ETHYLENE OXIDE POLYMERS

1. Introduction

Poly(ethylene oxide) [25322-68-3] (PEO) is a water-soluble, thermoplastic polymer produced by the heterogeneous polymerization of ethylene oxide. The white, free-flowing resins are characterized by the following structural formula:

$$-(CH_2CH_2O)_n-$$

The resins are available in a broad range of molecular weight grades, from as low as 100,000 to over 7×10^6. Although most commonly known as poly(ethylene oxide) resins, they are occasionally referred to as poly(ethylene glycol) or polyoxyethylene resins. The CAS Registry Number of these resins is also used for low molecular weight oligomers of ethylene oxide, eg, tetraethylene glycol.

2. Physical Properties

2.1. Crystallinity. At molecular weights of 1×10^5–1×10^7, poly(ethylene oxide) forms a highly ordered structure. This has been confirmed by NMR and X-ray diffraction patterns and by the sharpness of the crystalline melting point (62–67°C). However, the highest degree of crystallinity (ca 95%) is obtained at a molecular weight of 6000. The polymer chain contains seven structural units per fiber identity period (1.93 nm) (1). The diffraction pattern of the monoclinic unit cell of poly(ethylene oxide) contains four molecular chains, in which $a = 0.796\,\text{nm}$, $b = 1.311\,\text{nm}$, $c = 1.939\,\text{nm}$, and $\text{b} = 124°48'$. Infrared studies show that the oxygen atoms of the crystalline polymer are in the gauche configuration. Because of this arrangement, the intermolecular dipole forces are oriented along the axis of the helix and ca 15 monomer units are involved within a single repeat unit. The heat of fusion of the polymer is 8.3 kJ (1980 cal) per structural unit (2). The high molecular weight poly(ethylene oxide) resins are of the spherulitic structure (3). Proper annealing of a melt-cast film produces a distinct lamellar structure. The molecular conformation of poly(ethylene oxide), as determined by the use of X-ray diffraction, IR, and Raman spectroscopic methods, is shown in Figure 1.

2.2. Density. Although the polymer unit cell dimensions imply a calculated density of 1.33 g/cm^3 at 20°C, and extrapolation of melt density data indicates a density of 1.13 g/cm^3 at 20°C for the amorphous phase, the density actually measured is 1.15–1.26 g/cm^3, which indicates the presence of numerous voids in the structure.

2.3. Glass-Transition Temperature. The glass transition temperature, T_g, of poly(ethylene oxide) has been measured over the molecular weight range of 10^2–10^7 (4,5). The T_g–molecular weight relationship is shown in Figure 2. These data indicate a rapid rise in the transition temperature to a maximum of −17°C for a molecular weight of 6000. The highest percentage of crystalline character develops at that molecular weight, and it is at that point that T_g is the highest. Beyond this point, chain entanglement reduces crystallinity.

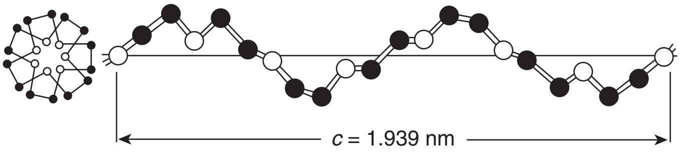


Fig. 1. Molecular conformation of poly(ethylene oxide).

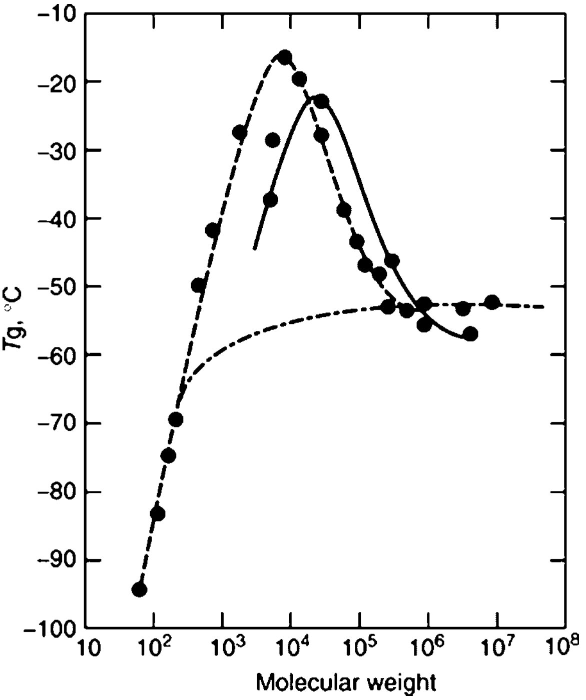


Fig. 2. Glass-transition temperature–molecular weight relationship for poly(ethylene oxide): (—) represents classical T_g–mol wt relationship; (- —), data from Ref. 6; and (– –), data from Ref. 4.

2.4. Solubility. Poly(ethylene oxide) is completely soluble in water at room temperature. However, at elevated temperatures (>98°C) the solubility decreases. It is also soluble in several organic solvents, particularly chlorinated hydrocarbons. Aromatic hydrocarbons are better solvents for poly(ethylene oxide) at elevated temperatures. Solubility characteristics are listed in Table 1.

Aqueous poly(ethylene oxide) solutions of higher molecular weight (ca 10^6) become stringy at polymer concentrations less than 1 wt%. At concentrations of 20 wt%, solutions become nontacky elastic gels; above this concentration, the solutions appear to be hard, tough, water-plasticized polymers.

Concentration and Molecular Weight Effects. The viscosity of aqueous solutions of poly(ethylene oxide) depends on the concentration of the polymer solute, the molecular weight, the solution temperature, the concentration of dissolved inorganic salts, and the shear rate. Viscosity increases with concentration and this dependence becomes more pronounced with increasing molecular weight. This combined effect is shown in Figure 3, in which solution viscosity is presented as a function of concentration for various molecular weight polymers.

