Kirk-Othmer Encyclopedia of Chemical Technology.

POLYETHERS, PROPYLENE OXIDE POLYMERS

Propylene oxide and other epoxides undergo homopolymerization to form polyethers. In industry the polymerization is started with multifunctional compounds to give a polyether structure having hydroxyl end groups. The hydroxyl end groups are utilized in a polyurethane forming reaction. This article is mainly concerned with propylene oxide (PO) and its various homopolymers that are used in the urethane industry.

Poly(propylene oxide) [25322-69-4] may be abbreviated PPO and copolymers of PO and ethylene oxide (EO) are referred to as EOPO. Diol poly(propylene oxide) is commonly referred to by the common name poly(propylene glycol) (PPG). Propylene oxide [75-56-9] and poly(propylene oxide) and its copolymers, with ethylene oxide, have by far the largest volume and importance in the polyurethane (PUR) and surfactant industry compared to all other polyepoxides. Articles reviewing propylene oxide (1), poly(propylene oxide) (2–4), other poly(alkylene oxides) (4), and polyurethanes (5–7) are cited to lead the interested reader to additional detail not in the scope of this article.

Homopolymers of PO and other epoxides are named a number of ways: after the monomer, eg, poly(propylene oxide) (PPO) or polymethyloxirane; from a structural point of view, polyoxypropylene or poly(propylene glycol); or from the *Chemical Abstracts* (CA) name, poly[oxy(methyl-1,2-ethanediyl)], α-hydro-ω-hydroxy-. Common names are used extensively in the literature and in this article.

1. History

Propylene oxide was discovered in 1860 in Wurz's laboratory (8). It became an important commercial industrial chemical after World War II when its importance in polyurethanes was recognized. As a general guide, polyethers give softer, more resilient foams (qv) with better hydrolytic resistance than polyesters, whereas the polyester-based foams have greater tensile strength and better resistance to oils, solvents, and oxidation. Bayer (9) received one of the first patents which was applied for in 1951 and granted in 1960. This patent used polyethers but was limited to poly(ethylene oxide). A patent for copolymers of PO and EO, which were used as surfactants (qv), was granted in 1954 (10). Flexible foam systems based on 80:20 (2,4- and 2,6-isomer ratio) toluene diisocyanate (TDI) and PO polymers or EOPO copolymers [9003-11-6] were introduced in the United States in 1957. That year Mobay offered commercial prepolymers based on these ingredients.

1.1. Uses of Poly(propylene oxide)

The vast majority of uses of PPO and EOPO copolymers are in polyurethanes, surfactants, and the medical area. Many but by no means all other applications follow. Taking advantage of their surfactant properties (especially EOPO copolymers), they have been used as lubricants (10–17), dispersants (18–21), antistatic agents (22–24), foam control agents (25–28), in printing inks (29, 30), in printing processes (31), and as a solubilizers (32). PPO and EOPO copolymers have been used in aqueous hydraulic fluids (33–37) and in coolant compositions (38). They are used in secondary oil recovery operations (39, 40), as plastic additives (41, 42), in nonpolyurethane

Table 1. U.S. Capacity for Propylene Oxide[a]

Producer	Location	Capacity, 10^3 t	Process
Arco Chemical	Bayport, Tex.; Channelview, Tex.	1.05	indirect oxidation
Dow	Freeport, Tex.	0.5	chlorohydrin
	Plaquemine, La.	0.22	chlorohydrin
Texaco	Port Neches, Tex.	0.18	indirect oxidation
Total		*1.95*	

[a] Ref. 57.

adhesives (43), and in propellant compositions (44). In the medical field they find applications as protective bandages (45–49), in drug delivery systems (qv) (50–53), in organ preservation (54), in dental compositions (55), and as a fat substitute (56).

2. Propylene Oxide Monomer

2.1. Synthesis

The total annual production of PO in the United States in 1993 was 1.77 billion kg (57) and is expected to climb to 1.95 billion kg with the addition of the Texaco plant (Table 1). There are two principal processes for producing PO, the chlorohydrin process favored by The Dow Chemical Company and indirect oxidation used by Arco and soon Texaco. Molybdenum catalysts are used commercially in indirect oxidation (58–61). Capacity data for PO production are shown in Table 1 (see Propylene oxide).

Miscellaneous synthesis methods for propylene oxide include the following. Arco received a patent (62) for producing PO and other epoxides in an integrated process involving air oxidation of a secondary alcohol in the presence of a titanium silicate catalyst. A 1993 Olin patent (63) described the production of PO by a noncatalytic, gas-phase oxidation process. In this process a gaseous mixture of propylene, oxygen, and acetaldehyde is allowed to react at a temperature in the range of 200 to $\sim 350^\circ$C and at a pressure up to about 6.8 MPa (1000 psig). Propylene oxide is obtained in 42% selectivity at low propylene conversion. This process has potential because of its simplicity and could be realized if the selectivity and conversion are improved. Several groups have reported that PO and other epoxides can be microbiologically synthesized from alkenes (64–69), some even producing chiral epoxides (70–76). PO can be prepared electrochemically and pilot-scale reactors have been described (77–79). There have been several reports of the direct oxidation of propene with hydrogen peroxide (80, 81).

2.2. Purification

A three-phase distillation for producing high purity PO has been reported (82). PO can be purified in the laboratory by refluxing with a drying agent, such as calcium hydride, then fractionally distilling (83). Texaco has reported that PO can be purified by extractive distillation (84–89).

2.3. Optically Active PO

The synthesis of optically pure PO has been accomplished by microbial asymmetric reduction of chloroacetone [78-95-5] (90). (*S*)-2-Methyloxirane [16088-62-3] (PO) can be prepared in 90% optical purity from ethyl (*S*)-lactate in 44% overall yield (91). This method gives good optical purity from inexpensive reagents without the need for chromatography or a fermentation step. (*S*)-PO is available from Aldrich Chemical Company, having a specific rotation $[\alpha]_D^{20} - 7.2$ ($c = 1$, $CHCl_3$).

Table 2. Physical Properties of Propylene Oxide[a]

Property	Value
molecular weight	58.08
boiling point, °C	33.9
dp/dt, kPa/°C[b]	3.70
vapor pressure constants[c]	
A	6.095
B	1065.27
C	226.283
freezing point, °C	−104.4
coefficient of thermal expansion α[d]	0.00151^{20}
refractive index n_D	
at 20°C	1.36603
25°C	1.36322
viscosity η, mPa·s(= cP)	
at 0°C	0.41
25°C	0.28
heat of vaporization ΔH_v, kJ/mol[e]	28.75^{34}
heat of combustion ΔH_c, kJ/mol[e]	−1917
heat capacity, C_p, J/(mol·K)[e]	120.37
critical temperature, °C	209.1
solubility in water, at 20°C, wt %	40.5
solubility of water in, at 20°C, wt %	12.8
flash point, closed cup, °C	−35.0
explosive limits in air, wt %	
upper	21.5
lower	2.1
specific gravity at 20°C	0.830

[a] Refs. 4, 92, and 93.

[b] To convert kPa to mm Hg, multiply by 7.5

[c] For $\log P = A - (B/T)$ or the Antoine equation $\log P = A - [B/(T + C)]$ ·
$d\alpha = 1/V(\partial V/\partial T)_P = (d_1/d_2) - 1/(T_2 - T_1)$. Superscript is temperature, °C.

[e] To convert J to cal, divide by 4.184.

2.4. Physical Properties

The physical properties of PO are shown in Table 2.

3. Propylene Oxide Polymers

Propylene oxide and other epoxides polymerize by ring opening to form polyether structures. Either the methine, CH–O, or the methylene, CH_2–O, bonds are broken in this reaction. If the epoxide is unsymmetrical (as is PO) then three regioisomers are possible: head-to-tail (H–T), head-to-head (H–H), and tail-to-tail (T–T) dyads, ie, two monomer units shown as a sequence. The anionic and

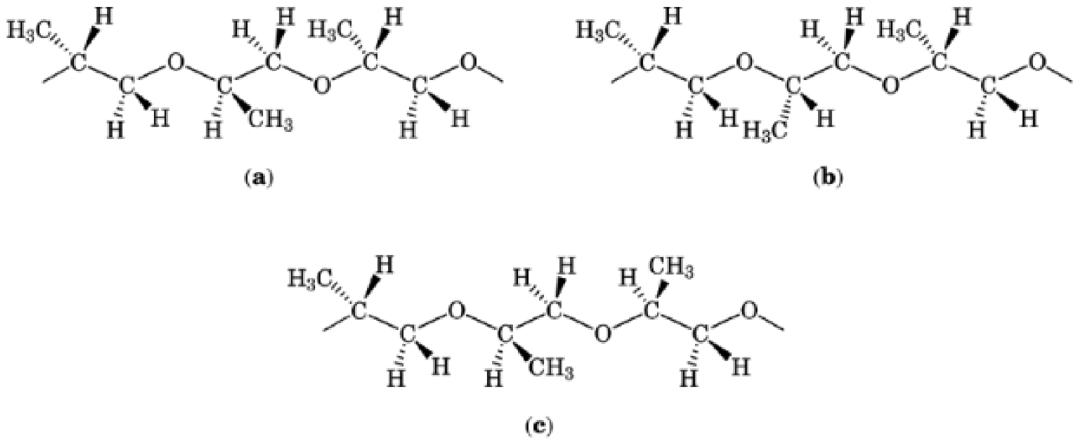
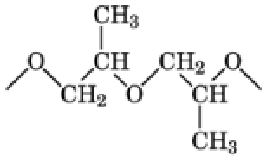
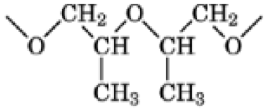


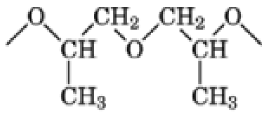
Fig. 1. Triad sequences for stereoregular poly(propylene oxide) where (**a**) shows isotactic (RRR or SSS), (**b**) syndiotactic (RSR or SRS), and (**c**) heterotactic (RRS or SSR, or SRR or RSS) units.



