Polyoxyalkylenes

ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

This article deals with polyoxyethylene, polyoxypropylene, and polytetrahydrofuran or poly (1,4-epoxybutane). Other names include poly (ethylene oxide), PEO; poly(propylene oxide), PPO; and poly(tetramethylene oxide), PTMO. Strictly speaking, the latter polymer is not derived from an alkene and thus is not a poly (alkylene oxide); however, it is included here, and the term poly(alkylene oxides) is used as a collective term for these three polymers. The poly(alkylene oxides) have an ether linkage in their main chain backbone and thus are polyethers. They are described by the repeat unit

$$-[(CH_2)_x-CHR-O]-$$

Poly(ethylene oxide):	R=H, x=1
Poly(propylene oxide):	R=CH_3, x=1
Poly(tetramethylene oxide):	R=H, x=3

Many details about the alkylene oxides and their polymers are given in [1].

2. Properties

Physical Properties. Typical physical properties of PEO, PPO, and PTMO are presented in Table 1. Except for PTMO, these polyethers can be linear or branched and are commercially available in a broad range of molecular masses from less than a few hundred to several million.

Low molecular mass polymers of ethylene oxide are clear, essentially colorless liquids and become partially crystalline solids at a molecular mass of ca. 800. As the molecular mass increases, they change from soft waxy solids to hard waxes. At high molecular mass, they are tough thermoplastics. Polyoxyethylenes of less than ca. 20 000 number-average molecular mass are usually referred to as poly(ethylene glycols). The crystalline polymer is spherulitic, has a unit cell (see Table 2) with four molecular chains, and has a fiber identity period of seven repeat units in two helical turns. The molecules are in an array of dihedral symmetry with twofold axes. One axis bisects the carbon – carbon bond and the other passes through the ether oxygens.

The glass transition temperature of PEO is listed as − 52 °C in Table 1; however, this is the value for a high molecular mass, partially crystalline polymer. This parameter is complicated by crystallinity in the molecular mass range 10^3 –10^5 [22], and abnormal values as high as − 17 °C are found for the polymer with M=6000, which is known to have the highest crystallinity (ca. 95 %). Macrospherulites or spherulites that can be seen without magnification have been prepared [23].

PEO is soluble in water, chlorinated hydrocarbons, aromatic hydrocarbons, methyl ethyl ketone, 2-ethoxyethyl acetate, butyl acetate, cy-clohexanone, esters, dimethylformamide, and

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Table 1. Selected physical properties of the poly(alkylene oxides)

	Poly(ethylene oxide)	Poly(propylene oxide)	Poly(tetramethylene oxide)
Density, g/cm^3			
Amorphous	1.127 – 1.128[a] [2]	ca. 1.01 – 1.025[a] [3]	0.975 (25 °C) [4]
Crystalline	1.21 (20 °C) [5]	1.096 (25 °C) [6]	1.07 – 1.08 [7]
Melting point, °C			
High molecular mass	65 [5]	75 [8]	58 – 60 [9]
Oligomeric[b]	30 – 50 [10]	[c]	10 – 45
Glass transition temperature, °C	– 52 [11]	– 73 to – 78 [12]	– 86 [4], [12]

[a] d_{20}^{20}.
[b] M_n ca. 400 – 3000.
[c] Liquid under ambient conditions.

other solvents [1]. It has a solubility parameter of 10.3 [24]. It is insoluble in ethers and aliphatic hydrocarbons. Mark – Houwink constants for the intrinsic viscosity/molecular mass relationship $[\eta]=KM^a$ are given in Table 3. In water, PEO exhibits an inverse solubility – temperature behavior, becoming less soluble as the temperature is increased.

Intermolecular or association complexes between PEO and other compounds are readily formed due to the strong hydrogen bonding character of the ether oxygens. These complexes, which involve PEO and polymeric acids such as poly(acrylic acid) [35], urea, and thiourea [36], as well as various other inorganic and organic compounds [1], [37], have potential applications in mechanochemical energy conversion systems [38], chemical valves for altering the porosity of membranes [39], and biosensors and carriers for controlled drug delivery [40]. Alkali-metal salt complexes have electrical properties that make them of interest as battery electrodes [41].