The dependence of the intrinsic viscosity [h] on molecular weight M for these polymers can be expressed by the Mark-Houwink relationship:

$$[\eta] = KM^a$$

Table 1. **Solubility of Poly(ethylene oxide)[a] in Several Solvents[b]**

	Temperature	
Solvent[c,d]	Resin dissolves on heating >25°C, °C	Resin precipitates on cooling, °C
Dissolves at room temperature in		
water		<0
carbon tetrachloride		<0
acetonitrile		<0
ethylene dichloride		<0
trichloroethylene		<0
methylene dichloride		<0
benzene		2
2-propanol (91%)		2
dimethylformamide		14
methanol		20
methyl ethyl ketone		20
Dissolves with heating in[e]	30	20
toluene		
xylene	30	20
acetone	35	20
Cellosolve[f] acetate	35	25
anisole	40	0
1,4-dioxane	40	4
ethyl acetate	40	25
ethylenediamine	40	26
dimethyl Cellosolve[f]	40	27
Cellosolve[f] solvent	45	28
ethanol (dry)	45	31
Carbitol solvent	50	32
n-butanol	50	33
butyl Cellosolve[f]	50	33
n-butyl acetate	50	34
2-propanol (dry)	50	36
methyl Cellosolve[f]	50	46

[a] Mol. wt. = (1–50) × 10^5.

[b] Ref. 6.

[c] Solution concentration = ca 1 wt%.

[d] All solvents except 2-propanol (91%) were carefully dried before testing.

[e] The polymer was insoluble in 1,3-butanediol, ethylene glycol, and glycerol at all temperatures.

[f] Registered trademark of Union Carbide Corp.

The constants K and a for high molecular weight poly(ethylene oxide) in several solvents at various temperatures are summarized in Table 2.

Temperature Effect. Near the boiling point of water, the solubility–temperature relationship undergoes an abrupt inversion. Over a narrow temperature range, solutions become cloudy and the polymer precipitates; the polymer cannot dissolve in water above this precipitation temperature. In Figure 4, this limit or cloud point is shown as a function of polymer concentration for poly(ethylene oxide) of 2×10^6 molecular weight.

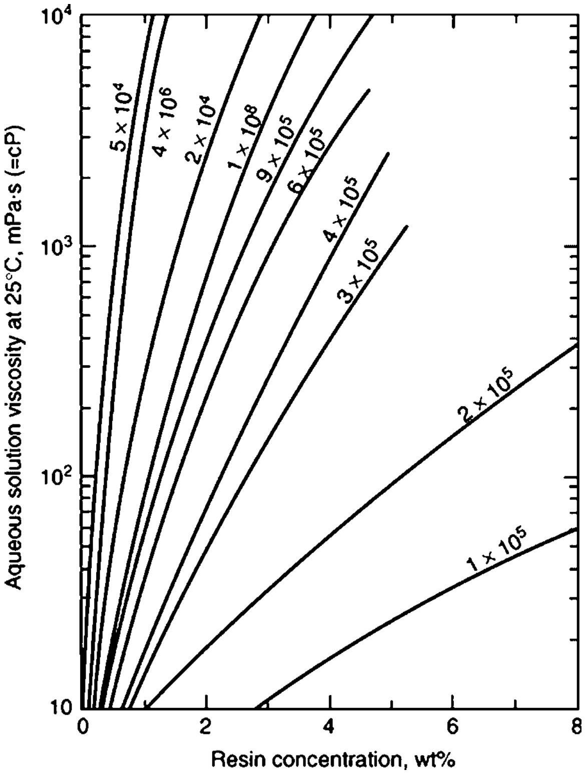


Fig. 3. Solution viscosity vs concentration for ethylene oxide polymers (7). The molecular weight of the polymer is indicated on each curve.

The viscosity of the aqueous solution is also significantly affected by temperature. In polymers of molecular weights $(1-50) \times 10^5$ the solution viscosity may decrease by one order of magnitude as the temperature of measurement is increased from 10 to 90°C. Figure 5 shows this effect.

Effects of Salts. The presence of inorganic salts in aqueous solutions of poly(ethylene oxide) reduces the upper temperature limit of solubility and viscosity. The upper temperature limit of solubility decreases in proportion to the

Table 2. **Mark–Houwink Constants for Poly(ethylene oxide)**

Solvent	Temperature, °C	$K \times 10^5$	a	Approx. M	Ref.
water	25	11.92	0.76	$(5-40) \times 10^5$	8
	35	6.4	0.82	10^4-10^7	9
	45	6.9	0.91	10^4-10^7	9
$0.45\,M$ K2SO$_4$ (aq)	35	130	0.5	10^4-10^7	9
$0.39\,M$ MgSO$_4$ (aq)	45	100	0.5	10^4-10^7	9
benzene	25	39.7	0.686	$(8-500) \times 10^4$	10
	30	61.4	0.64	$(3-20) \times 10^5$	7