H–T



H–H



T–T

coordination polymerization of PO results in nearly all (95–98%) H–T sequences because the S_N2 attack occurs on the least substituted carbon atom, the methylene carbon. A small amount of the other sequences are also found and can be identified by nmr. Tacticity describes stereoregular polymers and indicates the orderliness of the succession of configurational repeating units in the main chain of the polymer. PPO from anionic polymerization always results in an atactic polymer which is a regular polymer (H–T), the molecules of which have equal numbers of possible configurational base units in a random sequential distribution. On the other hand, certain coordination catalysts produce a stereoregular isotactic polymer which can be described in terms of only one species of configurational unit, having chiral or prochiral atoms in the main chain, in a single sequential unit. A triad, a sequence of three monomer units, is necessary to show this behavior (Fig. 1). PPO would have an excess of one enantiomer only if optically active PO were used as starting material.

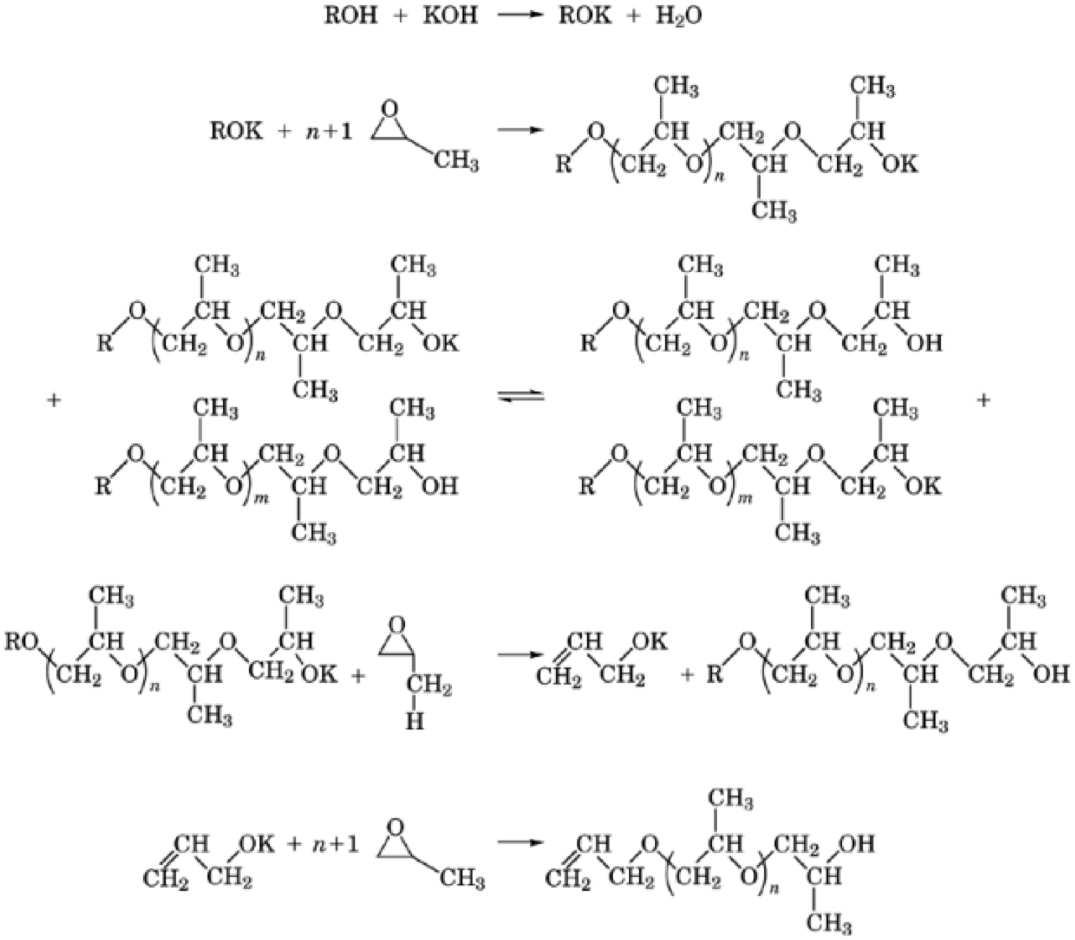


Fig. 2. Reaction scheme for the anionic polymerization of propylene oxide.

3.1. Base-Catalyzed Polymerization Of Propylene Oxide

3.1.1. The Reaction

Most polyether polyols used commercially for urethanes and surfactants are produced by anionic polymerization. The bases of choice are potassium hydroxide or sodium hydroxide. The sequence of reactions leading to polymer are shown in Figure 2. Reaction 2 is the formation of alkoxide ion with the formation of water which is normally removed. ROH (ROK) is commonly referred to as the starter. Reaction 2 is the propagation reaction and the rate depends on catalyst and PO concentration. Reaction 2 is a proton-transfer reaction which is very fast and gives rise to the narrow molecular weight distribution normally seen in commercial polyether polyols. Reaction 2 shows the generation of allyl alkoxide which in turn polymerizes with PO to form monofunctional polyetherol (Reaction 2). Another reaction which is not shown is the isomerization of allyl alkoxide to propenyl alkoxide. The unsaturation present at the end of anionic polymerization is nearly all allyl but isomerization to propenyl occurs in unneutralized polymerizates (94). In measurements of the rate of isomerization (allyl $\longrightarrow$ propenyl) simple second-order kinetics were found; the rate = $k_2[allyl][base]$ (94). The activation energy is 116 kJ/mol (27.7 kcal/mol) over a temperature range 90–130°C.

Table 3. Charges for a 3000 Molecular Weight Glycerol-Initiated PPO Triol

Charges	Wt, g	Moles of hydroxyl	Hydroxyl equivalents	Hydroxyl number contribution
glycerol	178.0	1.93	5.80	54.23
potassium hydroxide, 90%	36.0	0.58	0.58	
water from KOH	−14.0			
propylene oxide (PO)	5822			
water from PO	0.6	0.03	0.06	0.56
unsaturation[a]		0.14	0.14	1.35
−K + H[b]	−22.0	−0.58	−0.58	
Total[c]	*6000*	*2.10*	*6.00*	*56.14*

[a] Unsaturation is normaly expressed meq/g but it is convenient to convert it to hydroxyl units for charge circulation.

[b] The replacement of K by H in the equation $\mathrm{ROK + H_2O \longrightarrow ROH\ (polyol) + KOH}$.

[c] The functionality can be calculated from the hydroxyl equivalents and hydroxyl moles: $f = 3.00/2.10 = 2.86$.

Tetrabutylammonium benzoate has been used as a catalyst for the polymerization of PO over the temperature range 40–108°C and the yield of polymer was typically low (2–78%); a large amount of unsaturation was present due to chain transfer (95). When synthetic hydrotalcite, $\mathrm{Mg_6Al_2(OH)_{16}CO_3{\cdot}4\ H_2O}$, is used to polymerize PO and is activated by calcining at 450°C, a quantitative yield of PPO is obtained at 50°C in 2 hours (96). At Olin, POLY-L polyols have been produced with reduced unsaturation, but the catalyst used to produce them has not been disclosed (97). The use of zinc hexacyanocolbaltate to prepare low unsaturation polyols has been reported (98).

3.1.2. General Procedure of Base Catalysis

This yields a 3000 number-average molecular weight triol. In order to make this polyol in a reasonable amount of time, high temperature and consequently high pressure are required; therefore a stainless steel autoclave reactor is employed instead of a glass apparatus. The reactor is nominally 3.78 L (1 gal) in size, and has the following features: an oxide addition tube which extends to the bottom of the vessel and is pointed toward a high speed stirrer; a means of adding the oxide at a constant rate such as a pump or a flow controller; an inlet for vacuum or inert gas; a means to monitor the temperature and pressure (the oxide feed rate should also be monitored to give reproducible results); a charge port to add starter and catalyst; a water and steam inlet and outlet for cooling and heat; a high speed stirrer; a water jacket to help control the temperature; and a discharge port.

The charges for this polyol are shown in Table 3. Glycerol and 90% KOH are charged to the autoclave which is then purged with nitrogen. The charge of glycerol is only 3% of the total charge and may not be enough material for efficient stirring. A 4 or 5 mol PO adduct of glycerol can be made and used as the starter. The reactor is pressurized with nitrogen to 450 kPa (50 psig), where it is held for 15 min to check for leaks. The pressure is relieved and the reactor is heated to 105°C. Then the reactor is evacuated to 8 kPa (60 mm Hg), and the required amount of water is removed by stripping. The oxide is then added at a constant rate (600–900 g/oxide per mole initiator) in 5 h at 105°C. The pressure is not allowed to exceed 722 kPa (90 psig) during the addition.

