Alkylene Oxides and Their Polymers

SURFACTANT SCIENCE SERIES

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Preface

Alkylene oxides are interesting molecules that are used in a wide variety of ways. They are used in monomeric form as reactive intermediates to prepare low-molecular-weight chemicals that find application as solvents, pharmaceuticals, and surfactants. Ethylene oxide, for example, is used as a sterilant and as an intermediate. The utility of alkylene oxides and their polymers is far-reaching and includes the automotive, pharmaceutical, cosmetic, metal-working, mining, industrial coating, textile, construction, home furnishings, and other industries.

The poly(alkylene oxide)s are an unusual family of polymeric materials because of the extremely diverse and critical functions they perform in commercial use. To most consumers, these materials are often hidden in the fine print that describes compositions on labels, in material safety data sheets, and in handling documents. To scientists, the poly(alkylene oxide)s are known as distinct materials that are available in a wide range of molecular weights, from dimer to polymers of tens of millions, and yet remain well-characterized species of controlled molecular-weight distribution and known structure and configuration. These polymers can form ionic or molecular complexes and can provide mixtures with wide ranges of compatibilities, solubilities,

and electrical conductivities. The poly(alkylene oxide)s are in many ways high-molecular-weight phase-transfer agents exhibiting some of the host-guest specificity of the crown-ethers. The polyether glycols have been used in this way biochemically to permit controlled penetration of cell membranes and in frozen cell preservation.

Commercial polymers of alkylene oxides are prepared from a relatively few basic monomers: ethylene oxide, propylene oxide, butylene oxide, and epichlorohydrin. (Contrary to what can be found in the literature, poly(tetramethylene oxide) or poly-(tetrahydrofuran) is not derived from an alkylene and is not an alkylene oxide polymer.) The low-molecular-weight polymers are usually liquids with viscosities that depend on composition and degree of polymerization. These compounds are used as surfactants, lubricants, hydraulic fluids, quenchants, and emollients. The high-molecular-weight polymers are solids that may be amorphous or partially crystalline, depending on the same factors and on stereoregularity, with solubilities ranging from water soluble, hydrophilic, and oil resistant to oil soluble. The high-molecular-weight water-soluble polymers are used to modify the flow properties of water solutions and slurries and as selective coagulants in water treatment.

Elastomers can be obtained from atactic poly(propylene oxide), polyepichlorohydrin, and epichlorohydrin/ethylene oxide copolymers. Incorporated in polymers and plastics known as urethanes, the poly(alkylene oxide)s are found in automobile parts and seating, in snowmobile and other recreational vehicles, and as motor housings for machinery. In urethane foams, they are found in thermal insulation of appliances, in construction, in automotive seating and padding, in home carpet underlayment, in sports clothes, and in the upholstery of home and office furnishings. Poly(alkylene carbonate)s prepared from alkylene oxides and carbon dioxide are new materials that have utility as ceramic binders and foam castings and are being investigated for other uses.

The broad range of physical properties, chemical characteristics, and compatibilities makes these oligomers and polymers interesting materials for researchers in the laboratory, for product development personnel, and for consumers. They touch our lives in some manner every day.

F. E. Bailey, Jr.
Joseph V. Koleske

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1

Introduction: The Poly(alkylene oxide)s

I. THE POLYMERS OF THE 1,2-ALKYLENE OXIDES AND MAJOR COMMERCIAL USES (1-4)

The poly(alkylene oxide)s are linear or branched-chain polymers that contain ether linkages in their main polymer chain structure and are derived from monomers that are vicinal cyclic oxides, or epoxides, of aliphatic olefins, principally ethylene and propylene and, to a much lesser extent, butylene. These polyethers are commercially produced over a range of molecular weights from a few hundred to several million for use as functional materials and as intermediates. Lower polymers are liquids, increasing in viscosity with molecular weight. The high polymers can be thermoplastic. Solubilities range from hydrophilic water-soluble polymers that are principally derived from ethylene oxide, to hydrophobic, oil-soluble polymers of propylene oxide and butylene oxide. A wide variety of copolymers is produced, both random copolymers and block copolymers. The latter may be used for their surface-active characteristics.

This unusual family of materials performs extraordinarily diverse commercial functions (see Table 1). As distinct polymers, the poly(alkylene oxide)s are of great value to polymer scien-

TABLE 1 Uses of the Poly(alkylene oxide)s
(From Refs. 3 and 4.)