Polymers of propylene oxide remain clear, almost colorless liquids or amorphous solids over broad ranges of molecular mass. They can be prepared as amorphous or stereoregular polymers, with stereoregularity resulting in crystallinity. Polyoxypropylenes with $M<$ca. 20 000 are usually referred to as poly(propylene oxide) polyols, and these polymers are by far the most important products from a commercial standpoint. They are usually marketed as di- and trihydroxyl polyols that are available in a broad range of molecular mass. (The third hydroxyl group comes from the initiator; for example if glycerine, which is the most common initiator for PPO polyols, is used, the PPO grows off all three hydroxyl groups and a trifunctional polyol results.) High molecular mass PPO polymers are used as specialty rubber and represent only a small worldwide demand of about 1000 t/a. The crystalline polymer has a unit cell (see Table 2) that contains two chains in a bowed zigzag conformation, with the methyl group of one molecule located between the ether oxygen and methylene group of the adjacent molecule.

PPO is soluble in most organic solvents. Very low molecular mass polyols (< 1000) are insoluble in aliphatic hydrocarbons such as hexane due to the high hydroxyl content. However, polyols with such high hydroxyl contents do have some solubility in water. Mark – Houwink constants for the intrinsic viscosity/molecular mass relationship $[\eta]=K\,M^a$ are given in Table 3.

Although not so thoroughly studied as those of poly(ethylene oxide), association complexes of

Table 2. Crystal data for poly(alkylene oxides)

	Poly(ethylene oxide) [13–15]	Poly(propylene oxide) [16], [17]	Poly(tetramethylene oxide) [18–21]
Unit cell	Monoclinic	Orthorhombic	Monoclinic
a, nm	0.796	1.04	0.548 – 0.561
b, nm	1.311	0.467	0.873 – 0.892
c, nm	1.939	0.716	1.207 – 1.225
β	124.8°		134.2 – 134.5°

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Table 3. Mark – Houwink constants for poly(alkylene oxides)

Solvent	Temperature, °C	$K \times 10^5$	a	Approximate molecular mass range	Average molecular mass	Reference
Poly(ethylene oxide)						
Water	30	12.5	0.78	$10^4 - 10^7$	Weight	[25]
Water	35	6.4	0.82	$10^4 - 10^7$	Weight	[26]
Aq. 0.45 M K_2SO_4	35	130	0.50	$10^4 - 10^7$	Weight	[26]
Aq. 0.39 M $MgSO_4$	45	100	0.50	$10^4 - 10^7$	Weight	[26]
Benzene	25	39.7	0.69	$8 \times 10^4 - 5 \times 10^6$	Weight	[27]
Carbon tetrachloride	20	69	0.61	200 – 10 000	Number	[28]
Toluene	35	145	0.70	400 – 4000	Number	[29]
Poly(propylene oxide)						
Acetone	25	75.5	0.56	1000 – 4000	Number	[30]
Benzene	20	11.1	0.77	700 – 3300	Number	[31]
Benzene	25	11.2	0.77	$3 \times 10^4 - 7 \times 10^5$	Weight	[32]
Toluene	20	20.8	0.72	700 – 3300	Number	[31]
Toluene	25	12.9	0.75	$3 \times 10^4 - 7 \times 10^5$	Weight	[32]
Poly(tetramethylene oxide)						
Benzene	30	131	0.60	$3 \times 10^4 - 10^6$	Weight	[33]
Cyclohexane	30	176	0.54	$3 \times 10^4 - 10^6$	Weight	[33]
Ethyl acetate	30	42.2	0.65	$3 \times 10^4 - 10^6$	Weight	[33]
Toluene	28	25.1	0.78	$3 \times 10^4 - 10^5$	Number	[34]

poly(propylene oxide) are also known. These complexes are formed with a variety of salts such as lithium perchlorate [42] and metal halides, particularly chlorides [43]. Complexes of propylene oxide – ethylene oxide block copolymers with sodium and lithium salts exhibit marked increases in electrical conductivity [44] as compared to the uncomplexed copolymers.

Tetrahydrofuran can be polymerized to high molecular mass, but the commercially available poly(tetramethylene oxide) diols have molecular masses of ca. 650 – 3000 and a narrow molecular mass distribution. Although these polyols are usually crystalline in nature, their narrow molecular mass distribution [45] makes them easy to use, since even partial melting yields a product with effectively the same molecular mass distribution as that of a completely melted product. The crystalline polymer has a monoclinic unit cell whose characteristic dimensions are given in Table 2.