The mixture is kept for 3 hours at 105°C after the oxide addition is complete. By this time, the pressure should become constant. The mixture is then cooled to 50°C and discharged into a nitrogen-filled bottle. The catalyst is removed by absorbent (magnesium silicate) treatment followed by filtration or solvent extraction with hexane. In the laboratory, solvent extraction is convenient and effective, since polyethers with a molecular weight above about 700 are insoluble in water. Equal volumes of polyether, water, and hexane are combined and shaken in a separatory funnel. The top layer (polyether and hexane) is stripped free of hexane and residual

Table 4. Common Starters for Polyurethane Polyols

Name	Abbreviation	CAS Registry Number	f	Mol wt	OH No.
water			2	18	6233.3
propylene glycol	PG	[57-55-6]	2	76.1	1474.4
dipropylene glycol	DPG	[110-98-5]	2	134.2	836.1
glycerol	Gly	[56-81-5]	3	92.1	1827.4
trimethylolpropane	TMP	[77-99-6]	3	134.2	1254.1
pentaerythritol	PE	[115-88-5]	4	136.2	1647.6
ethylenediamine	EDA	[107-15-3]	4	60.1	3733.8
toluenediamine	TDA	[25376-45-8]	4	122.2	1836.3
sorbitol	Sorb	[50-70-4]	6	182.2	1847.4
sucrose	Suc	[57-50-1]	8	342.3	1311.1

water. The hydroxyl number, water, unsaturation value, and residual catalyst are determined by standard titration methods.

3.1.3. Hydroxyl Number

The molecular weight of polyether polyols for urethanes is usually expressed as its hydroxyl number or percent hydroxyl. When KOH (56,100 meg/mol) is the base, the hydroxyl number is defined as 56,100/equivalent weight (eq wt). Writing the equation as eq $\text{wt} = 56{,}100$/OH No. allows one to calculate the equivalents of polyol used in a urethane formulation, and then the amount of isocyanate required. The molecular weight can be calculated from these equations if the functionality, f, is known: mol wt = $f^{*}\text{eq wt}$.

The hydroxyl number can be determined in a number of ways such as acetylation, phthalation, reaction with phenyl isocyanate, and ir and nmr methods. An imidazole-catalyzed phthalation has been used to measure the hydroxyl number for a number of commercial polyether polyols and compared (favorably) to ASTM D2849 (uncatalyzed phthalation) (99). The uncatalyzed method requires two hours at 98°C compared to 15 minutes at the same temperature.

3.1.4. Starters

Nearly any compound having an active hydrogen can be used as starter (initiator) for the polymerization of PO. The common types are alcohols, amines, and thiols. Thus in Figure 2 ROH could be RNH_2 or RSH. The functionality is derived from the starter, thus glycerol results in a triol. Some common starters are shown in Table 4. The term starter is preferred over the commonly used term initiator because the latter has a slightly different connotation in polymer chemistry. Table 5 lists some homopolymer and copolymer products from various starters.

3.1.5. Unsaturation Value

The reaction temperature, catalyst concentration, and type of counterion of the alkoxide affect the degree of unsaturation. The tendency for rearrangement of PO to allyl alcohol is greatest with lithium hydroxide and decreases in the following order (100): $Li^{+} > Na^{+} > K^{+} > Cs^{+}$. The amount of unsaturation also increases with number-average molecular weight (M_n) suggesting that the rate of polymerization decreases relative to the rate of isomerization (chain transfer). The maximum molecular weight of base-catalyzed PPO, limited to 6000 by the ratio of polymerization, k_p, to transfer, k_{tr}, is about $k_p/k_{tr} \approx 100$. A theoretical upper limit to the molecular weight of PPO has been calculated.

The unsaturation present at the end of the polyether chain acts as a chain terminator in the polyurethane reaction and reduces some of the desired physical properties. Much work has been done in industry to reduce unsaturation while continuing to use the same reactors and holding down the cost. In a study (102) using

Table 5. CAS Numbers for Some Polyols Listed in the TSCA Inventory

Homopolymer		Copolymer	
Composition[a]	CAS Registry Number	Composition[a]	CAS Registry Number
PG–PO	[25322-69-4]	PO–EO	[9003-11-6]
Gly–PO	[25791-96-2]	PG–PO–EO	[53637-25-5]
TMP–PO	[25723-16-4]	Gly–PO–EO	[9082-00-2]
PE–PO	[9051-49-4]	TMP–PO–EO	[52624-57-4]
EDA–PO	[25214-63-5]	PE–PO–EO	[30374-35-7]
TDA–PO	[63641-63-4]	EDA–PO–EO	[26316-40-5]
Sorb–PO	[52625-13-5]	TDA–PO–EO	[67800-94-6]
Suc–PO	[9049-71-2]	Suc–PO–EO	[26301-10-0]

[a] The abbreviation for the composition has the form initiator–1st oxide–2nd oxide. The abbreviations for the initiators are shown in Table 4. PO and EO are propylene oxide and ethylene oxide, respectively.

18-crown-6 ether with potassium hydroxide to polymerize PO, a rate enhancement of approximately 10 was found at 110°C and slightly higher at lower temperature. The activation energy for this process was found to be 65 kJ/mol (mol ratio, $r = 1.5$ crown ether/KOH) compared to 78 kJ/mol for the KOH-catalyzed polymerization of PO. It was also feasible to prepare a PPO with $M_n \sim 10,000$ having narrow distribution at 40°C with added crown ether ($r = 1.5$) (103). The polymerization rate under these conditions is about the same as that without crown ether at 80°C.

Unsaturation value can be determined by the reaction of the allyl or propenyl end group with mercuric acetate in a methanolic solution to give acetoxymercuric methoxy compounds and acetic acid (ASTM D4671-87). The amount of acetic acid released in this equimolar reaction is determined by titration with standard alcoholic potassium hydroxide. Sodium bromide is normally added to convert the insoluble mercuric oxide (a titration interference) to mercuric bromide. The value is usually expressed as meq KOH/g polyol which can be converted to OH No. units using multiplication by 56.1 or to percentage of vinyl using multiplication by 2.7.

3.2. Acid Catalysis

The ring-opening polymerization of PO using acid catalysts has been extensively studied. The products range from isomerization of PO to low molecular weight oligomers (104–111). Measurement of the kinetics of hydration of PO to PG using an ion-exchange resin catalyst (acid) showed that the order of reaction for PO was 0.43 for homogenous reaction and 0.55 under heterogenous conditions (112). The activation energies obtained for the homogenous and heterogenous reactions were 51.5 and 53.4 kJ/mol, respectively. Studies (113) of the reaction of PO with boron trifluoride etherate catalyst showed varying results with different solvents. In dioxane, the isomerization to propionaldehyde proceeded smoothly and selectively. In THF, copolymerization of PO and THF was observed. In benzene the primary product was low mol wt PPO. In another study (111) the oligomerization PO using $BF_3(C_2H_5)_2O$ stopped before the monomer was completely exhausted. Substituted vinyl bromides were studied as photoinitiators in combination with onium salts for cationic polymerization of cyclohexene oxide, CHO (110). The product had a mol wt range of 200–2000 and a rate enhancement of approximately 10 was observed for irradiated samples over onium salt alone. The vinyl radicals generated by irradiation were oxidized by onium ions and the vinyl cation thus formed initiated the cationic polymerization of monomers such as cyclohexene oxide. Phosphoric acid has been used as a catalyst for the oligomerization of EO (109).

Chemicals responsible for odor in some PUR foams were synthesized by polymerization of PO in CH_2Cl_2 with $BF_3(C_2H_5)_2O$ catalyst (114). The yield was 25% volatile material and 75% polymeric material. The 25% fraction consisted of dimethyldioxane isomers, dioxolane isomers, DPG, TPG, crown ethers, tetramers, pentamers, etc, and 2-ethyl-4,7-dimethyl-1,3,6-trioxacane (acetal of DPG and propionaldehyde). The latter compound is mainly responsible for the musty odor found in some PUR foams. This material is not formed under basic conditions but probably arises during the workup when acidic clays are used for catalyst removal.

3.3. Coordination Polymerization of PO

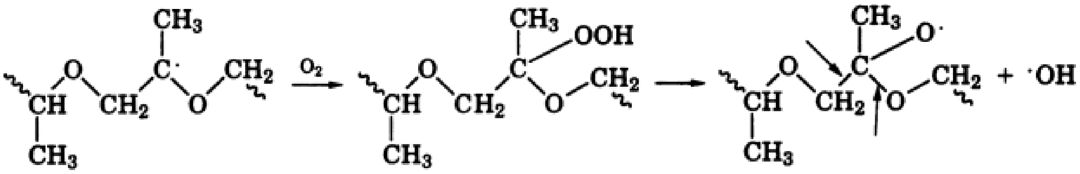
A variety of ring-opening polymerization catalysts, called coordination catalysts, have been reported. Among them are organoaluminum and organozinc compounds that have been modified with alcohols, ketones, phenols, and others. These polymerizations are characterized by controlled molecular weight with narrow molecular weight distribution and result in some amount of stereoregular polymer. The process is described as living polymerization, defined as consisting only of initiation and propagation reactions with no termination or chain-transfer reactions. Another way of saying this is that polymerization can be stopped by cutting off the flow of monomer and can be restarted by adding a new monomer. The end of the reaction is reached when a reagent such as acetic acid to hydrolyze the metal species is added. The term immortal polymerization has been used (115). In immortal polymerization the mixture continues to initiate polymerization until the reaction is specifically quenched. Many groups have studied the mechanism of immortal polymerization. It was found that the propagation and chain transfer could be accelerated by use of a Lewis acid such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (115). Living polymerization especially with metalloporphyrins has been reviewed (116). An organozinc complex has been used to polymerize *tert*-butylethylene oxide and the polymerization compared to that of PO (117). Partially stereoregular PPO has been separated on glass beads using isooctane as the eluent and controlling the temperature based on desired stereoregularity and mol wt (118, 119).

