.*, 1993; Opgenorth, 1987).

The key to the environmental fate of polycarboxylates lies in their tendency for physical-chemical removal from the waste stream following the use of detergents and other cleaners that contain the polymers. Since detergents are primarily discharged into municipal wastewater treatment facilities, it is necessary to focus on removal occurring in or before the treatment plant.

Two different mechanisms of removal appear to be important for polycarboxylates in conventional wastewater treatment. Based on the results of a Continuous Activated Sludge (CAS) test, environmentally realistic concentrations of a 4,500 Mw polyacrylate exhibited 45-80% removal, depending on the extent of settling in the

clarifier and the amount of suspended solids leaving the system in the effluent (Freeman *et al.*, 1993; Hamilton, Reinert and Freeman, 1996). This removal decreases slightly with increasing polyacrylate influent concentrations, but under typical conditions results in approximately 50% elimination.

In the case of the 70,000 Mw copolymer, treatment removal is about 97% as measured in a laboratory activated sludge treatment plant test (5-20 mg/L test concentration) (Schumann, 1991). This removal occurs mainly through a precipitation of calcium polycarboxylate (which can occur in wastewater before or during treatment) in combination with sorption onto sludge. A study directly comparing the polyacrylate to the copolymer in a laboratory activated sludge treatment plant test has not been run. Thus, it is difficult to assess whether the differences in removal between the two polycarboxylates at environmentally realistic conditions are significant. It is clear that concentration dependent removal observed for the polyacrylate is not an issue for the copolymer. Removal of the 70,000 Mw copolymer at levels higher than those calculated for the environment is still 94% as measured by a Semi-continuous Activated Sludge (SCAS) test (Opgenorth, 1987).

Finally, in another aspect of wastewater treatment, chemical treatment is often used to remove wastewater components which are readily precipitated, such as phosphates. Laboratory simulations of a wastewater plant chemical treatment process have shown that almost 100% of a polycarboxylate will be removed after treatment with ferric chloride precipitant, if concentrations of the precipitant are over 30 mg/L as FeCl₃.

Thus, the data summarized here for both polycarboxylates support the conclusion that wastewater treatment systems will

TABLE 1
Summary of Polycarboxylate Biodegradation and Removal in Sewage Treatment

Test	4,500 Mw Polyacrylate	70,000 Mw Copolymer
Semi-continuous Activated Sludge	37.5% removal ^{a,b}	94% removal ^c
CO ₂ evolution	8.1% CO ₂ evolution ^{a,d}	20% CO ₂ evolution ^d
Batch Activated Sludge	15.6% CO ₂ evolution ^a	17.9% CO ₂ evolution ^b
Continuous Activated Sludge	Typically 50% overall removal @ 1 mg/L test concentration but dependent on effluent solids ^e	82% overall removal @ 3mg/L test concentration ^d
Lab scale treatment plant		97% overall removal @ 5-20 mg/L test concentration ^f
Continuous Activated Sludge with FeCl ₃ added	98% removal @ 3 mg/L test concentration ^{b,d}	

^a Freeman and Bender, 1993 ^b Chiaudani and Poltronieri, 1990 ^c Opgenorth, 1987 ^d Opgenorth, 1992

^e Hamilton *et al.*, 1996 ^f Schumann, 1991

substantially reduce the polycarboxylate influent concentrations to very low levels entering receiving waters (Table 1).

Solubility

Polycarboxylates and especially their alkali metal salts are readily soluble in water but are insoluble in organic solvents, such as alcohols or hydrocarbons (Opgenorth, 1992). Polycarboxylates can form sparingly soluble complexes with calcium ions in natural waters. This can impact on polycarboxylate environmental fate through removal of precipitated calcium/polycarboxylate complexes with the sludge in sewage treatment plants.