Solvents for PTMO, which has a solubility parameter of 17.3 – 17.6 [46], include aromatic hydrocarbons such as benzene and toluene, chlorobenzene, dichloromethane, chloroform, carbon tetrachloride, esters such as ethyl acetate, and nitrobenzene. Low molecular mass products are soluble in acetone, alcohols, and similar polar solvents. The polymers are insoluble in aliphatic hydrocarbons such as heptane, hexane, pentane, and petroleum ether. Only cursory studies of association complexes of PTMO have been conducted [43].

Chemical Properties. Poly(alkylene oxides) are chemically characterized as usually having primary (PEO and PTMO) and secondary (PPO) hydroxyl end groups [47]. PEO and PPO have been prepared with a variety of end groups including allyl or propenyl ethers, which arise during polymerization of ethylene oxide and propylene oxide through the termination reaction [48]; carboxyl [49], [50]; amine [51]; cyano [52]; and vinyl ether [53]. Alkyl or aryl ester terminated PEOs are used as nonionic surfactants [54], [55], and alkoxy-terminated PEOs prepared from alcohols or other monohydroxyl compounds are used for similar purposes as well as in cosmetic and pharmaceutical preparations. In addition to primary hydroxyl termination, PTMOs have been prepared with a majority of primary amino terminal groups [56]. Isocyanate-terminated poly (propylene oxides) and poly(tetramethylene oxides) are known as isocyanate-terminated prepolymers for preparation of polyurethanes.

Copolymers of various types can be prepared from the alkylene oxides. The best known of these are the polyurethanes, though they are not normally prepared from the poly(ethylene oxides). Polyurethanes are formed in a rearrange-

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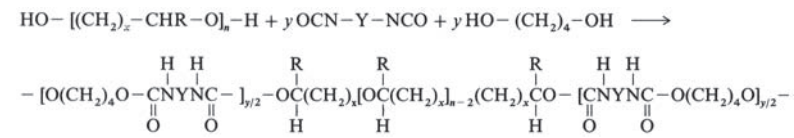

Figure 1. Formation of polyurethanes

ment reaction from poly(alkylene oxide) polyols, short chain diols such as 1,4-butanediol and ethylene glycol, and multifunctional isocyanates. The reaction takes place at relatively low temperatures, including room temperature, as depicted in the general, idealized manner (Fig. 1) where Y represents the residue of a polyfunctional isocyanate without its isocyanato groups. (In this generalization, it should be noted that the starter molecule for the poly(alkylene oxide) is omitted. If the alkylene oxide involved were propylene oxide, on the average both end groups would have been secondary hydroxyl groups.)

This unit would be the average repeating unit in the final polyurethane. A wide variety of isocyanates are used, including toluene-2,4-diisocyanate, 4,4′-diphenylmethane diisocyanate and its polymeric forms, 4,4′-dicyclohexylmethane diisocyanate, and isophorone diisocyanate. The latter two isocyanates are used when light-stable polyurethanes are required.

Urethane acrylates are formed by preparing an isocyanate-terminated prepolymer and then capping it with a hydroxyalkyl acrylate. These acrylate-terminated oligomers are widely used in radiation curable coatings.

Isocyanate-terminated PTMO polyols have been marketed as Adiprene (Du Pont) and Vibrathane (Uniroyal) precursors. Block copolymers of poly(tetramethylene oxide) and poly (butylene terephthalate) are marketed as Hytrel (Du Pont) for a variety of end uses.

Other copolymers include the very important ethylene oxide – propylene oxide copolymers [57], which occur in random, block, and graft form. Random copolymers are usually prepared from mixtures of monomers, and block copolymers by alternately feeding the two monomers. Block copolymers are often used as surfactants, metal lubricants, and functional fluids. Most of the block copolymers have poly(ethylene oxide) as the hydrophilic block and poly(propylene oxide) as the hydrophobic block. Other hydrophobic blocks include poly(styrene oxide), poly (tetramethylene oxide), and polystyrene [58]. ABA block copolymers of poly(1-proline) and amine-terminated PEO [59], as well as those of poly(ε- caprolactone) [60] and polyesters [61] grown onto hydroxyl-terminated PEO, have been prepared. A well-known graft copolymer, hydroxyethyl cellulose (→ Cellulose Ethers) [62], [63] is formed by swelling cellulose in a caustic solution and then adding ethylene oxide to the hydroxyl groups of the anhydroglucose units. Silica [64], gelatin and collagen [65], and chitin [66] are other polymeric substrates to which ethylene oxide has been grafted. Low molecular mass PEOs terminated with 1,2,4-triazoline-3,5-dione have been grafted onto polybutadiene [66].