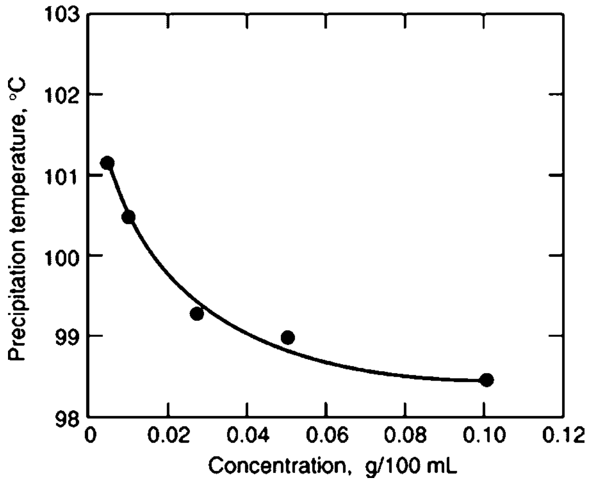
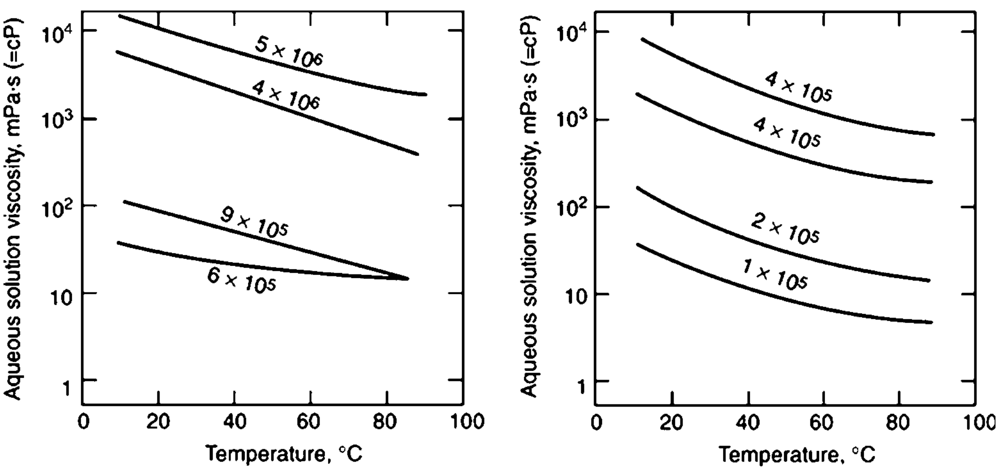


Fig. 4. Upper temperature limit for solubility of poly(ethylene oxide) in water. Molecular weight is 2×10^6 (3).

concentration and valence of the ionic species present. The size of the ions is also important; eg, smaller hydrated ions have the greatest effect. The effect of a number of inorganic salts on the upper temperature limit of solubility of poly(ethylene oxide) in water is illustrated in Figure 6. The decrease in temperature is nearly a linear function of salt concentration. However, this salting-out effect cannot always be correlated with the ionic strength principle. For example, potassium and magnesium sulfate have approximately the same effect, but potassium halides are widely different. Thus, it appears that the anion has the



(a) (b)

Fig. 5. Solution viscosity vs temperature: (**a**) 1.0 wt% solution and (**b**) 5.0 wt% solution (11) for polymers of various molecular weights, indicated on the curves.

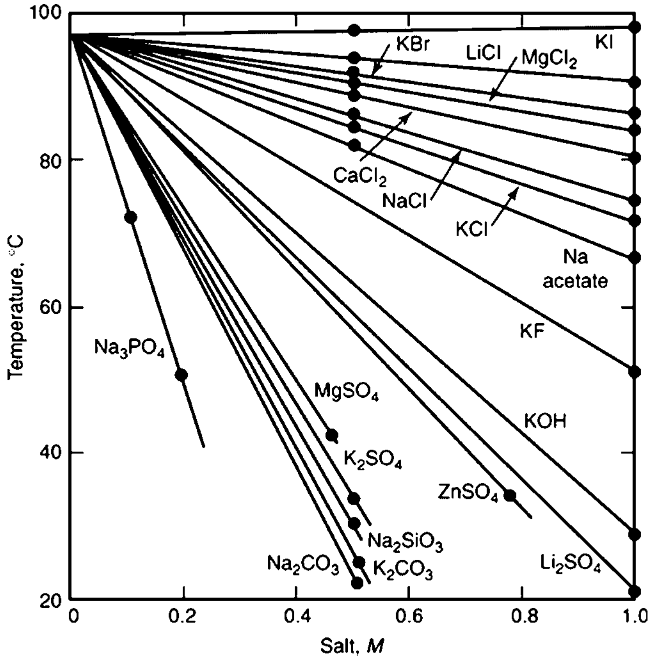


Fig. 6. Upper temperature limit of solubility in salt solution. Resin concentration is 5.0 wt% (7).

greater effect on the upper temperature limit of solubility. The effectiveness of anions to reduce the θ temperature of aqueous poly(ethylene oxide) solution decreases in the following order: $PO_4^{3-} > HPO_4^{2-} > S_2O_3^{2-} > H_2PO_4^{-} > F^{-} > HCO_2^{-} > CH_3CO_2^{-} > Br^{-} > I^{-}$. The order for cations was found to be $K^{+} \approx$; $Rb^{+} \approx$; $Na^{+} \approx$; $Cs^{+} > Sr^{2+} > Ba^{2+} \approx$; $Ca^{2+} > NH^{+}{}_{4} > Li^{+}$ (12). The presence of inorganic salts in solutions of poly(ethylene oxide) also can reduce the hydrodynamic volume of the polymer, with attendant reduction in intrinsic viscosity; this effect is shown in Figure 7.

Effect of Shear. Concentrated aqueous solutions of poly(ethylene oxide) are pseudoplastic. The degree of pseudoplasticity increases as the molecular weight increases. Therefore, the viscosity of a given aqueous solution is a function of the shear rate used for the measurement. This relationship between viscosity and shear rate for solutions of various molecular weight poly(ethylene oxide) resins is presented in Figure 8.

2.5. Thermoplasticity. High molecular weight poly(ethylene oxide) can be molded, extruded, or calendered by means of conventional thermoplastic processing equipment (13). Films of poly(ethylene oxide) can be produced by the blown-film extrusion process and, in addition to complete water solubility, have the typical physical properties shown in Table 3. Films of poly(ethylene oxide) tend to orient under stress, resulting in high strength in the draw direction. The physical properties, melting behavior, and crystallinity of drawn films have been studied by several researchers (14–17).