3.3.1. Procedure for Porphyrin–$(C_2H_5)_2AlCl$ Catalyst

The following procedure is considered typical (120). The reaction of tetraphenylporphyrin with pyrophoric diethylaluminum chloride was carried out in a Pyrex flask fitted with a three-way stopcock. The flask containing the porphyrin (1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added to dissolve the porphyrin. To this solution was added $(C_2H_5)_2AlCl$ (1.2 mmol) in 20% excess to the porphyrin. After about 4 h, the volatile materials were removed under reduced pressure from above the reaction mixture to leave crystalline materials, which were used as the polymerization catalyst. Dichloromethane (20 mL) was added to the catalyst and the mixture was cooled with liquid nitrogen. Purified PO (200 mmol) was added by trap-to-trap distillation to the cooled catalyst. Polymerization was carried out at room temperature for several days. A large amount of methanol was added to stop the polymerization. The volatile compounds were removed under reduced pressure. This procedure gave a 100% yield of polymer having mol wt of 10,000 and polydispersity of 1.13. The catalyst was removed by dissolving the residue in THF and filtering off the insoluble catalyst residue.

3.4. Autoxidation of PPO

PPO is prone to oxidation, as are short-chain aliphatic ethers. The mechanism of oxidation has been studied both with and without added stabilizers. The oxidation is initiated by the formation of a radical on the carbon (usually secondary) α to the ether oxygen. The radical is then trapped by oxygen to form an α-alkoxy hydroperoxide (121). The hydroperoxide decomposes unimolecularly to give an oxy radical and a hydroxyl radical (eq. **6**). The oxy radical **(1)** can follow two paths to products: the first occurs from split of the C–C bond (indicated by arrow) and leads to an acetate end group (and acetic acid), a formate end group, one chain scission, and two moles of water formed per two moles of oxygen consumed; the second path occurs from split of the C–O bond (indicated by arrow) and leads to formation of methyl ketone and an alcohol group for one mole of oxygen consumed (122).


(6)

(1)

The autoxidation of PPO is characterized by having an induction period which becomes longer upon addition of increasing amounts of an antioxidant such as 2,6-di-*tert*-butyl-4-methylphenol, more commonly referred to as butylated hydroxy toluene (BHT) (123). Both the induction period and rate of reaction are sensitive to temperature. The rate of autoxidation is independent of molecular weight and therefore the autoxidation must occur randomly along the chain and not on the end groups. The formation of phenyl urethane end groups increases the induction period and decreases the rate of oxygen consumption.

The tendency of aliphatic ethers toward oxidation requires the use of antioxidants such as hindered phenolics (eg, BHT), secondary aromatic amines, and phosphites. This is especially true in polyether polyols used in making polyurethanes (PUR) because they may become discolored and the increase in acid number affects PUR production. The antioxidants also reduce oxidation during PUR production where the temperature could reach 230°C. A number of new antioxidant products and combinations have become available (115, 120, 124–139) (see Antioxidants).

4. Manufacture of Polyols

A list of polyol producers is shown in Table 6. Each producer has a varied line of PPO and EOPO copolymers for polyurethane use. Polyols are usually produced in a semibatch mode in stainless steel autoclaves using basic catalysis. Autoclaves in use range from one gallon (3.785 L) size in research facilities to 20,000 gallon (75.7 m^3) commercial vessels. In semibatch operation, starter and catalyst are charged to the reactor and the water formed is removed under vacuum. Sometimes an intermediate is made and stored because a 30–100 dilution of starter with PO would require an extraordinary reactor to provide adequate stirring. PO and/or EO are added continuously until the desired OH No. is reached; the reaction is stopped and the catalyst is removed. A uniform addition rate and temperature profile is required to keep unsaturation the same from batch to batch. The KOH catalyst can be removed by absorbent treatment (140), extraction into water (141), neutralization and/or crystallization of the salt (142–147), and ion exchange (148–150).

5. Characterization and Properties of Polyethers

5.1. Viscosity

In the molecular weight range of 200–6000, PPO polyols are liquids. The viscosity depends on the functionality. Polyols with higher functionality have higher viscosity at a given equivalent weight. At low equivalent weight the viscosity depends strongly on the initiator. Monols and diols decrease the viscosity of a triol. PPO polyethers used for flexible foam have a viscosity of approximately 600 mPa·s (=cP). Polyethers for rigid foam have short chains and are therefore viscous. Some polyethers initiated by toluenediamine, which gives a tetrol, and used for rigid foams have a viscosity range of 10,000–100,000 mPa·s. Some high functionality sucrose-initiated polyols have viscosity as high as 10^6 mPa·s. Many sucrose-initiated polyols are co-initiated with lower functionality

Table 6. Polyether[a] Producers for Urethane Applications

Company	Location	Trademark	Annual capacity, 10^3 t
Arco[b] Chemical Co.	Channelview, Tex.	Arcol	77
	Conroe, Tex.		45
AC West Virginia Polyols Co.			200
BASF Corp.	Geismar, La.	Pluracol	82
	Wyandotte, Mich.		36
	Washington, N.J.		77
Bayer[c]	Baytown, Tex.	Multranol	70
	New Martinville, W. Va.		32
E. R. Carpenter Co., Inc.	Bayport, Tex.	Carpol	125
Dow Chemical U.S.A.	Freeport, Tex.	Voranol	227
Olin Corp.	Brandenburg, Ky.	Poly-G	114[d]
Pelron Corp.	Lyons, Ill.	PEL-RIG PEL-FLEX PEL-PPG	1.4
Stepan Co.	Milsdale, Ill.	Stepanol	3.6
ICI Corp.	Geismar, La.		
Total			*1090*

[a] Each company has a full line of products including PPG (diols) and glycerol adducts, as well as other initiator adducts.
[b] Texaco sold its polyol product line and a tolling agreement to Arco in 1987.
[c] Formerly Miles (formerly Mobay).
[d] Plus 18,000 t non-PUR product.

materials such as glycerol to reduce the viscosity of the final product. The viscosity of mixtures of diols and triols is intermediate and can be estimated from the weight fraction of the components.

In measurements (151) of the viscosity—temperature—mol wt relationship for PPO diols and triols the viscosity of PPG diols was found to be independent of shear rate, that is they are Newtonian fluids. A plot of viscosity vs reciprocal temperature ($\eta - 1/T$) of a series of PPO diols or triols gives a family of straight lines; higher mol wt gives higher viscosity. A plot of viscosity vs mol wt is a straight line but breaks at a limiting viscosity corresponding to a mol wt of ca 600 where no further decrease is observed. This means that a Mark-Houwink relationship should fail for mol wt less than 600. Equation 7 gives a polydispersity-corrected limiting viscosity number–molecular weight relationship for PPO in benzene solution at 25°C (152).

$$[\eta] = 0.000246\ M^{0.71}\ (\mathrm{dL/g}) \qquad (7)$$

This value differs by a factor of 2 from that of the often quoted relationship (153) shown by equation 8.

$$[\eta] = 0.000129\ M_v^{0.75}\ (\mathrm{dL/g}) \qquad (8)$$

5.2. Nmr Studies

^{1}>H- and ^{13}C-nmr has been valuable in elucidating the structure of PPO and copolymers of EO and PO, especially since high field nmr has become widely available.

The primary and secondary hydroxyl content in polyethers has been determined by high field (360 MHz) ^{1}H-nmr of trichloroacetyl isocyanate (TAIC)-modified polymers (154). Methylene or methine protons in the α-position are shifted and both are well resolved for integration. When the molar range of secondary hydroxyl groups is 10–90%, 5–8% accuracy is claimed (154). The resonance due to allylic end groups confounds the signal at 4.43 but is separable. ^{1}H-nmr (300 and 500 MHz) has been used to determine the number-average molar masses and molar ratio of the double-bond content of anionically polymerized PO over a range of conversions (136). Triad sequences of statistical and block copolymers of EO and PO were measured using resolution enhancement and subspectrum editing techniques (155). ^{13}C-nmr has been used to differentiate between random and block copolymers, and study persistence ratio (a measure of the deviation from fully random statistics), mean sequence length of EOPO sequences, triad probabilities, and starter and end groups (156). In ^{1}H and ^{13}C studies (157), to characterize the end groups in PPO polymers, it was found that the peaks corresponding to propenyl end groups were only observed in freshly prepared solutions and disappeared in about two days due to hydrolysis by trace DCl in the $DCCl_3$, producing propanol and a CH_2OH end group. Dipropylene glycol (DPG) and tripropylene glycol (TPG) prepared from chiral PO using an aluminum complex has been studied by means of a J-modulated spin echo technique ^{13}C-nmr (158). Findings were applied to a racemic oligomer ($\mathrm{DP} = 11$) and it was possible to identify central and terminal units. End-group carbon atoms present large configurational effects compared to internal carbon atoms. Measurement of relaxation times of PPO complexed with sodium trifluoromethanesulfonate using ^{13}C-nmr demonstrated the influence of polyether–salt interactions on local segmental motion of the polymer chains (159). Relaxation time,T_1, decreases with decreasing temperature for uncomplexed PPO but increases with decreasing temperature for complexes. Increasing the salt concentration to create more virtual cross-links causes PPO lifetime, τ_0, to increase rapidly. This behavior is unusual.