Partitioning Between Soil and Water

Lysimeter tests show that polycarboxylates generally exhibit a strong tendency to attach to a solid phase such as soil particles. A small, highly mobile component of the polymer has been observed in laboratory testing from the low molecular weight fraction of the molecular weight distribution. However, it is unlikely that this mobile fraction will even reach soils, since this fraction will be biodegraded in prior wastewater treatment. More importantly, the largest part of the molecular weight distribution is stationary and the non-mobile phase was found to be 84-93% of the material adsorbed onto sand (Chiaudani *et al.*, 1990). Polymer is also bound strongly to activated sludge, and partition coefficients (K_d 's) in static systems are in the range of 2,600-8,600 (Hamilton *et al.*, 1996). Thus, even this largest component of the polycarboxylate will most likely reach only the top layers of soil upon which the sludge is spread and will not impact upon soils underneath landfills where sludge might be stored. Once a polycarboxylate is bound to a soil or sludge, it is unlikely to be eluted from it by surface or ground waters.

Effects on Remobilization of Heavy Metals

Testing did not reveal any influence of polycarboxylates on the removal or mobilization of heavy metals found in wastewaters. The concentrations of copper, nickel, cadmium, lead and zinc in typical wastewaters were monitored in the presence and absence of polymer. No effect on metals remobilization was detected between the polymer and control systems, even though the conditions of testing were exaggerated by using concentrations of both the 4,500 Mw polyacrylate and 70,000 Mw copolymer above those expected to be in waste waters (Chiaudani *et al.*, 1990; Freeman *et al.*, 1993; Opgenorth, 1987).

Exposure Aquatic

The average concentration of detergent polycarboxylates in U.S. municipal wastewater influents is estimated to be 0.7 mg/L using the modeling program WW-TREAT (Cowan, Larson, Feijtel and Rapaport, 1993). This

estimate is based on total detergent product use (58 MM lbs. or 26,310,000 kg per year), domestic water use (average per capita usage of 400 L/day) and population (250 million).

Plant Influent =

$$\frac{26,310,000 \text{ kg}}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \times 10^6 \text{ mg}}{\text{kg}} \times \frac{\text{.day}}{250 \text{ MM} \times 400 \text{ L}} = \frac{0.72 \text{ mg/L}}{\text{(ppm)}}$$

Actual detection and measurement of low level polycarboxylates in environmental matrices are subject to numerous interferences principally from the humic substances found in wastewaters and surface waters. It has been demonstrated that significant removal of a polycarboxylate takes place during wastewater treatment, and it is accepted that the treated effluent will be diluted upon discharge to receiving waters so that the concentration of any residual polycarboxylate will be further reduced. It can be estimated (again using WW-TREAT) that the concentration of polycarboxylates will be ~0.03 mg/L below the outfall of the wastewater treatment facility, assuming at least 55% removal and a dilution factor of 10 (U.S. Environmental Protection Agency, 1991).

Plant Effluent =

$$\frac{0.7 \text{ mg/L} \times (1-0.55)}{10} = \frac{0.03 \text{ mg/L}}{\text{(ppm)}}$$

Bioaccumulation in aquatic organisms is unlikely due to the high water solubility of polycarboxylates (Opgenorth, 1992). Also, it is assumed that only substances with average molecular weights less than 600 can pass through biological membranes (Zitko, 1981).

Terrestrial

Sludge containing adsorbed or precipitated polycarboxylates may be landfilled or used as agricultural fertilizer. In this case the concentration of polymer in sludge-amended soils can be estimated to be 0.1 mg/kg soil at the time of application (Cowan *et al.*, 1993; Holman, 1981), with some limited biodegradation reducing this level over time (assuming a 0.2 kg/m² sludge application rate, soil depth of 0.2 m and a soil density of 1600 kg/m³).

ENVIRONMENTAL EFFECTS

Aquatic

Both polycarboxylates studied show chronic no-observed effect concentrations (NOEC) of approximately 6 mg/L in *Daphnia magna* or greater in other aquatic organisms. This represents a conservative estimate of the lowest aquatic NOEC, since it has been reported that the *Daphnia* test results in unrealistically low toxicity values

arising from a physical effect rather than a toxic effect (Opgenorth, 1987).