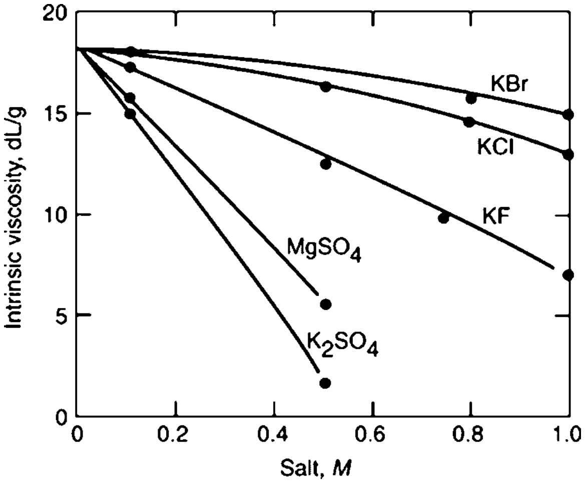


Fig. 7. Effects of salts on the intrinsic viscosity of poly(ethylene oxide) at 30°C. Molecular weight is 5.5×10^6 (3).

At 100−150°C above the melting point, the melt viscosities of these polymers may exceed 10 kPa · s (10^5 P) (Fig. 9). These high melt viscosities indicate extremely high molecular weight. Melt viscosities are relatively unaffected by temperature changes but are directly proportional to the molecular weight of the polymer. Thus, polymers with molecular weights of (1−3) × 10^5 are usually used for applications involving thermoplastic forming processes.

2.6. Polymer Blends. The miscibility of poly(ethylene oxide) with a number of other polymers has been studied, eg, with poly(methyl methacrylate) (18–23), poly(vinyl acetate) (24–27), polyvinylpyrrolidinone (28), nylon (29), poly(vinyl alcohol) (30), phenoxy resins (31), cellulose (32), cellulose ethers

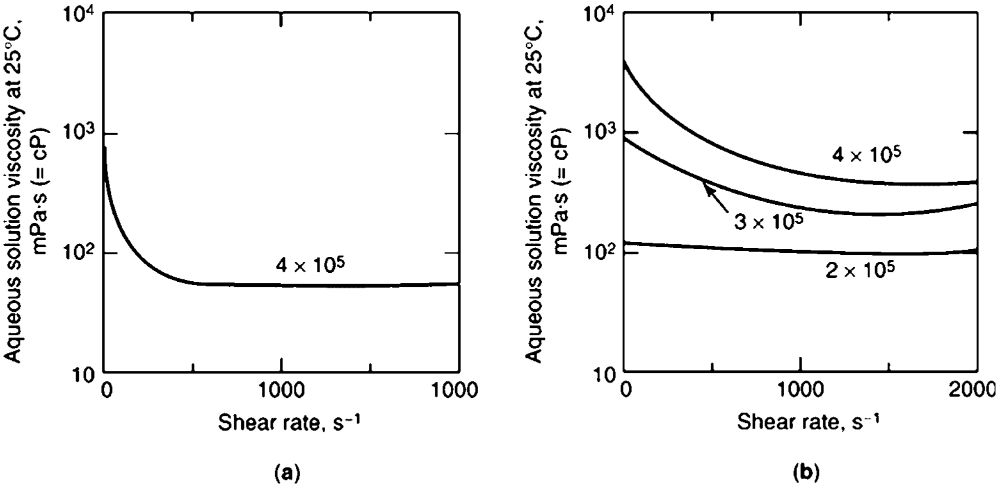


Fig. 8. Effect of shear on aqueous solution viscosities of poly(ethylene oxide) resins: (**a**) 1.0 wt% solution; (**b**) 5.0 wt% solution (7). Each curve represents a different molecular weight.

Table 3. **Typical Physical Properties of Poly(ethylene oxide) Film**

Property	Value
specific gravity	1.2
tensile strength, MP[a]	
machine direction	16
transverse direction	13
secant modulus, MP[a]	
machine direction	290
transverse direction	480
elongation, %	
machine direction	550
transverse direction	650
tear strength, kN/m	
machine direction	100
transverse direction	240
dart Impact at 50% failure, kN/m[b]	80
release time in water, s	15
O_2 transmission, μmol/(m · s · Gpa)[c]	85.8
melting point, °C	67
heat-sealing temperture, °C	71–107
cold-crack resistance, °C	−46

[a] To convert MPa to psi, multiply by 145.

[b] To convert kN/m to lbf/in., multiply by 57.14.

[c] To convert μmol/(m · s · Gpa) to cm^3 · mil/($in.^2$ · d · atm), multiply by 5.

(33), poly(vinyl chloride) (34), poly(lactic acid) (35), polyhydroxybutyrate (36), poly(acrylic acid) (37), polypropylene (38), polyethylene (39), and poly(styrene-*co*-maleic anhydride) (40). The crystallization behavior of representive PEO blends have been studied using time-resolved wide- and small-angle X-ray scattering (41).

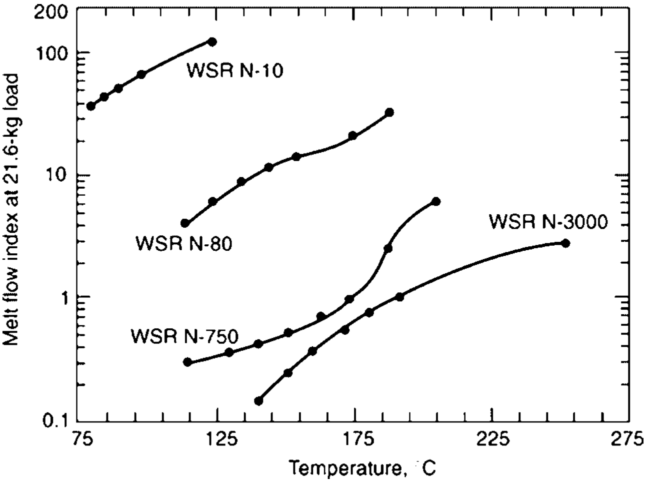


Fig. 9. Melt flow index as a function of temperature for varying molecular weights of poly(ethylene oxide). WSR = Polyox water-soluble resins.