^{13}C-nmr was used to analyze the stereoregularity of PPO prepared with the diphenylzinc–water system at various ($H_2O/(C_6H_5)_2Zn$) ratios (160). Two nmr methods were used to determine the primary hydroxyl content of EOPO copolymers (161). The first method was integration of the ^{13}C-nmr resonance from the carbon bearing the hydroxyl group. The second method used ^{19}F-nmr of trifluoroacetic acid derivatives. The ^{13}C method had good accuracy and easy sample preparation but poor sensitivity and precision. The ^{19}F method had good sensitivity and precision but poor accuracy (probably because of workup during derivatization) and difficult sample preparation. These tests are called ASTM 4273-83 methods A and B. Two-dimensional J-resolved spectroscopy was used to separate overlapping multiplets in atactic PPO (162). Proton chemical shift is sensitive to triad sequences but the homonuclear coupling constants for head-to-head monomer units are the same regardless of stereosequence.

A ^{13}C-nmr study of regioisomers (eg, H–T, H–H, T–T) of oligomeric poly(propylene glycol) has been done (163). A method for determining the number-average functionality and functionality distribution of polyether polyols based on measured intensities of relevant end groups observed by ^{13}C-nmr has been described (164). Chromium(III) acetylacetonate, $Cr(acac)_3$, was used as a relaxation reagent and allows analysis to be speeded up by decreasing relaxation times. Chemical shift reagent $Eu(DPM)_3$ has been used to measure the molecular weight of PPO (165). The molecular weight values found were within a few percent of the values reported by suppliers. This method is not practical due to the ease of use and accuracy of gpc compared to the expense of the shift reagents. Multipulse ^{13}C-nmr INEPT and DEPT techniques have been used for the determination of PPO microstructure (166). The ^{13}C-nmr chemical shifts were also calculated using the γ-gauche effect for various dyad sequences (166).

5.3. Refractive Index

The effect of mol wt (1400–4000) on the refractive index (RI) increment of PPG in benzene has been measured (167). The RI increments of polyglycols containing aliphatic ether moieties are negative: $d\eta/dc$ (mL/g) $= -0.055$. A plot of RI vs $1/M$ is linear and approaches the value for PO itself (109). The RI, density, and viscosity of PPG–salt complexes, which may be useful as polymer electrolytes in batteries and fuel cells have been measured (168). The variation of RI with temperature and salt concentration was measured for complexes formed with PPG and some sodium and lithium salts. Generally, the RI decreases with temperature, with the rate of change increasing as the concentration increases.

5.4. Infrared Spectroscopy

The following bands are seen in the ir spectrum of PPG: 2970, 2940, 2880 cm^{-1} (C–H stretch, m); 1460, 1375 cm^{-1} (C–H bend, m); 1100, 1015 cm^{-1} (C–O stretch, m) of which the 2940 and 1015 band are specific. The latter are also present in copolymers of EO and PO. Absorptions due to unsaturated end groups are found at 1650 cm^{-1} (allyl ether) and 1672 cm^{-1} (1-propenyl ether). The O–H stretching band at 3470 cm^{-1} shows the greatest variation for different hydroxyl number polyols and has been used to estimate the hydroxyl number (169).

5.5. Chromatography

One gpc study (170) of low molecular weight polyethers used two systems: THF solvent and PLgel columns and water with TSK gel column sets. In THF the elution volume depends predominantly on chain length, whereas in water the composition as well as chain length influences the elution volume. THF is a good solvent for PPO homopolymer and EOPO copolymers. Gpc calibration is typically done with poly(ethylene glycol) (PEG) or polystyrene standards but the latter tend to overestimate the mol wt of PPO. In some cases unsaturated polyethers can be resolved as a shoulder on the low mol wt side of the main peak. In many cases it is possible to see additives in polyols, but quantitation is difficult owing to the low sensitivity of the RI detector. Additives are better determined by gc or hplc. An on-line gpc analyzer for the detection of PO and EO in the polymerization reactor has been described (171). The system consists of a PL aquagel column, a RI detector, and a sampling valve that allows on-stream measurement. This system was evaluated over the range 8% to $<0.3\%$ PO and compared favorably with that calculated from the vapor pressure. Another study used a gpc system consisting of Fractogel TSK columns, water–acetonitrile as the eluent, and PEG–PEO calibration standards.

The composition of PPG–PEG blends has been determined using gpc with coupled density and RI detectors. PEG and PPG have different response factors for the density and RI detectors which were exploited (173). An hplc system with CHROMPAC RP-18C_{18} column at 298°C and acetonitrile–water or methanol–water as the mobile phase has been used to gather information about the functionality of PPO (174).

Reversed-phase hplc has been used to separate PPG into its components using evaporative light scattering and uv detection of their 3,5-dinitrobenzoyl derivatives. Acetonitrile–water or methanol–water mixtures effected the separation (175). Polymer glycols in PUR elastomers have been identified (176) by pyrolysis-gc. The pyrolysis was carried out at 600°C and produced a small amount of ethane, CO_2, propane, and mostly propylene, CO, and CH_4. The species responsible for a musty odor present in some PUR foam was separated and identified by gc (Supelco SP-2100 capillary column) (114). Unsaturated oligomers up to allyl-penta PG from a pentane extraction of polyol have also been separated and identified (114).

5.6. Solubility

PPO polyols with a molecular weight below 700 are water soluble. The triol is slightly more water soluble than the diol. The solubility in water decreases with increasing temperature. This inverse solubility causes a cloud point which is important in characterizing copolymers of propylene oxide and ethylene oxide.

Polyethers prepared from propylene oxide are soluble in most organic solvents. The products with the highest hydroxyl number (lowest molecular weight) are soluble in water, not in nonpolar solvents such as hexane. The solubility of 3000 molecular weight triols is high enough in solvents such as toluene, hexane, and methylene chloride that the triols can be purified by a solvent extraction process.

The following components of solubility parameters for PPO have been obtained (177): $\delta_d = 16.3 \pm 1$, $\delta_p = 4.7 \pm 0.5$, $\delta_h = 7.4 \pm 0.5$, and $\delta_0 = 18.5 \pm 1.2$ with units $(\mathrm{J/mL})^{1/2}$. The determination was based on the use of three mixtures of solvents. For each mixture, the point of maximum interaction between the mixture and the polyol was obtained from the maximum value of the intrinsic viscosity. The parameter δ_d

Table 7. Water Solubility of PO Polyols[a]

	Solubility, wt %	
Polyol description	at 23°C	at 50°C
2000 mol wt diol	5.3	3.6
2000 mol wt diamine	7.3	5.4
3000 mol wt triol	4.8	4.1
5000 mol wt triol	2.8	

[a] Ref. 178

measures dispersion; δ_p, polar bonding; δ_h, hydrogen bonding; and δ_o is the Hildebrand solubility parameter which is the radius vector of the other orthogonal solubility parameters. Water solubility of PPO has been determined using turbidimetric titration (178) (Table 7).

5.7. Mass Spectrometry

Field desorption mass spectrometry has been used to analyze PPO (179). Average molecular weight parameters (M_n and M_w) could be determined using either protonated (MH^+) or cation attachment (MNa^+) ions. Good agreement was found between fdms and data supplied by the manufacturer, usually less than 5% difference in all cases up to about 3000 amu. Laser desorption Fourier transform mass spectrometry was used to measure PPG ion and it was claimed that ions up to m/z 9700 (PEG) can be analyzed by this method (180).

5.8. Density

At low equivalent weight, the specific gravity (density) of polyethers depends on the initiator and at high equivalent weight it depends on the alkylene oxide. The effects of molecular weight on specific gravity are minor. Most commercial products have a specific gravity of 1.005–1.020 at 25°C unless they are of low hydroxyl equivalent weight. The specific gravity of PPO diol can be calculated from the hydroxyl number by the linear equation sp gr (25°C) = $0.000127 \times (\text{hydroxyl number}) + 0.9976$ over the molecular weight range 2000–7000.

The specific volume (mL/g) of PPO is inversely proportional to the molecular weight (181) and is described by $\text{sp vol} = 1.0013 - 2.524/M_n$. The temperature dependence of the specific volume is given by $V_{sp} = 1.000 + 0.0007576\,(T - 25)$ over the temperature range 25–80°C (94).

5.9. Other Properties

The glass-transition temperature for PPO is $T_g \sim 190\ \text{K}$ and varies little with molecular weight (182). The temperature dependence of the diffusion coefficient of PPO in the undiluted state has been measured (182).