A particularly useful class of grafted poly (propylene oxide) polyols was discovered in 1966 [67], [68]. These so-called polymer polyols are composed of vinyl polymers (e.g., acrylonitrile, styrene) and copolymers which are grafted to PPO or to PEO- capped PPO. They are produced by adding the vinyl monomers to the PPO polyol and dispersing them by agitation. A catalyst is then added to polymerize the vinyl monomers, which are believed to graft or partially graft to the polyol. The polymer polyol retains the end-group hydroxyl functionality, which is thus available for reaction with, for example, isocyanates. The vinyl polymer, which is incompatible with the polyol, is present in the form of a stable dispersion that acts as a reinforcing filler. These polymer polyols are used to manufacture polyurethane foams that have enhanced moduli while maintaining other desirable characteristics. Commercial products contain either grafted polyacrylonitrile or acrylonitrile – styrene copolymers, and they are used in high-resiliency automotive seating [69], microcellular elastomers [70], and other high-performance applications.

A deficiency of polyethers is their susceptibility to oxidation. PEO degrades by an autoxidation mechanism that is associated with formation and cleavage of intrachain hydroperoxides [72], [72]. Mechanical actions such as high shear can also cause degradation [73]. Hydroperoxide

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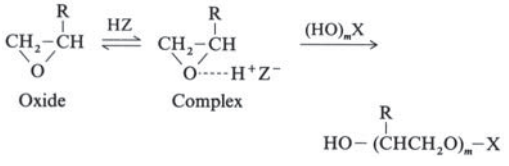
formation is facilitated by heavy metal ions, strong acids, and ultraviolet light. PPO and PTMO degrade by both chain scission and cross-linking [74], [75]. A number of investigations indicate that aromatic compounds such as substituted phenols, cresols, and quinones [76–78], mixtures of aliphatic amines and dihydric phenols (e.g., hydroquinone, *tert*-butylhydroquinone) [79], carbamates [80], and similar compounds function as stabilizers. A prime stabilizer for the poly(alkylene oxides) is 2,6-di-*tert*-butyl-4-methylphenol. Stabilization during storage is usually effected with 200 – 300 ppm of the stabilizer. However, in end uses involving solutions or slab stock polyurethane foam produced in bun form [1, p. 237] from poly(propylene oxide) polyols, 1000 – 5000 ppm are used to compensate for the long times at high temperature that are encountered due to retention of the heat of polymerization caused by the excellent insulation properties of the foam.

3. Production

Ethylene oxide was first polymerized in 1863 by Wurtz [81], who heated the oxide with water in a sealed tube. Earlier, in 1859, Lourenço [82] had obtained the polymer from ethylene glycol and ethylene bromide. Seven decades later Staudinger and Lohmann [83] prepared a number of polymers with a variety of catalysts, including alkali and alkaline earth metals.

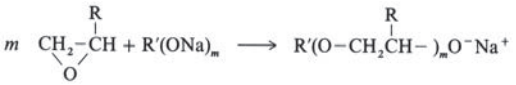
There are three main ring-opening reactions for the polymerization of ethylene oxide and propylene oxide: acid, base, and coordinate initiation. Acid or cationic initiation [84–86] with an acid, HZ, involves addition of an active-hydrogen compound such as an alcohol or glycol, $(HO)_mX$ (m=1 – 4), to the 1,2-epoxide ring. In the initiation step, an oxonium complex forms and ring opening takes place by cleavage of the oxygen – carbon bond to form an initiated species that is available for propagation.



In the propagation step, n molecules of oxide are added to give a polymer having the formula $HO-[(CHRCH_2O)_n]_m-X$. Termination can occur by proton transfer, which yields an unsaturated product, or by anion transfer, which generates the starting acid.