3. Chemical Properties

3.1. Association Complexes. The unshared electron pairs of the ether oxygens, which give the polymer strong hydrogen bonding affinity, can also take part in association reactions with a variety of monomeric and polymeric electron acceptors (42,43). These include poly(acrylic acid), poly(methacrylic acid), copolymers of maleic and acrylic acids, tannic acid, naphtholic and phenolic compounds, as well as urea and thiourea (44–49).

When equal amounts of solutions of poly(ethylene oxide) and poly(acrylic acid) are mixed, a precipitate, which appears to be an association product of the two polymers, forms immediately. This association reaction is influenced by hydrogen-ion concentration. Below ca pH 4, the complex precipitates from solution. Above ca pH 12, precipitation also occurs, but probably only poly(ethylene oxide) precipitates. If solution viscosity is used as an indication of the degree of association, it appears that association becomes more pronounced as the pH is reduced toward a lower limit of about 4. The highest yield of insoluble complex usually occurs at an equimolar ratio of ether and carboxyl groups. Studies of the poly(ethylene oxide)–poly(methacrylic acid) complexes indicate a stoichiometric ratio of three monomeric units of ethylene oxide for each methacrylic acid unit.

These association reactions can be controlled. Acetone or acetonylacetone added to the solution of the polymeric electron acceptor prevents insolubilization, which takes place immediately upon the removal of the ketone. A second method of insolubilization control consists of blocking the carboxyl groups with inorganic cations, ie, the formation of the sodium or ammonium salt of poly(acrylic acid). Mixtures of poly(ethylene oxide) solutions with solutions of such salts can be precipitated by acidification.

Poly(ethylene oxide) associates in solution with certain electrolytes (50–54). For example, high molecular weight species of poly(ethylene oxide) readily dissolve in methanol that contains 0.5 wt% KI, although the resin does not remain in methanol solution at room temperature. This salting-in effect has been attributed to ion binding, which prevents coagulation in the nonsolvent. Complexes with electrolytes, in particular lithium salts, have received widespread attention on account of the potential for using these materials in a polymeric battery. Variable temperature IR studies have been used to explain the structural changes in these systems (55). The use of complexes of poly(ethylene oxide) in analytical chemistry has also been reviewed (56).

3.2. Oxidation. Because of the presence of weak C–O bonds in the backbone, high molecular weight polymers of ethylene oxide are susceptible to oxidative degradation in bulk, during thermoplastic processing, or in solution. The mechanistic aspects of poly(ethylene oxide) oxidation have been reviewed (57). During thermoplastic processing at elevated temperature, oxidative degradation is manifested by a rapid decrease in melt viscosity with time. In aqueous solution at ambient temperatures, the decay of solution viscosity also is an indication of oxidative degradation, and the rate of decay is increased by the presence of traces of chlorine, peroxides, permanganate, or persulfate and certain transition-metal ions such as Cu^{+}, Cu^{2+}, Cu^{3+}, Fe^{3+}, and Ni^{2+}. A combination of these agents can lead to severe viscosity losses.

Several stabilizers are useful in minimizing oxidative degradation during thermoplastic processing or in the bulk solid. Phenothiazine, hindered phenolic antioxidants such as butylated hydroxytoluene, butylated hydroxyanisole, and secondary aromatic amines in concentrations of 0.01–0.5% based on the weight of polymer, are effective.

Aqueous solutions can be stabilized against viscosity loss by addition of 5–10 wt% anhydrous isopropyl alcohol, ethanol, ethylene glycol, or propylene glycol. The manganous ion (Mn^{2+}) also is an effective stabilizer at concentrations of 10^{-5}–10^{-2} wt% of the solution.

4. Manufacture and Processing

4.1. Heterogeneous Catalytic Polymerization. The preparation of polymers of ethylene oxide with molecular weights greater than 100,000 was first reported in 1933. The polymer was produced by placing ethylene oxide in contact with an alkaline-earth oxide for extended periods (58). In the 1950s, the low yield and low polymerization rates of the early work were improved upon by the use of alkaline-earth carbonates as the catalysts (59). Further improvements in reaction rates and polymerization control have led to the commercial availability of poly(ethylene oxide) of varying molecular weights.

The polymerization of ethylene oxide to produce high molecular weight polymer involves heterogeneous reaction with propagation at the catalyst surface. The polymerization can involve anionic or cationic reactions of ethylene oxide that generally produce lower molecular weight products. The mechanism for production of extremely high molecular weight polymers is thought to involve a coordinate anionic reaction where ethylene oxide is coordinated with a metal atom of the catalyst and is then attacked by an anion. The various polymerization mechanisms have been described (60).

Catalysts capable of polymerizing ethylene oxide to high molecular weight polymers include many metal compounds. Among those reported are alkaline-earth carbonates and oxides (61), alkyl zinc compounds (62–64), alkyl aluminum compounds and alkoxides (65–67), and hydrates of ferric chloride, bromide, and acetate (68,69). Other catalysts include various alkyls and alkoxides of aluminum, zinc, magnesium, and calcium, and mixtures of these materials with various other inorganic salts. The preparation and utilization of the various catalysts have also been described (70,71). The molecular weight of the polymer appears to be controlled by the catalyst systems as well as by polymerization conditions. Rigid control of catalyst preparation and raw material quality appear to be mandatory for successful laboratory preparation of high molecular weight poly(ethylene oxide).

4.2. Polymer Suspensions. Poly(ethylene oxide) resins are commercially available as fine granular solids. However, the polymer can be dispersed in a nonsolvent to provide better metering into various systems. Production processes involve the use of high shear mixers to disperse the solids in a nonsolvent vehicle (72–74).