The thermal conductivity of PPO is approximately 0.16 W/($\text{m}\cdot\text{K}$) for a 3000 mol wt polyol and 0.15 W/($\text{m}\cdot\text{K}$) for a 5000 mol wt polyol. The thermal conductivity is relatively insensitive to the temperature. The specific heat of PPO varies with temperature but not with the molecular weight. At 25°C the specific heat is 1950 J/(kg·°C) and at 150°C it is 2300 J/(kg·°C). Intermediate values can be interpolated with the following equation:

$$\text{specific heat}\ (\text{J}/(\text{kg}\cdot{}^\circ\text{C})) = 2.84 \times \text{temperature}\ ({}^\circ\text{C}) + 1875$$

6. Health and Safety

Propylene oxide is highly reactive. It reacts exothermically with any substance that has labile hydrogen such as water, alcohols, amines, and organic acids; acids, alkalies, and some salts act as catalysts.

Propylene oxide is a primary irritant, a mild protoplasmic poison, and a mild depressant of the central nervous system. Skin contact, even in dilute solution (1%), may cause irritation to the eyes, respiratory tract, and lungs. Propylene oxide is a suspected carcinogen in animals. The LC_{50} (lowest lethal concentration by inhalation in rats) is 4000 mg/kg body weight. The LD_{50} (oral) is 930 mg/kg. The LD_{50} (dermal) is 1500 mg/kg. The TWA (8-h exposure) is 100 ppm and the STEL (15-min exposure) is 150 ppm.

PPO and EOPO copolymers are low hazard–low vapor pressure liquids. Contact with skin, eyes, or inhalation cause irritation. There are no known acute or chronic affects associated with polyols. First aid for contact with polyols involves washing the affected area with water. The flash point of PPO is greater than 93°C.

BIBLIOGRAPHY

"Propylene Oxide Polymers and Higher 1,2-Epoxide Polymers" under "Polyethers" in *ECT* 3rd ed., Vol. 18, pp. 633–645, by R. A. Newton, Dow Chemical USA.

Cited Publications

1. D. Kahlich, U. Wiechern, and J. Lindner, in B. Elvers, S. Hawkins, and G. Schulz, eds., *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. **A22**; VCH Publishers, Inc., New York, 1993, 239–260.
2. S. D. Gagnon, 273–307; and N. Clinton, and P. Matlock, 225–273, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **6**, John Wiley and Sons, Inc., New York, 1986.
3. F. E. Bailey, in Ref. 1, Vol. A21; 1992, 579–589.
4. L. C. Pizzini and J. T. Patton, Jr., 145–167; F. W. Stone, and J. J. Stratta, 103–145; J. Furukawa, and T. Saegusa, 175–195; and L. C. Pizzini, J. T. Patton, Jr., 168–175, in H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds., *Encyclopedia of Polymer Science and Technology*, Vol. **6**, John Wiley and Sons, Inc., New York, 1967.
5. R. W. Body, and V. L. Kyllingstad, in Ref. 2, 307–322.
6. D. Dieterich, and K. Uhlig, in Ref. 3, 665–716.
7. R. A. Briggs, and E. E. Gruber, in Ref. 4, 195–209.
8. B. Osner, *Bull. Soc. Chim. Fr.*, 235 (1860).
9. U.S. Pat. 2,948,691 (Aug. 9, 1960), E. Windemuth, H. Schnell, and O. Bayer, (to Bayer).
10. U.S. Pat. 2,674,619 (Apr. 6, 1954), (to Wyandotte Chemical Corp.).
11. Eur. Pat. 460,317 (Dec. 11, 1991), (to Ethyl Petroleum Additives, Ltd., U.K.).
12. Eur. Pat. 244,733 (Nov. 11, 1987), G. C. Weitz (to American Polywater Corp.).
13. U.S. Pat. 4,555,549 (Nov. 26, 1985), R. L. Camp, E. M. Dexheimer, and M. J. Anchor, (to BASF Corp.).
14. U.S. Pat. 4,452,711 (June 5, 1984), J. T. Laemmie (to Aluminum Co. of America, USA).
15. U.S. Pat. 4,414,121 (Nov. 8 1983), R. P. Aiello.
16. U.S. Pat. 4,402,839 (Sept. 6, 1983), (to Mobil Oil Corp., USA).
17. H. S. Koenig and G. M. Bryant, *Text. Res. J.* **50**, 1 (1980).
18. U.S. Pat. 4,560,482 (Dec. 24, 1985), G. P. Canevari (to Exxon Research and Engineering Co., USA).
19. U.S. Pat. 4,505,716 (Mar. 19, 1985), (to ITT Corp., USA).
20. U.S. Pat. 4,441,889 (Apr. 10, 1984), S. Mark (to Gulf and Western Industries, Inc., USA).
21. Eur. Pat. 158,996 (Oct. 23, 1985), W. McCormick (to Adamantech, Inc., USA).
22. WO Pat. 9,205,220 (Apr. 2, 1992), S.H.-P Yu and T. R. Mass (to B.F. Goodrich Co., USA).
23. U.S. Pat. 4,542,095 (Sept. 17, 1985), D. J. Steklenski and J. E. Littman (to Eastman Kodak Co., USA).
24. U.S. Pat. 4,304,562 (Dec. 8, 1981), J. A. Bolan and M. A. Grimmer (to Drackett Co., USA).
25. WO Pat. 9,101,171 (Feb. 7, 1991), M. S. Dahanayake (to GAF Chemicals Corp., USA).

26. U.S. Pat. 4,836,951 (June 6, 1989), (to Union Carbide Corp., USA).
27. U.S. Pat. 4,510,067 (Apr. 9, 1985), A. C. Ozmeral (to BASF Corp.).
28. U.S. Pat. 4,411,810 (Oct. 25, 1983), D. R. Dutton, E. J. Parker, R. A. Ott, and J. G. Otten (to BASF Corp.).
29. U.S. Pat. 5,098,478 (Mar. 24, 1992), R. Krishnan, R. W. Bassemir, and T. C. Vogel (to Sun Chemical Co.).
30. Eur. Pat. 397,431 (Nov. 14, 1990), H. Tomita and Y. Sonoda (to Kabushiki Laisha Kako Co., Ltd.).
31. Eur. Pat. 469,724 (Feb. 5, 1992), C. R. Frisby (to McGean-Rohco, Inc.).
32. U.S. Pat. 4,528,075 (July 9, 1985), M. J. Anchor and R. L. Camp (to BASF Corp.).
33. Eur. Pat. 359,071 (Mar. 21, 1990), L. Levrero, F. Granata, and R. Latorrata (to BP Chemicals Ltd., U.K.).
34. U.S. Pat. 4,548,726 (Oct. 22, 1985), B. J. Morris-Sherwood, E. C. Brink, Ir., D. R. McCoy, and E. E. McEntire (to Texaco).
35. U.S. Pat. 4,552,686 (Nov. 12, 1985), B. J. Morris-Sherwood and E. C. Brink Jr, (to Texaco Inc., USA).
36. U.S. Pat. 4,543,199 (Sept. 24, 1985), L. F. Kuntschik and C. L. Dowe (to Texaco Inc., USA).
37. U.S. Pat. 4,481,125 (Nov. 6, 1984), R. V. Holgado (to E. F. Houghton and Co., USA).
38. Can Pat. 2,027,303 (Apr. 12, 1991), S. T. Hirozawa and D. E. Coker (to BASF Corp.).
39. U.S. Pat. 5,057,234 (Oct. 15, 1991), R. G. Bland and D. K. Clapper (to Baker Hughes, Inc., USA).
40. U.S. Pat. 4,780,220 (Oct. 25, 1988), T. E. Peterson (to Hydra Fluids, Inc., USA).
41. WO Pat. 9,115,542 (Oct. 17, 1991), J. S. Peanasky, J. M. Long, and R. P. Wool (to AGRI-Tech Industries, Inc., USA).
42. U.S. Pat. 4,857,593 (Aug. 15, 1989), P. S. Leung, E. D. Goddard, and F. H. Ancker (to Union Carbide Corp., USA).
43. WO Pat. 9,114,727 (Oct. 3, 1991), G. M. Vanhaeren (to Exxon Chemical Ltd., U.K.).
44. U.S. Pat. 4,343,664 (Aug. 10, 1982), S. Iyer (to U.S. Dept. of the Army).
45. U.S. Pat. 5,160,328 (Nov. 3, 1992), J. V. Cartmell and W. R. Sturtevant (to NDM Aquisition Corp., USA).
46. Eur. Pat. 481,600 (Apr. 22, 1992), N. I. Payne, M. Gibson, and P. M. Taylor (to American Cyanamid Co.).
47. U.S. Pat. 4,879,109 (Nov. 7, 1989), R. L. Hunter (to Emory University, USA).
48. D. Attwood, J. H. Collett, and C. J. Tait, *Int. J. Pharm.* **26**, 25 (1985).
49. R. M. Nalbandian, R. L. Henry, K. W. Balko, D. V. Adams, and N. R. Neuman, *J. Biomed. Mater. Res.* **21**, 1135 (1987).
50. Eur. Pat. 441,307 (Aug. 14, 1991), Y. Kawasaki and Y. Suzuki (to Showa Yakuhin Kako Co., Ltd.).
51. Eur. Pat. 122,799 (Oct. 24, 1984), R. C. Harrison (to Amersham International PLC, U.K.).
52. S. Miyazaki and co-workers, *Chem Pharm. Bull.* **34**, 1801 (1986).
53. T. K. Law, T. L. Whateley, and A. T. Florence, *J. Controlled Release* **3**, 279 (1986).
54. WO Pat. 9,013,307 (Nov. 15, 1990), G. Collins and W. Wicomb.
55. Eur. Pat. 464,545 (Jan. 8, 1992), M. Shibuya and S. Ishii (to Showa Yakuhin Kako Co., Ltd.).
56. Eur. Pat. 481,717 (Apr. 22, 1992), C. F. Cooper (to ARCO Chemical Technology, Inc.).
57. *Chem. Mark. Rep.*, (Apr. 1993).
58. Y.-C. Yen and C.-S. Liu, *Ethylene Oxide/Propylene Oxide, Process Economics Report 2D*, Stanford Research Institute, Menlo Park, Calif., 1985.
59. U.S. Pat. 5,101,052 (Mar. 31, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
60. U.S. Pat. 5,107,067 (Apr. 21, 1992), E. T. Marquis, K. P. Keating, J. R. Sanderson, and W. A. Smith (to Texaco Inc.).
61. U.S. Pat. 5,093,509 (Mar. 3, 1992), R. A. Meyer and E. T. Marquis (to Texaco Chemical Co.).
62. U.S. Pat. 5,214,168 (May 25, 1993), J. G. Zajacek and G. L. Crocco (to Arco Chemical Technology, L.P.).
63. U.S. Pat. 5,241,088 (Aug. 31, 1993), J. L. Meyer, B. T. Pennington, and M. C. Fullington, (to Olin Corp.).
64. A. Q. H. Habets-Cruetzen and J. A. M. De Bont, *Appl. Microbiol. Biotechnol.* **26**, 434 (1987).
65. T. Imai and co-workers, *Appl. Environ. Microbiol.* **52**, 1403 (1986).
66. V. Subramanian, *J. Ind. Microbiol.* **1**, 119 (1986).
67. L. E. S. Brink and J. Tramper, *Enzyme Microb. Technol.* **8**, 281 (1986).
68. N. R. Woods and J. C. Murrell, *Bitechnol. Lett.* **12**, 409 (1990).
69. G. A. Kovalenko and V. D. Sokolovskii, *React. Kinet. Catal. Lett.* **48**, 447 (1992).
70. C. A. G. M. Weijers, E. J. T. M. Leenen, N. Klijn, and J. A. M. De Bont, *Meded. Fac. Landbouwwet., Rijksuniv. Gent.* **53**(4b), 2098 (1988).
71. M. Mahmoudian and A. Michael, *J. Ind. Microbiol.* **11**, 29 (1992).
72. S. H. Stanley and H. Dalton, *Biocatalysis* **6**(3), 163 (1992).
73. S. Li, C. Gao, and A. Liu, *Chin. Chem. Lett.* **2**(4), 303 (1991).