Brønsted or Lewis acids such as $AlCl_3$, $SnCl_4$, PF_6, and BF_3 are used as initiators. The reaction is very fast, molecular mass is relatively low, and molecular-mass distribution is broad.

Base or anionic initiation [87–89] takes place in the following manner, where R′ is usually an alkyl group.



Propagation takes place in a manner similar to that described above. Termination can be by hydrogen abstraction from the backbone, which results in terminal unsaturation and formation of a new initiation site, or by rearrangement of the active species.

Polymerization rates for the two mechanisms when perchloric acid and sodium methoxide are used are given in Table 4 for a few selected alkylene oxides.

Anionic initiators are usually metal alkoxides such as sodium or potassium methoxide or ethoxide. The reaction is usually slower than that obtained with acid initiation, except for epichlorohydrin and glycidol [90], [91]; relatively high molecular masses can be obtained and the molecular mass distribution is relatively narrow.

Ionic coordinative polymerization [92–95] involves a complex of a metal, M, such as Al, Sn, Fe, Mg, Li, etc., with ligands, L (e.g., OH, OR, Cl) that coordinates in an ionic manner with the oxygen atom of the epoxide. Complexation is followed by nucleophilic attack by the ligand,

Table 4. Polymerization rate for selected alkylene oxides relative to ethylene oxide [90], [91]

Oxide	Initiator	
	Perchloric acid	Sodium ethoxide
Epichlorohydrin	0.065	4.8
Ethylene oxide	1.0	1.0
Propylene oxide	54	0.5
Isobutylene oxide	5100	0.06

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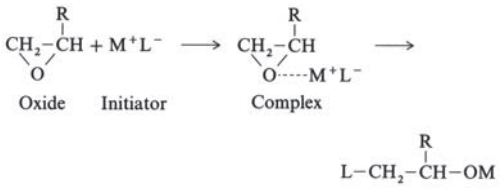
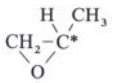
which results in opening of the oxirane ring to give an initiated species that can undergo propagation to form the polymer chain.

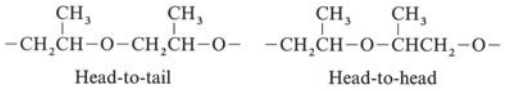


There are two categories of ionic coordination initiators [94], [96]. Initiators in the first category involve the formation of metal – oxygen coordination bonds, and those in the second category are alkaline earth compounds that have an anionic surface capable of coordinating with the oxide monomer.

In the case of propylene oxide, the monomer has an asymmetric carbon atom (C^*)



and when the ring is opened this asymmetric center is incorporated in the polymer chain. PPO can contain both head-to-tail and head-to-head sequences.

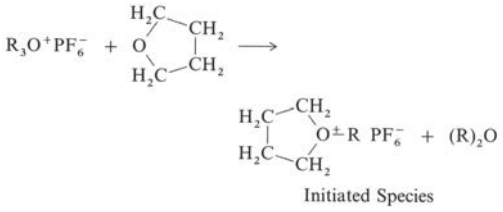


The head-to-tail sequences are formed by the expected carbon – oxygen cleavage between the methylene group and the oxygen atom of the epoxide, whereas the head-to-head sequences occur when unexpected cleavage takes place between the methyl-substituted carbon and the oxirane oxygen. Up to 30 % head-to-head structure has been found in certain polyoxypropylenes [97], [98].

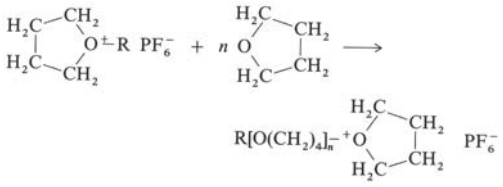
Tetrahydrofuran was first polymerized by Meerwein and Kroning in 1937 [99], [100]. An I.G. Farbenindustrie patent [101] indicates that polymers of this monomer were the subject of numerous investigations from 1939 to 1943. Ring strain, a necessity for favorable polymerization, is small in this monomer compared to other cyclic ethers [102], and thus THF has less tendency to polymerize than ethylene oxide and propylene oxide. Although commercial polymers are dihydroxyl functional and low in molecular mass, a high molecular mass polymer with a melting point above 100 °C has been reported [103].