4.3. Thermoplastic Processing. Poly(ethylene oxide) resins can be thermoplastically formed into solid products, eg, films, tapes, plugs, retainers, and fillers. Through the use of plasticizers, poly(ethylene oxide) can be extruded, molded, and calendered on conventional thermoplastic processing equipment. Sheets and films of this resin are heat sealable (75,76).

4.4. Irradiation and Cross-Linking. Exposure of poly(ethylene oxide) to ionizable radiation (gamma irradiation, electron beam, or ultraviolet light) can result in molecular weight breakdown or cross-linking, depending on the environmental conditions. If oxygen is present, hydroperoxides are formed and chain scission leads to an overall decrease in molecular weight (77). However, in the absence of oxygen, cross-linking becomes the preferred reaction (78,79,90). The resulting polymer network exhibits hydrogel properties of high water capacity (81,82).

Studies of the cross-linking mechanism and structure of the cross-linked polymer indicate that a complex network of cross-linked chains of varying lengths is present (83–86). When the cross-linking is performed in solution, the cross-links can be both intermolecular and intramolecular; the overall structure of the cross-linked polymer is the combined result of chain scission, intramolecular bonding, and intermolecular bonding. Under conditions of high aggregation in solution, for example, high concentration, intermolecular cross-linking is preferred and a continuous gel is formed. When the polymer is not aggregated in solution, intramolecular cross-linking predominates, and microgels, rather than a cohesive gel network, are formed. Detailed positron annihilation studies have been used to reveal the evolution of small pore structure for semicrystalline PEO under gamma irradiation (87).

5. Economic Aspects

Only Japan and the United States have significant commercial facilities for the production of poly(ethylene oxide) resins. In Japan, Meisei Chemical Works Ltd. produces Alkox and Sumitomo Seika Kagaky Co., Ltd. produces PEO. In the United States, The Dow Chemical Corp. produces Polyox. Precise figures have not been released on capacities or annual production.

6. Specifications, Standards, and Quality Control

The primary quality control measure for these resins is the concentrated aqueous solution viscosity, which is related to molecular weight. Specifications for POLYOX are summarized in Table 4. Additional product specifications frequently include moisture content, particle-size distribution, and residual catalyst by-product level.

7. Analytical and Test Methods

7.1. Molecular Weight. Measurement of intrinsic viscosity in water is the most commonly used method to determine the molecular weight of poly(ethy-

Table 4. **Aqueous Solution Viscosity Specifications for Polyox Resins**[a]

Grade	Approximate M_w	Concentration wt%	Brookfield Viscometer Spindle Number	Speed, rmp	Viscosity at 25°C, Pa · s[b]
WSR-308	8×10^6	1.0	2	2	10,000–15,000
WSR-303	7×10^6	1.0	2	2	7,500–10,000
COAG	5×10^6	1.0	2	2	5,500–7,500
WSR-301	4×10^6	1.0	1	2	1,650–5,500
WSRN-60K	2×10^6	2.0	3	10	2,000–4,000
WSRN-12K	1×10^6	2.0	1	10	400–800
WSR-1105	9×10^5	5.0	2	2	8,800–17,600
WSR-205	6×10^5	5.0	2	2	4,500–8,800
WSRN-3000	4×10^5	5.0	1	2	2,250–4,500
WSRN-750	3×10^5	5.0	1	10	600–1000
WSRN-80	2×10^5	5.0	1	50	65–115
WSRN-10	1×10^5	5.0	1	50	12–50

[a] Ref. 88.

[b] To convert Pa · s to Poise, multiply by 10.

lene oxide) resins. However, there are several problems associated with these measurements (89,90). The dissolved polymer is susceptible to oxidative and shear degradation, which is accelerated by filtration or dialysis. If the solution is purified by centrifugation, precipitation of the highest molecular weight polymers can occur and the presence of residual catalyst by-products, which remain as dispersed, insoluble solids, further complicates purification.

A number of techniques, including static and dynamic light scattering (91), viscometry (92), and gel-permeation chromatography (GPC) with low angle laser light-scattering detection (93), have been used to study the behavior of poly(ethylene oxide) in solution. Dynamic light scattering (94,95) has also been used to determine the molecular weight distribution of poly(ethylene oxide) and to study crystallization from dilute solutions (96,97).

Attempts to measure average molecular weight and molecular weight distribution of poly(ethylene oxide) for molecular weights above 1 million, using GPC, are extremely difficult because of the effect of shear on the high molecular weight polymer molecules in the GPC column and the lack of adequate standards for calibration of the columns. However, one group has been successful in using high speed gel filtration to fractionate high molecular weight poly(ethylene oxide) and provide materials with narrow molecular weight distributions suitable for use as standards for GPC (98). An alternative method for average molecular weight determination is cloud point titration (99) (see Molecular Weight Determination).

7.2. Aqueous Solution Viscosity. A special solution preparation method is used for one type of measurement of aqueous solution viscosity (100). The appropriate amount of poly(ethylene oxide) resin is dispersed in 125 mL of anhydrous isopropyl alcohol by vigorous stirring. Because the resin is insoluble in anhydrous isopropyl alcohol, a slurry forms and the alcohol wets the resin particles. An appropriate amount of water is added and stirring is slowed to about 100 rpm to avoid shear degradation of the polymer. In

Table 4, the nominal resin concentration reported is based on the amount of water present and ignores the isopropyl alcohol.