74. R. L. Kelley, D. E. Hoefer, J. R. Conrad, V. J. Srivastava, and C. Akin, in C. Akin and J. I. Smith, eds., *Gas, Oil, Coal, Environ. Biotechnol.* 2nd ed., Gas Technology, Chicago, Ill., 1990, 433–455.
75. M. Shimoda, Y. Seki, and I. Okura, *J. Mol. Catal.* **78**(2), L27 (1993).
76. S. H. Stanley, A. O'L. Richards, M. Suzuki, and H. Dalton, *Biocatalysis* **6**(3), 177 (1992).
77. K. Scott, C. Odouza, and W. Hui, *Chem. Eng. Sci.* **47**(9–11), 2957 (1992).
78. L. Franke, A. Zimmer, and K. Seibig, *Chem. Ing. Tech.* **64**(7), 652 (1992).
79. J. D. Lisius and P. W. Hart, *J. Electrochem. Soc.* **138**(12), 3678 (1991).
80. U.S. Pat. 5,214,168 (May 25, 1993), J. Zajacek (to Arco Chemical).
81. R. L. Burwell, Jr., *Chemtracts: Inorg. Chem.* **3**(6), 344 (1991).
82. A. Zhou, B. Zhu, and H. Chen, in X. I. A. Hou, ed., *Proceedings of the International Conference on Petroleum Refining and Petrochemical Processing*, Vol. 3; Beijing, China, 1991, 1176–1182.
83. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents, Techniques of Chemistry*, 4th ed., Vol. **II**, John Wiley and Sons, Inc., New York, 1986.
84. U.S. Pat. 5,154,803 (Oct. 13, 1992), E. T. Marquis, G. P. Speranza, Y. H. E. Sheu, W. K. Culbreth, III, and D. G. Pottratz (to Texaco Chemical Co.).
85. U.S. Pat. 5,154,804 (Oct. 13, 1992), E. T. Marquis, G. P. Speranza, Y. H. E. Sheu, W. K. Culbreth, III, and D. G. Pottratz (to Texaco Chemical Co.).
86. U.S. Pat. 5,139,622 (Aug. 18, 1992), E. T. Marquis, G. P. Speranza, Y. H. E. Sheu, W. K. Culbreth, III, and D. G. Pottratz (to Texaco Chemical Co.).
87. U.S. Pat 5,116,466 (May 26, 1992), E. T. Maarquis, G. P. Speranza, Y. H. E. Sheu, W. K. Culbreth, III, and D. G. Pottratz, (to Texaco Chemical Co.).
88. U.S. Pat. 5,116,467 (May 26, 1992), E. T. Marquis, G. P. Speranza, Y. H. E. Sheu, W. K. Culbreth, III, and D. G. Pottratz, (to Texaco Chemical Co.).
89. U.S. Pat. 5,116,465 (May 26, 1992), E. L. Yeakey and E. T. Marquis (to Texaco Chemical Co.).
90. C. A. G. M. Weijers, M. J. J. Litjens, and J. A. M. de Bont, *Appl. Microbiol. Biotechnol.* **38**(3), 297 (1992).
91. R. G. Ghirardelli, *J. Am. Chem. Soc.* **95**, 4987 (1973).
92. *Propylene Oxide*, Technical bulletin, Arco. Chemical Co., Philadelphia, Pa.
93. J. A. Riddick and W. B. Bunger, *Organic Solvents, Techniques of Chemistry*, 3rd ed., Vol. **II**, Wiley-Interscience, New York, 1970.
94. G. Yu, F. Heatley, C. Booth, and T. G. Blease, *J. Polym. Sci., Part A: Polym. Chem.* **32**, 1131 (1994).
95. X. Chen and M. Van De Mark, *J. Appl Polym. Sci.* **50**, 1923 (1993).
96. S. Kohjiya, T. Sato, T. Nakayama, and S. Yamashita, *Makromol. Chem., Rapid Commun.* **2**, 231 (1981).
97. A. T. Chen and co-workers, "Comparison of the Dynamic Properties of Polyurethane Elastomers Based on Low Unsaturation Polyoxypropylene Glycols and Poly(tetramethylene oxide) Glycols," *Polyurethanes World Congress 1993*, Vancouver, B.C., Canada, Oct. 10–13, 1993.
98. N. Barksby and G. L. Allen, "Low Monol Polyols and Their Effects in N. Barksby and G. L. Allen, "Low Monol Polyols and Their Effects *Polyurethanes World Congress 1993*, Vancouver, B.C., Canada, Oct. 10–13, 1993.
99. M. A. Carey, S. L. Wellons, and D. K. Elder, *J. Cell. Plast.*, 42 (1984).
100. J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*; Wiley-Interscience, New York, 1963.
101. A. Penati, C. Maffezzoni, and E. Moretti, *J. Appl. Polym. Sci.* **26**, 1059 (1981).
102. J. Ding, C. Price, and C. Booth, *Eur. Polym. J.* **27**, 891 (1991).
103. J. Ding, F. Heatley, C. Price, and C. Booth, *Eur. Polym. J.* **27**, 895 (1991).
104. U.S. Pat. 4,223,160 (Sept. 16, 1980), L. G. Hess (to Union Carbide Corp., USA).
105. P. Brüzga, J. V. Grazulevicius, R. Kavallünas, R. Kublickas, and I. Liutviniene, *Polym. Bull.* **30**, 509 (1993).
106. I. I. Abu-Abdoun, *Eur. Polym. J.* **28**, 73 (1992).
107. I. I. Abu-Abdoun, *Eur. Polym. J.* **29**, 1445 (1993).
108. A. Martinez, F. Mijangos, and L. M. Leon, *Eur. Polym. J.* **22**, 243 (1986).
109. T. Biela and P. Kubisa, *Makromol. Chem.* **192**, 473 (1991).
110. N. Johnen, S. Kobayashi, Y. Yagci, and W. Schnabel, *Polym. Bull.* **30**, 279 (1993).
111. S. S. Ivanchev and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **18**, 2051 (1980).
112. R. Jaganathan, R. V. Chaudhari, and P. A. Ramachandran, *AIChe J.* **30**, 1 (1984).
113. S. Sugiyama, S. Ohigashi, K. Sato, S. Fukunaga, and H. Hayashi, *Bull. Chem. Soc. Jpn.* **62**, 3757 (1989).