Terrestrial

In terrestrial organisms, the NOEC of polycarboxylates is 225 mg/kg soil or greater for earthworms and a variety of plants (corn, soybean, wheat, etc.). Table 2 provides a more complete listing of acute and chronic toxicity test results for polycarboxylates.

RISK ASSESSMENT

Aquatic

Toxicity data indicate that polycarboxylates are practically non-toxic to aquatic test species under U.S. EPA toxicity

classification guidelines (the lowest EPA category of toxicity). The 4,500 Mw polyacrylate and the 70,000 Mw copolymer have lethal concentrations for 50% of the test population, LC₅₀s (or depending on the test protocol, effect concentrations on 50% of the test population, abbreviated EC₅₀s), greater than 100 mg/L. In addition, both polycarboxylates have chronic NOECs of approximately 6 mg/L in *Daphnia magna* (the most sensitive aquatic species tested). In comparison, the estimated detergent polycarboxylate concentration in surface waters is 0.03 mg/L.

A U.S. EPA "assessment factor" (AF) can be applied to address the uncertainty of the toxicity testing. In this case a factor of 10 is appropriate based on the extent of testing done (Bascietto, Hinckley, Plafkin and Slimak, 1990). The environmental concentration of polycarboxylates, estimated to be 0.03 mg/L, is substantially less than the NOEC/AF of 0.6 mg/L.

TABLE 2
Summary of Ecotoxicity Data for Polycarboxylates

Ecotoxicity	4,500 Mw Polyacrylate ^a	70,000 Mw Copolymer ^b
Bacteria		
- sludge O ₂ /glucose consumption (EC ₅₀)	>100 mg/L	—
- Robra O ₂ consumption test (EC ₁₀)	—	>200 mg/L
- modified O ₂ consumption test (EC ₁₀)	—	>400 mg/L
- Bringmann-Kuehn method (EC ₁₀)	—	180 mg/L
- luminous bacteria method (EC ₂₀)	—	>200 mg/L
Algae		
- <i>Scenedesmus subspicatus</i> (growth, EC ₁₀)	180 mg/L	>200 mg/L
Hydra		
- colony multiplication (EC ₅₀)	—	136 mg/L
Daphnia magna		
- acute (48 hr, immobilization, EC ₅₀)	>1000 mg/L	>200 mg/L
- reproductive (21 days, NOEC)	5.6 mg/L	6.2 mg/L
Fish		
Acute:		
- trout (96 hr, LC ₅₀)	700 mg/L	—
- bluegill sunfish (96 hr, LC ₅₀)	>1000 mg/L	—
- zebra fish (96 hr, LC ₅₀)	>200 mg/L	—
- golden orfe (96 hr, LC ₅₀)	—	>200 mg/L
Chronic:		
- larval test (zebra fish, 6 weeks, NOEC)	—	>40 mg/L
- sublethal test (zebra fish, 14 days, NOEC)	—	>40 mg/L
- early life stage (fathead minnow, NOEC)	56 mg/L	—
Plant		
- corn, wheat, soybean (growth inhib., NOEC)	225 mg/kg soil	—
- oat (growth inhib., NOEC)	—	400 mg/kg soil
Earthworm		
- acute (96 hr, LC ₅₀)	>1000 mg/kg soil	>1600 mg/kg soil

^a Freeman and Bender, 1993; Opgenorth, 1992 ^b Chiodani and Poltronieri, 1990; Opgenorth, 1992

Terrestrial

For terrestrial species, the most sensitive organism tested had a NOEC of 225 mg/kg soil. The estimated concentration of polycarboxylates in soils, 0.1 mg/kg, is less than the NOEC/AF of 22.5 mg/kg (U.S. EPA, 1994). Thus, these polymers are acceptable for use in detergents from an environmental viewpoint.