THF is a nucleophilic monomer that forms a tertiary oxonium ion during initiation and only polymerizes by a cationic ring-opening mechanism [104–108]. A variety of mechanisms for formation of the tertiary oxonium ion are known. These include direct alkylation or acylation, in situ formation from reactive organic halides and metal salts or Lewis acids, and direct addition of strong protic acids to the oxygen atom. For example [109], direct alkylation of the monomer by exchange with trialkyloxonium salts illustrates the initiation reaction.

Propagation then takes place by collisions between the initiated species and THF, whereby



only collisions that occur at the α- carbon atom of the THF molecule result in propagation.



Water, oxygen, and other nucleophilic reagents can be used to terminate the polymerization.

Industrial poly(tetramethylene oxides) are hydroxyl terminated, and control of the termination reaction is important to the process. Hydroxyl groups, which have a profound effect on molecular mass, can be formed if strong protic acids are used to form the initiated species [110], [111]. The proton gives rise to an hydroxyl group on the end of the propagating species, and when water is used to terminate the polymerization, a second hydroxyl group is formed and the initiator acid is regenerated.

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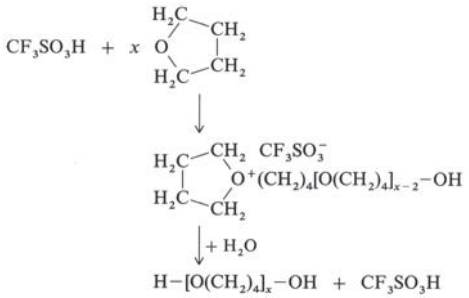

4. Toxicity [112]

Poly(ethylene oxides) have a very low single-dose oral toxicity that decreases with increasing molecular mass. Single-dose oral LD_{50} values in g/kg, for polymers of 200, 1000, 2000, and 6000 are, respectively, 34, 45, 45, and > 50 for male rats; 28, 32, > 50, and > 50 for female rats; 14, (not available), > 50, and > 50 for male rabbits; and 34, > 50, > 50, and > 50 for mice. PEOs of 400, 1540, and 4000 molecular mass were fed to dogs at a 2 % level in the diet with no adverse effect. When fed to rats at 2 %, PEO of 400 molecular mass had no effect, and at 4 % PEOs of 1540 and 4000 molecular mass had no effect. Doubling the dietary amounts for rats resulted in weight loss, an increase in liver weight, and slight histologic changes in the liver with the 400 compound, an increase in liver weight with the 1540 compound, and weight loss with the 4000 compound. Feeding of a 4 000 000 molecular mass compound at 5 % (rat) and 2 % (dog) diet had no detectable effect after 24 months. Testing with a radioactively labeled sample of the high molecular mass PEO indicated no significant absorption of the polymer from the gastrointestinal tract of the rat or dog.

PEOs do not appear to cause appreciable irritation to the eyes of rabbits. Skin irritation is apparently absent, which is attested to by the wide use of these compounds in cosmetic preparations. Overall, there are no reported adverse effects or human injuries from handling of PEOs [111].

Poly(propylene oxides) of molecular mass ca. 200 – 2000 have a single-dose oral toxicity that is noticeable, and they have mild eye irritability. They are not irritating to the skin, and even though there is some absorption through the skin, they do not appear to present a serious industrial health hazard. Inhalation of mists, particularly of the low molecular mass compounds (ca. 400 to 1200), could be hazardous. The low molecular mass compounds are rapidly adsorbed from the gastrointestinal tract and are potent CNS stimulants that readily cause cardiac arrhythmia. Excitement and convulsions are apparent within minutes after oral administration. Higher molecular mass compounds (> 2000) are very low in toxicity by all administration routes and do not stimulate the CNS. Oral LD_{50} values (rat) in g/kg for polymers of 400, 1200, and 4000 molecular mass are 1.6, 1.4, and > 15 for males and 2.1, 1.1, and > 15 for females, respectively.