7.3. Analysis for Poly(ethylene oxide). Another special analytical method takes advantage of the fact that poly(ethylene oxide) forms a water-insoluble association compound with poly(acrylic acid). This reaction can be used in the analysis of the concentration of poly(ethylene oxide) in a dilute aqueous solution. Freshly prepared poly(acrylic acid) is added to a solution of unknown poly(ethylene oxide) concentration. A precipitate forms, and its concentration can be measured turbidimetrically. Using appropriate calibration standards, the precipitate concentration can then be converted to concentration of poly(ethylene oxide). The optimum resin concentration in the unknown sample is 0.2–0.4 ppm. Therefore, it is necessary to dilute more concentrated solutions to this range before analysis (101). Low concentrations of poly(ethylene oxide) in water may also be determined by viscometry (102) or by complexation with KI_3 and then titration with $Na_2S_2O_3$ (103).

8. Health and Safety Factors

Poly(ethylene oxide) resins are safely used in numerous pharmaceutical and personal care applications. Poly(ethylene oxide) resins show a low order toxicity in animal studies by all routes of exposure. Because of their high molecular weight, they are poorly adsorbed from the gastrointestinal tract and are completely and rapidly eliminated (104). The resins are not skin irritants or sensitizers, nor do they cause eye irritation.

Considerable interest has been shown in poly(ethylene oxide) for diverse applications in food, drug, and cosmetic products. Such uses fall within the scope of the Federal Food, Drug, and Cosmetic Act. The U.S. Food and Drug Administration (FDA) has recognized and approved the use of poly(ethylene oxide) for specific food and food packaging uses. USP/NF grades of Polyox water-soluble resins (The Dow Chemical Co.) that meet all requirments of the United States Pharmacopeia/National Formulary (USP/NF) are available for pharmaceutical applications (105).

9. Uses

Significant use properties of poly(ethylene oxide) are complete water solubility, low toxicity, unique solution rheology, complexation with organic acids, low ash content, and thermoplasticity.

9.1. Pharmaceutical and Biomedical Applications. On account of its low toxicity and unique properties, poly(ethylene oxide) is utilized in a variety of pharmaceutical and biomedical applications.

Denture Adhesives. Fast hydration and gel-forming properties are ideally mated to produce a thick, cushioning fluid between the dentures and gums (106). The biologically inert nature of poly(ethylene oxide) helps reduce unpleasant odors and taste in this type of personal care product. The use of PEO blends has also been shown as a means to optimize denture adhesive properties (107).

Mucoadhesives. Poly(ethylene oxide) has good adhesive properties to mucosal surfaces because of its high molecular weight, linear molecules, and fast hydration properties. *In vivo* results have shown that the duration of adhesion increases with molecular weight up to 400,000. Further increase in molecular weight results in a concomitant decrease in adhesive properties, most likely because of the swelling of the resulting hydrogel (108). The mucoadhesive properties have been utilized in the design of buccal-sustained drug delivery systems (109,110) and occular delivery systems (111).

Ophthalmic Solutions. The viscoelastic properties of poly(ethylene oxide) produce unique benefits for vitreous fluid substitution for ophthalmic surgery. Solutions of high molecular weight poly(ethylene oxide) have been used as vehicles for therapeutics for the eye (112) and as a contact lens fluid for hard or gel-type lenses (113). A treated lens appears to have a high viscosity layer at the low shear rates that occur on the inside surface. This provides a thick, comfortable cushioning layer. At high shear rates caused by the blinking eyelid, the apparent viscosity is much lower. This allows the lid to move smoothly and effortlessly over the outside surface of the lens. Unlike the cellulosics, poly(ethylene oxide) does not support bacterial growth. Lens solutions are easier to keep sterile.

Wound Dressings. Cross-linked poly(ethylene oxide) solutions form hydrogels which contain about 90–97% of water. These hydrogels are clear, transparent, permeable to gases, and absorb 5–100 times their weight in water. Such characteristics make these hydrogels interesting materials for wound dressings. Compared to other occlusive dressings, these hydrogels have shown the promotion of rapid healing (114). Release of therapeutic substances from these dressings has been demonstrated (115,116).

Oral Drug Release. The dissolution rate of tableted poly(ethylene oxide) depends on the molecular weight and particle-size distribution. High molecular weight resin provides an excellent tablet binder for sustained drug release from matrix tablets (117–119) (see Controlled Release Technology. Agricultural). The good flow properties and compressibility of poly(ethylene oxide) powder can be advantageously exploited in preparing tablets by direct compression. The high swelling capacity of high molecular weight poly(ethylene oxide) tablets when exposed to intestinal fluids has been successfully used in osmotic delivery systems for water-insoluble drugs (120–123). A detailed review of these osmotic systems is available (124). A zero-order drug release has been reported from films produced from poly(ethylene oxide) and polycaprolactone. The change in drug release profile with respect to film composition, thickness, and morphology has been described (125). Novel PEO matrix systems aimed at gastric delivery and chewable forms have been described (126,127). The thermoplastic properties of PEO lend themselves to the use of extrusion methods in the preparation of oral delivery systems (128,129).

Biomaterials with Low Thrombogenicity. Poly(ethylene oxide) exhibits extraordinary inertness toward most proteins and biological macromolecules. The polymer is therefore used in bulk and surface modification of biomaterials to develop antithrombogenic surfaces for blood contacting materials. Such modified surfaces result in reduced concentrations of cell adhesion and protein adsorption when compared to the nonmodified surfaces (130,131).

Lubricious Coatings for Biomaterials. Coatings of poly(ethylene oxide) when dry are tactile. If brought into contact with water, the poly(ethylene oxide) hydates rapidly and forms a lubricious coating. This type of technology is of great interest for biomedical devices introduced into the human body, such as catheters and endotracheal tubes, and for sutures (132–135).