CONCLUSION

The use of polycarboxylates in cleaning formulations has no adverse impact on the environment based on toxicological and environmental fate testing. The low levels of polycarboxylates in wastewater streams are significantly reduced in treatment plants through sorption and/or precipitation of the polymer. Acute and chronic toxicity tests indicate that under U.S. EPA criteria, polycarboxylates are "practically non-toxic" to aquatic organisms. Based on a comparison between the estimated environmental concentrations and the lowest no-observed effect concentrations, polycarboxylates are being used at acceptable levels.

REFERENCES

- Bascietto, J., D. Hinckley, J. Plafkin and M. Slimak, 1990. Ecotoxicity and environmental risk assessment, *Environ. Sci. Technol.* 24(1):10-15.
- Billmeyer, Jr., F.W., 1962. *Textbook of Polymer Science*, Interscience Publishers, New York.
- Chiaudani, G. and P. Poltronieri, 1990. Study on the environmental compatibility of polycarboxylates used in detergent formulations, *Ing. Ambientale*, 11:1-43.
- Cowan, C.E., R.J. Larson, T.C. Feijtel and R.A. Rapaport, 1993. An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants, *Water Res.* 27(4):561-573.
- Freeman, M.B. and T.M. Bender, 1993. An environmental fate and safety assessment for a low molecular weight polyacrylate detergent additive, *Environ. Technol.*, 14:101-112.
- Freeman, M.B., Y.H. Paik, G. Swift, R. Wilczynski, S.K. Wolk and K.M. Yocom, 1996. Biodegradability of polyacrylates: structure-activity studies, *Hydrogels and Biodegradable Polymers for Bioapplications* (R.M. Ottenbrite, S.J. Huang, K. Park, eds.) ACS Symposium Series 627, American Chemical Society, Washington, DC, 118-136.
- Goin, J.L., with L.P. Somogyi, H. Janshekar and Y. Ishikawa, 1995. Water-soluble polymers, *Chemical Economics Handbook*, SRI International, Menlo Park, CA.
- Hamilton, J.D., K.H. Reinert and M.B. Freeman, 1996. Aquatic risk assessment of a polycarboxylate dispersant polymer used in laundry detergents, *J. Tox. Environ. Health*, 49(1):67-82.
- Holman, W.F., 1981. Estimating the environmental concentrations of consumer product components, *Aquatic Toxicology and Hazard Assessment: Fourth Conference, ASTM STP 737* (D.R. Branson and K.L. Dickson, eds.) American Society for Testing and Materials, Conshohocken, PA, 159-182.
- Jones, C.E., 1993. *Development of Chlorine-stable Polymers*, presentation to the 84th American Oil Chemists' Society Meeting and Expo, Anaheim, CA.
- Opgenorth, H.-J., 1987. Environmental tolerance of polycarboxylates, *Tenside Surfact. Det.* 24(6):366-369.
- Opgenorth, H.-J., 1992. Polymeric Materials Polycarboxylates, *The Handbook of Environmental Chemistry, Volume 3, Part F* (N.T. de Oude, ed.) Springer-Verlag, Berlin, 337-350.
- Schumann, H., 1991. Elimination properties of polyelectrolytes in biological wastewater purification processes, *Tenside Surfact. Det.* 28(6):452-459.
- U.S. Environmental Protection Agency, 1991. *Technical Support Document for Water Quality-based Toxics Control*, Office of Water, Washington, DC, EPA/505/2-90-001, 52.
- U.S. Environmental Protection Agency, 1994. *A Review of Ecological Case Studies From a Risk Assessment Perspective, Volume 2*, ORD, Washington, DC, EPA/630/R-94/003.
- Zitko, V., 1981. Uptake and excretion of chemicals by aquatic fauna, *Ecotoxicology and the Aquatic Environment* (P.M. Stokes, ed.) Pergamon Press, New York, 67-78.