114. S. H. Harris, P. E. Kreter, and C. W. Polley, "Characterization of Polyurethane Foam Odor Bodies," *Polyurethanes World Congress 1987*, Aachen, Germany.
115. M. Akatsuka, T. Aida, and S. Inoue, *Macromolecules* **27**, 2820 (1994).
116. S. Inoue and T. Alda, *Chemtech*, 28 (1994).
117. T. Tsuruta and Y. Hasebe, *Macromol. Chem. Phys.* **195**, 427 (1994).
118. K. Alyürük and K. Hartani, *Polymer* **30**, 2328 (1989).
119. K. Alyürük, T. Özden, and N. Çolak, *Polymer* **27**, 2009 (1986).
120. T. Aida and S. Inoue, *Macromolecules* **14**, 1166 (1981).
121. U. Hähner, W. D. Habicher, and K. Schwetlick, *Polym. Degrad. Stabil.* **34**, 111 (1991).
122. P. J. F. Griffiths, J. G. Hughes, and G. S. Park, *Eur. Polym. J.* **29**, 437 (1993).
123. U. Hähner, W. D. Habicher, and K. Schwetlick, *Polym. Degrad. Stabil.* **34**, 119 (1991).
124. R. G. Skorpenske, A. K. Schrock, and G. E. Beal, "Antioxidant Behavior in Flexible Polyurethane Foam," *33rd Annual Polyurethane Technical/Marketing Conference*, Orlando, Fla., Sept. 30–Oct. 3, 1990.
125. L. B. Barry and M. C. Richardson, "Novel AO System for Polyether Polyol Stabilization," *33rd Annual Polyurethane Technical/Marketing Conference*, Orlando, Fla., Sept. 30–Oct. 3, 1990.
126. L. B. Barry and M. C. Richardson, "A Less Volatile Performance Equivalent to BHT for Polyether Polyol Stabilization," *Polyurethane World Congress 1993*, Vancouver, B.C., Canada, Oct. 10–13, 1993.
127. L. B. Barry and M. C. Richardson, "Recent Developments in L. B. Barry and M. C. Richardson, "Recent Developments *34th Annual Polyurethane Technical/Marketing Conference*, New Orleans, La., Oct. 21–24, 1992.
128. R. A. Hill, "New Antioxidant Package for Polyether Polyols, with Reduced Fogging Behaviour," *34th Annual Polyurethane Technical/Marketing Conference*, New Orleans, La., Oct. 21–24, 1992.
129. U.S. Pat. 4,904,745 (Feb. 27, 1990), S. Inoue and T. Aida (to Kanegafuchi Kagaka Kogyo).
130. S. Asano, T. Aida, and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1148 (1985).
131. T. Yasuda, T. Aida, and S. Inoue, *Bull. Chem. Soc. Jpn.* **59**, 3931 (1986).
132. Y.-S. Gal, B. Jung, W.-C. Lee, and S.-K. Choi, *J. M. S.-Pure Appl. Chem.* **30**, 531 (1993).
133. S. Inoue, T. Aida, Y. Watanabe, and K.-I. Kawaguchi, *Makromol. Chem., Macromol. Symp.* **42**, 365 (1991).
134. Y. Watanabe, T. Aida, and S. Inoue, *Macromolecules* **23**, 2612 (1990).
135. S. Murouchi, Y. Hasebe, and T. Tsuruta, *Makromol. Chem., Rapid Commun.* **11**, 129 (1990).
136. Ga-E. Yu, A. J. Masters, F. Heatley, C. Booth, and T. G. Blease, *Macromol. Chem. Phys.* **195**, 1517 (1994).
137. Eur. Pat. Appl. 18,609 (Nov. 12, 1980), (to Hoechst A-G).
138. M. P. Calcagno, F. Lopez, J. M. Contreras, M. Ramirez, and F. M. Rabagliati, *Eur. Polym. J.* **27**(8), 751 (1991).
139. Z. Oktem, A. Sari, K. Alyuruk, *Eur. Polym. J.* **29**(5), 637 (1993).
140. Eur. Pat. Appl. 418,533 (Mar. 27, 1991), A. Penati, E. Moretti, C. Maffezzoni, G. Agopian, and B. Mazdrakov (to Pressindustria SpA, Verila State Enterprises, Italy).
141. Ger. Offen. 3,016,113 (Oct. 29, 1981), H. Hetzel, P. Gupta, R. Nast, H. Echterhof, and U. Brocker (to Bayer A-G).
142. Ger. Offen. 3,907,911 (Sept. 13, 1990), P. Gupta, H. J. Sandhagen, and H. J. Rosenbaum (to Bayer A-G).
143. Eur. Pat. Appl. 383,333 (Aug. 22, 1990), T. Watabe, H. Takeyasu, T. Doi, and N. Kunii (to Asahi Glass Co., Ltd.).
144. Eur. Pat. Appl. 414070 (Feb. 27, 1991), P. Gupta, H. J. Sanndhagen, and H. J. Rosenbaum (to Bayer A-G).
145. U.S. Pat. 4,521,548 (June 4, 1985), J. D. Christen, H. B. Taylor, III (to Dow Chemical Co.).
146. Ger. Offen. 3,229,216 (Feb. 9, 1984), W. Straechle, R. Denni, and M. Marx (to F A-G).
147. U.S. Pat. 4,306,943 (Dec. 22, 1981) (to Daiichi Kogyo Seiyaku Co., Ltd.).
148. U.S. Pat. 4,985,551 (Jan. 15, 1991), J. G. Perry and W. A. Spelyng (to BASF Corp.).
149. U.S. Pat. 4,994,627 (Feb. 19, 1991), M. Cuscurida and A. J. Faske (to Texaco Chemical Co.).
150. U.S. Pat. 5,182,025 (Jan. 26, 1993), R. G. Duranleau, M. J. Plishka, and M. Cuscurida (to Texaco Chemical Co.).
151. C. Vervloet and D. E. Knibbe, *Cellular Polym.* **1**, 15 (1982).
152. P. Szewczyk, *J. Appl. Polym. Sci.* **31**, 1151 (1986).
153. G. Allen, C. Booth, and M. N. Jones, *Polymer* **5**, 195 (1964).
154. J. Loccufier, M. Van Bos, and E. Schacht, *Polym. Bull.* **27**, 201 (1991).
155. F. Heatley, Y.-Z. Luo, J.-F. Ding, R. H. Mobbs, and C. Booth, *Macromolecules* **21**, 2713 (1988).
156. W. Gronski, *Makromol. Chem.* **192**, 591 (1991).
157. F. Heatley, J. Ding, G. Yu, and C. Booth, *Makromol. Chem., Rapid Commun.* **14**, 819 (1993).
158. A. Le Borgne, M. Moreau, and V. Vincens, *Macromol. Chem. Phys.* **195**, 375 (1994).

159. J. P. Manning, C. B. Frech, B. M. Fung, and R. E. Frech, *Polymer* **32**, 2939 (1991).
160. F. M. Rabagliati and F. López, *Makromol. Chem., Rapid Commun.* **6**, 141 (1985).
161. C. L. LeBas and P. A. Turley, *J. Cell. Plast.*, 194 (1984).
162. M. D. Bruch, F. A. Bovey, and R. E. Cais, *Macromolecules* **18**, 1253 (1985).
163. C. Campbell, F. Heatley, G. Holcroft, and C. Booth, *Eur. Polym. J.* **25**, 831 (1989).
164. R. H. Carr, J. Hernalsteen, and J. Devos, *J. Appl Polym. Sci.* **52**, 1015 (1994).
165. F. F. Ho, *Polym. Lett.* **9**, 491 (1971).
166. F. C. Schilling and A. E. Tonelli, *Macromolecules* **19**, 1337 (1986).
167. N. Binboga, D. Kisakürek, and B. M. Baysal, *J. Polym. Sci. Polym. Phys.* **23**, 925 (1985).
168. W. Wixwat, Y. Fu, and J. R. Stevens, *Polymer* **32**, 1181 (1991).
169. J. Loertscher and F. Weesner, *Determination of Hydroxyl Number in Polyols by Mid-Infrared Spectroscopy*, Nicolet FT-IR Application Note (AN-9146), Nicolet Instrument Corp.
170. Y. Luo, and co-workers, *Eur. Polym. J.* **24**, 607 (1988).
171. C. W. Amoss, R. W. Slack, and L. R. Taylor, *J. Liq. Chromat.* **10**, 583 (1987).
172. J. Van Dam, P. Daenens, and R. Busson, *J. Appl. Polym. Sci.* **50**, 2115 (1993).
173. B. Trathnigg, *J. Liq. Chromat.* **13**, 1731 (1990).
174. A. V. Gorshkov and co-workers, *J. Chromatogr.* **523**, 91 (1990).
175. K. Rissler, H.-P. Künzi, and H.-J. Grether, *J. Chromatogr.* **635**, 89 (1993).
176. M. Furukawa, N. Yoshitake, and T. Yokoyama, *J. Chromatogr.* **435**, 219 (1988).
177. R. Mieczkowski, *Eur. Polym. J.* **27**, 377 (1991).
178. R. L. Tabor, K. J. Hinze, R. D. J. Priester, and R. B. Turner, “The Compatibility of Water with Polyols,” *34th Annual Polyurethane Technical/Marketing Conference*, New Orleans, La., Oct. 21–24, 1992.
179. R. P. Lattimer and G. E. Hansen, *Macromolecules* **14**, 776 (1981).
180. C. F. Ijames and C. L. Wilkins, *J. Am. Chem. Soc.* **110**, 2687 (1988).
181. L. S. Sandell and D. A. I. Goring, *Macromolecules* **3**, 50 (1970).
182. S. J. Mumby, B. A. Smith, E. T. Samulski, Li-P. Yu, and M. A. Winnik, *Polymer* **27**, 1826 (1986).

STEVEN D. GAGNON
BASF Corporation

Related Articles

Propylene oxide; Urethane polymers; Surfactants