9.2. Industrial Applications. Poly(ethylene oxide)s also have numerous industrial uses.

Flocculation. Poly(ethylene oxide)s of molecular weights greater than 4 million have been used as specialty flocculants. The ability of the PEO molecule to hydrogen-bond with the surface hydroxyl layers of silica, kaolinites, and other mineral oxides leads to adsorption of the polymer on the substrate. The balance between the hydrophilicity of the ether oxygen moiety and the hydrogen-bonding forces on the solid substrate results in a loop-tail conformation essential to flocculation. Some of the end uses for PEO as a flocculant are as a fines retention aid in the paper industry, a low pH flocculant of silica in beryllium, uranium, and copper mines that use acid leaching, and as a dewatering aid in industrial waste treatment. In the paper industry, PEO is widely used as a retention aid and pitch control agent in the newsprint industry (136–157). Typically, a phenol formaldehyde-type resin is added to the substrate before the addition of PEO. The chemical that is added before PEO has been referred to as an *enhancer*. Recent publications on designing enhancers that work with PEO have resulted in expanding the use of PEO in flocculation of several substrates (146,147,158,159).

Several technical articles suggest that the use of PEO increases the dewatering efficiency of mineral sludges significantly (160–176). In the mining industry, PEO is used to flocculate siliceous substrates at pH <2 during the acid leaching operations. The low pH stability provides PEO polymers with unique advantages in this application.

Drag Reduction. The addition of 0.03% of high molecular weight PEO (greater than 4 million) to aqueous solutions has resulted in a 100% increase in the flow rate at fixed pump pressures (177). The significant reduction in friction as a result of the addition of PEO has been attributed to supermolecular structure formation of PEO (178) and to expansion and orientation of the polymer in rotation-free draining flow (179,180). Drag reduction properties have been demonstrated by trials using fire hoses, which show that water travels 50% further because of the addition of small quantities of PEO. Investigations on the effect of Reynold's number, orifice size of the pumping device, and polymer blends have led to a better understanding for suitable drag-reducing systems that may use PEO (177–191). Degradation of PEO and point of addition of the polymer appear to play a significant role in successful manipulation of this property in end uses (192,193). Some references also suggest the use of this property in reducing arterial pressure in medical applications (190) and in ocean transport (194–197).

Binders in Ceramics, Powder Metallurgy, and Water-Based Coatings for Fluorescent Lamps. In coatings and ceramics applications, the suspension rheology needs to be modified to obtain a uniform dispersion of fine particles in the finished product. When PEO is used as a binder in aqueous suspensions, it is possible to remove PEO completely in less than 5 min by baking at temperatures of 400°C. This property has been successfully commercialized in several ceramic applications, in powder metallurgy, and in water-based coatings of fluorescent lamps (198–201).

Personal Care. The addition of PEO provides a silky feel to solid and liquid products. This unique lubricious property has been successfully exploited in formulation of razor strips (202,203) and in shampoos, detergents, and other personal care applications. The combination of water solubility and the ability to produce films and other devices by thermoplastic processing enables the use of the PEO in flushable articles (204–207). PEO has also been used as an antimisting agent in personal care and cleaning formulations (208) and has been shown to enhance the deposition of active ingredients to the hair and skin, as well as to act as a foam enhancer (209). Fundamental investigations have examined the interaction of PEO and surfactants in aqueous solutions (210–213).

Adhesives. High concentration ($>10\%$) solutions of poly(ethylene oxide) exhibit wet tack properties that are used in several adhesive applications (214). The tackiness disappears when the polymer dries, and this property can be successfully utilized in applications that require adhesion only in moist conditions. PEO is also known to form solution complexes with several phenolic and phenoxy resins. Solution blends of PEO and phenoxy resins are known to exhibit synergistic effects, leading to high adhesion strength on aluminum surfaces.

Acid Cleaners. The addition of PEO can significantly increase the viscosity of acid solutions. Highly viscous acid solutions are used in cleaning formulations for glass, ceramic, and metal surfaces. The increase in viscosity increases the contact time of the cleaning solution when it is sprayed on vertical surfaces. Some acids that can be thickened by using PEO are hydrochloric, sulfuric, phosphoric, and oxalic. The order of addition of the polymer and oxidative stabilizers appears to play an important role in formulating highly viscous acid solutions. The manufacturers provide several formulations to thicken different acids.

Drift and Mist Control. The pseudoplastic properties of PEO solutions reduce mist formation during spraying of aqueous solutions that contain PEO. This property is used in metal-working fluids to lower worker exposure to mists from the cutting and grinding aids. PEO may also be used to focus the spraying area of herbicides and water-based coatings.

Construction. The addition of PEO to concrete has been a subject of several investigations (215). Research studies and patent literature suggests that PEO can be used as a pumping aid to concrete, where the lubricity of PEO allows concrete to be pumped to longer distances (216–219). In addition, PEO is also used to disperse the water more uniformly in the concrete mixture, which promotes better uniformity of the concrete mixture. Formulations in the construction industry are proprietary and not easily available.

Batteries. Polymer electrolytes based on PEO have been widely reviewed (220,221). The prospect of using a thin-layer, flexible battery for applications ranging from cellular phones to electric vehicles has led to several patents (222,223) and research papers in this field. Typically, a salt such as potassium iodide, lithium triflate, or lithium perchlorate is complexed with PEO in a methylene chloride solvent. The solution complex is cast into thin films and the solvent is evaporated. The complex has been characterized; it is believed that the 7C2 helical structure of PEO allows an ideal structure for ion transport and leads to effective use as a battery. The dissociation of the anion−cation pair in the PEO salt complex has been attributed to the oxygen atoms, which form a cage around the cation and lead to ionic conductivity. The crystallinity of PEO at room temperature has limited the use of this technology to batteries that are used at temperatures higher than 65°C, the melting point of PEO. Research in the 1990s focuses on modifying the complex or the PEO molecule to overcome the crystallinity problem and in understanding the interaction of PEO with lithium salts (224–235).

9.3. Other Applications. PEO has also been used as an antistat additive (236,237), a water-soluble packaging material of seeds and fertilizers (238), and a rheology modifier in aqueous flexographic printing inks (239), and for the production of nanofibers containing multiwalled carbon nanotubes (240).

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