Nonionic surfactants
Polyols for urethane foams and elastomers
Antifoams
Calender lubricants
Circulating oils
Compressor lubricants (air, helium, hydrogen, natural gas, process gases)
Cosmetics (emollients, humectants, thickeners)
Cryogenic fluids
Gear oils
Greases
Heat-transfer fluids
Hydraulic fluids
Industrial coatings
Mandrel lubricants
Metal-working lubricants
Seal lubricants
Solder-assist fluids
Textile lubricants (fiber and machine lubricants)
Two-cycle engine lubricants
Vacuum pump lubricants

tists who may wish to have polymers with relatively simple basic structures that are well characterized, either linear or with controlled branching, over a high molecular-weight range. Such well-characterized polymers are readily prepared with narrow molecular-weight distributions and with controlled levels of polymer crystallinity. Poly(ethylene oxide), above a molecular

weight of about 1000, is a crystalline, linear polymer with a crystalline melting point that increases with molecular weight, approaching a melting point of about 67°C. Poly(propylene oxide) and poly(1,2-butylen oxide) can be prepared as amorphous or stereospecific polymers. These polyethers can form a wide variety of molecular and ionic complexes and provide, thereby, a broad range of compatibilities, solubilities, and electrical conductivities.

Lower molecular weight polymers of ethylene oxide, and copolymers of high ethylene oxide content, are water soluble. These polymers have been used for many years in cosmetics and pharmaceuticals as humectants and binders and have been used to impart surface lubricity in lotions and creams. Poly(ethylene oxide) adducts of higher alcohols and phenols are a principal class of nonionic surfactants. A higher polymer, CARBOWAXTM 20M, with a number average molecular weight of about 20,000, has been widely used as a packing in gas chromatograph columns.

High-molecular-weight polymers of ethylene oxide are miscible with water in all proportions at temperatures from the freezing point to near the boiling point, depending on polymer molecular weight. The polymers exhibit an inverse solubility-temperature relationship in water, having a lower consolute temperature near 100°C. At very high dilutions, poly(ethylene oxide) is an enormously effective drag-reduction agent in water (5) (Tom's Effect). At higher concentrations, it forms hydrogels. The polymer itself can be formed as a thermoplastic into a water-soluble film.

The lower molecular weight polymers of propylene oxide and propylene oxide adduct copolymers are used as surfactants, hydraulic fluids, and machine and metal-working lubricants. Propylene oxide adducts of polyhydroxy compounds, such as glycerine, trimethylolpropane, or pentaerythritol or sorbitol, are principal polyols used in making polyurethane elastomers, rigid thermal insulation, flexible foams, and coatings.

The poly(ethylene oxide)s and poly(propylene oxide)s described in this book are widely available in different molecular weights and functionalities. Table 2 is a listing of some of the various trade names or brand names and their sources for these polymers and their copolymers. Trade names for other products can be found at various appropriate places within the text.

TABLE 2 Trade Names or Brand Names for Poly(ethylene oxide)s and Poly(alkylene oxide)s and Their Copolymers

Trade name	Source
ACTOL	Allied-Signal Incorporated
ADEKA, ADEKA CARPOL	Asahi Denka Kogyo K.K.
AFTOL	Petrolite Corporation
ALKATRONIC	Alkaril Chemicals Inc.
ANTAROX	Sparmar Dispersants
AQUANOX	Baker Hughes Incorporated
AQUASURF	Baker Hughes Incorporated
ATLAS	Atlas Chemical Company
CP POLYOL	Corn Products Incorporated
CARBOWAX	Union Carbide Corporation
CARPOL	E. R. Carpenter, Incorporated
CARDANOL	Shell Chemical Company
DALTOLAC	ICI Limited
DESMOPHEN	Farbenfabriken Bayer A.G.
GAFTRONIC	GAF Corporation
EMERLUBE	Quantum Chemical Corporation
FOAMBREAK	Baker Hughes Incorporated
FOMREZ	Witco Corporation
HODAG	Hodag Chemical Corporation
ISONOL	Upjohn Company
JEFFOX	Texaco, Incorporated
MULTRANOL	Bayer U.S.A., Mobay Corp.
NALCO	Nalco Chemical Company
NIAX	Union Carbide Corporation
PLURACOL	BASF Corporation

TABLE 2 (Continued)

Trade name	Source
PLURONIC	BASF Corporation
POLY-G	Olin Corporation
PROPYLAN	Lankro Chemical Company, Mitsui K.K.
POLYOX	Union Carbide Corporation
POLYURAX	Pfizer Incorporated
SELECTRO	PPG Ind., Incorporated
SYNPERONIC	ICI American Holdings, Inc.
TETRONIC	BASF Corporation
THANOL	Arco Chemical Company
TRETOLITE	Petrolite Corporation
VISCO	Nalco Chemical Company
VORANOL	Dow Chemical U.S.A.
WITBRAKE	Witco Corporation

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