Poly(tetramethylene oxides) are commercially available in four number-average molecular masses (650, 1000, 2000, and 2900) as dihydroxyl functional compounds [113], [114]. Acute oral toxicity (LD_{50} in g/kg) for albino rats was 11.3, 18.8, and > 34 for the 650, 1000, and 2000 molecular mass polyols, respectively. Acute dermal toxicity in albino rabbits was 8.37, 10.25, and > 10.25 g/kg for the same polyols. The poly-ols are rated as being minimally irritating to the eyes and skin of albino rabbits [112]; however, a Material Safety Data Sheet indicates that the products may irritate the skin and eyes [115].

5. Handling

Most manufacturers and suppliers of poly (alkylene oxides) have detailed, current handling methods available for bulk, drum, and laboratory handling and storage, which should be consulted when working with the chemicals.

The poly(ethylene oxides) range from liquids at low molecular mass to hard waxes at moderate molecular mass, and to tough thermoplastics at high molecular mass (> ca. 100 000). They are not corrosive to most common construction materials. Although not strongly corrosive to copper and its alloys, some discoloration may occur if the compounds are kept in contact with copper-containing materials for prolonged times. Aqueous solutions of PEOs are corrosive to regular carbon steel; hence, stainless steel should be used for their storage. Tanks for bulk storage are usually made of plain carbon steel. For smaller quantities, lined steel drums are used to minimize the pickup of traces of iron [116]. When short storage times of a month or

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less are involved, storage under air is acceptable. For prolonged storage, particularly in hot climates or under heated conditions, the products should be kept under an inert (nitrogen) atmosphere. Since PEOs are hygroscopic, dry conditions are important for most uses. PEOs have low vapor pressures and are not fire hazards unless high temperatures are involved. For example, polymers of molecular mass 200, 1000, 4000, and 9000 have Cleveland Open Cup flash points of 171 –182 °C, 254 – 265 °C, 271 °C, and 271 °C, and Cleveland Closed Cup flash points of > 148 °C, > 177 °C, > 177 °C, and > 177 °C, respectively.

The poly(propylene oxides) are usually liquid, stable, noncorrosive compounds that have a very low vapor pressure. They are preferably stored at temperatures below 50 °C, usually in carbon steel tanks. However, if there is concern about the pickup of iron, tanks protected with a baked phenolic coating can be used [117]. PPOs should be blanketed with dry air or nitrogen to prevent absorption of moisture during storage. They are usually dried before use in polyurethane manufacture. Nitrogen is preferred for prolonged storage or storage at elevated temperature. They represent fire hazards only at high temperatures. For example, 400, 2000, and 4000 molecular mass polymers have Cleveland Open Cup flash points of 166 °C, 229 °C, and 229 °C, respectively.

The poly(tetramethylene oxides) are liquids or low-melting solids under ambient conditions. Mild steel and phenolic-lined steel tanks are suitable for storage. These products are not considered fire hazards unless high temperatures are encountered, and they have a Tag Open Cup flash point of > 163 °C. The compounds are unstable and may decompose at temperatures above 100 to 200 °C or at lower temperatures if in contact with high surface area substrates such as fibrous insulation [115]. When they decompose, very flammable tetrahydrofuran and carbon monoxide can be released.

6. Uses

Low molecular mass poly(ethylene oxides) (M<800) are usually used as intermediates for the manufacture of fatty acid ester surfactants that are used in a variety of formulated products. Illustrative of these products are soap or detergent suds control agents, foam stabilizers, fabric softeners, and optical brighteners. Typical detergents contain up to 20 % of a nonionic or anionic surfactant. Polymers with molecular mass of ca. 1000 – 2000 are low-melting waxes used in pharmaceutical ointments, cosmetic creams, and lotions. Their low toxicity, nonirritating nature, and smooth, creamy texture along with liquefaction at body temperatures make them particularly useful in cosmetic and pharmaceutical applications such as formulations for salves, suppositories, and ointments. Esters of these compounds are used as thickeners in cosmetic formulations.

The medium molecular mass PEO compounds, up to about 20 000, are hard, brittle waxes. They are used as adhesives, binders, plasticizers, molding compounds, wood impregnants, stiffening agents, and metal-working lubricants. Various PEOs are used in artifact preservation, particularly for items recovered after prolonged water immersion [118], [119]. In particular, copolymers of ethylene oxide and propylene oxide are often used in metal-working fluids and as quenchants, lubricants, and hydraulic fluids.

High molecular mass PEOs are used as textile sizes, as hydrodynamic friction reduction agents, in cosmetics and toiletries, as water-soluble films for seeds, in packaging, in adhesives, and in dentistry. The ability of the high molecular mass polymer to reduce hydrodynamic friction has led to applications in fire fighting and municipal sewage discharge control. The polymer is so effective in reducing the friction of water that it has been banned from use in competitive skiing and boating, where it markedly improved speed when incorporated into waxes and polishes. The association complexes of poly(ethylene oxide) have found use in controlled release of drugs, as adhesives, in artificial kidneys, and microencapsulation.

Poly(propylene oxides) are used as plasticizers, lubricants, solvents, softening agents, antifoaming agents, surface active agents, mold release agents, hydraulic fluid compositions, quenchants, and as intermediates in the production of resins (polyurethanes and alkyds). The largest use of the poly(propylene oxides) and ethylene-oxide- capped PPO polyols is in the production of polyurethane foams and elasto-

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mers. The main polyurethanes are those based on toluene-2,4-diisocyanate and 4,4′-diphenylmethane diisocyanate, although light-stable versions based on cycloaliphatic polyisocyanates are made for specialty end uses. The polyurethanes are used as automobile seating, automotive crash pads, furniture cushioning, insulation, bedding, packaging, carpet underlay, molded parts, and many other applications.

The low molecular mass poly(tetramethylene oxide) polyols are used in coatings, to make block copolymers that are used for fabricated parts, and polyurethanes used as elastomeric fibers (spandex fibers). PTMOs have FDA approval for use in polyurethanes and adhesives that come into direct contact with dry foods [120]. The fibers have low hysteresis loss, very good tensile strength, and good tear and abrasion resistance. They are particularly useful for clothing, support garments, knitwear, swimwear, and other similar end uses. No commercial uses are known for high molecular mass PTMO.

7. Economic Aspects [121]

Estimates of the worldwide production of poly (alkylene oxide) polyols for polyurethanes is given in Table 5. Poly(propylene oxide) polyols account for about 95 percent of the polyols produced for polyurethanes, and poly(tetramethylene oxide) polyols account for about 2 percent of the total.

It is difficult to estimate amounts produced for nonpolyurethane end uses since major companies use the same facilities to produce for both markets. The production for nonpolyurethane end uses is given in Table 5. The majority of the polyol for nonpolyurethane use is for surface active agents (40 %) and for functional fluids and lubricants (31 %). The remainder is used in a wide variety of end uses (see Chap. 6). In the United States, production is about 18.6 % poly(propylene oxides), 31.4 % poly(ethylene oxides), and 50 % ethylene oxide – propylene oxide copolymers. In Western Europe production is about 38 % PPO and PEO, and the remainder copolymers. In Japan production is about evenly divided between PPO, PEO, and copolymers.

The largest manufacturers are:

United States	ARCO, BASF, Dow, E. R. Carpenter, Mobay, Olin, and Union Carbide
Western Europe	ARCO, BASF, Bayer, Dow, Montedipe, and Shell
Japan	Asahi Denka, Asahi Olin, Dow, and Mitsui Toatsu
Republic of Korea	Korea Polyol and Miwon
Taiwan	Chiunglong Petrochemical

Although production of poly(tetramethylene oxide) polyols is included in the production values for polyols as given in Table 5, production of this specialty polyol is delineated by company in Table 6. Polyurethane fibers and elastomers produced from these polyols have tensile properties as good as or better than those of polyesters, together with especially good hydrolytic stability and excellent low hysteresis loss [122].

Table 5. Major worldwide production or consumption of poly(alkylene oxide) polyols [121]

Country	Production, 10^3 t
Production for polyurethane end uses	
Western Europe	931
United States	835
Japan	260
Korea and Taiwan	54
Total	2080
Production for nonpolyurethane end uses	
United States	159
Western Europe	92
Japan	57
Total	308

Table 6. Worldwide production of poly(tetramethylene oxides) [121]

Company	Production, 10^3 t	Trade name
United States		
Du Pont	30	Terethane
QO Chemicals	11	Polymeg
Wesern Europe		
BASF	4	PolyTHF
Du Pont (Netherlands)	30	Terethane
Japan		
Hodogaya Chemical	3	
Mitsubishi Kasei	4	
Sanyo Chemical	1	

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