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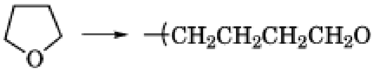
POLYETHERS, TETRAHYDROFURAN AND OXETANE POLYMERS

The polymerizations of tetrahydrofuran [1693-74-9] (THF) and of oxetane [503-30-0] (OX) are classic examples of cationic ring-opening polymerizations. Under ideal conditions, the polymerization of the five-membered tetrahydrofuran ring is a reversible equilibrium polymerization, whereas the polymerization of the strained four-membered oxetane ring is irreversible (1, 2).

The polymerization of tetrahydrofuran was first studied in the late 1930s (3, 4). In 1960, this work was summarized (4), and the literature on tetrahydrofuran polymers and polymerization has been growing ever since. Polytetrahydrofuran with hydroxy end groups has become a large-scale commercial product, used mainly as the flexible polyether segment in elastomeric polyurethanes and polyesters. It is commercially available under the trade names Terathane (Du Pont), Polymeg (QO Chemicals), and PolyTHF (BASF). Comprehensive review articles and monographs have been published (2, 5–8).

Tetrahydrofuran [1693-74-9] (tetramethylene oxide, 1,4-epoxybutane, oxolane) is a cyclic ether containing four methylene groups; the end groups are connected by an oxygen bridge. It has some internal strain resulting from repulsion of the eclipsed hydrogen atoms, and this small strain is sufficient to cause ring-opening polymerization under appropriate conditions.



The resulting linear polymer is called polytetrahydrofuran (PTHF), poly(tetramethylene oxide) (PTMO), poly(oxytetramethylene), or poly(tetramethylene ether) (PTME). It is filed under two CAS Registry Numbers, as poly(oxy-1,4-butanediyl) [26913-43-9] for the repeat-unit-based formula $(C_4H_8O)_n$ and under the monomer-based formula as tetrahydrofuran homopolymer [24979-97-3]. The most important difunctional derivative is the α,ω-dihydroxy-terminated polymer. It is called poly(tetramethylene ether) glycol (PTMEG, PTMG, PTG), poly(tetramethylene oxide) glycol, poly(oxytetramethylene) glycol (or diol), poly(1,4-oxybutylene) diol, or α,ω-dihydroxy poly(1,4-butanediyl), and is listed in *Chemical Abstracts* (CA) as α-hydro- ω-hydroxy poly(oxy-1,4-butanediyl [25190-06-1]. Poly(tetramethylene oxide) with other known end groups may be filed under still other names. For example, diamino poly(tetramethylene oxide) is indexed by CA as α-4-aminobutyl- ω-4-aminobutoxy poly(oxy-1,4-butanediyl) [27417-83-0].

The four-membered oxetane ring (trimethylene oxide [503-30-0]) has much higher ring strain, and irreversible ring-opening polymerization can occur rapidly to form polyoxetane [25722-06-9]:

Because of the high ring strain of the four-membered ring, even substituted oxetanes polymerize readily, in contrast to substituted tetrahydrofurans, which have little tendency to undergo ring-opening homopolymerization (5).

Polymers of tetrahydrofuran are relatively low melting, crystallizable materials, characterized by a low glass-transition temperature, T_g. It is possible to make THF polymers of almost any molecular weight. Above the melting point (ca 55°C), the high molecular weight homopolymer is a tough, somewhat elastomeric material. However, only the low molecular weight hydroxy-terminated oligomers have commercial applications. These materials, when incorporated as flexible soft segments into a polyurethane or polyester chain, impart useful elastomeric properties.

No oxetane polymer, either substituted or unsubstituted, has as of 1996 any commercial significance.

1. Tetrahydrofuran Polymers

1.1. Physical Properties

Some typical physical properties of high molecular weight poly(tetrahydrofuran) are summarized in Table 1. The type of end groups is not specified because in high molecular weight polymers, the effect of end groups becomes negligible. Tetrahydrofuran polymers crystallize readily near ambient temperature. Moderately high molecular weight polymers turn into waxy solids, whereas high molecular weight polymers display thermoplastic behavior. Typical mechanical properties of high molecular weight crystalline polytetrahydrofuran, as well as elastomeric properties of amorphous high molecular weight polymer, are also given in Table 1. Infrared and Raman spectroscopic studies have aided determination of the structure of polytetrahydrofuran (23–26), and nmr spectroscopy has been used in studies of the kinetics of polymerization and in end-group analysis (27–31). The principal absorptions and chemical shifts are well known, and many of them have been summarized (6).

The only THF polymers of commercial importance in the 1990s are diprimary low molecular weight poly(tetramethylene ether) glycols or their derivatives. These materials generally are waxy solids when crystallized and colorless viscous fluids when melted. Number-average molecular weights of the most widely used PTME glycols are 1000 and 2000. Polymer glycols are soluble in many polar organic solvents such as alcohols, esters, ketones, and aromatic hydrocarbons. The high molecular weight fractions are slightly soluble in aliphatic hydrocarbons; the low molecular weight fractions are slightly soluble in water. The polymeric glycols normally contain ca 300–1000 ppm of butylated hydroxytoluene (BHT) to prevent peroxide formation. They should be stored under nitrogen to prevent oxidation and moisture pickup, which could adversely affect later reactions and detract from the properties of the final product. The ether oxygens of PTHF greatly increase the solubility of PTHF in polar solvents as compared to hydrocarbon polymers. Solubility varies with molecular weight, but there are solvents, such as THF, that dissolve PTHF of all molecular weights. Lower molecular weight polymers dissolve more readily in more solvents and form less viscous solutions than higher molecular weight materials. Typical solvents for nearly all molecular weights include THF, toluene, methylene chloride, ethyl acetate, and other esters. Ethyl ether, alcohols, acetone, and water are solvents for lower molecular weight THF polymers. Nonsolvents are aliphatic hydrocarbons, eg, pentane, petroleum ether, and hexane. Narrow molecular weight distribution samples of PTHF can therefore be prepared by fractional precipitation from methanol–water (32), or solvent fractionation using a hydrocarbon (such as toluene or cyclohexane), methanol, and water (33–38). PTMEG of narrow molecular weight distribution can also be prepared by direct polymerization or depolymerization.

Intrinsic viscosity is often used to characterize tetrahydrofuran polymers. Intrinsic viscosities in a variety of solvents and Mark-Houwink constants for the equation $[\eta] = KM^{\alpha}$ have been determined for a wide variety

Table 1. Typical Properties of High Molecular Weight Polytetrahydrofuran

Property	Value	Reference
melting temperature, T_m, °C	43,58–60[a]	4,9,10
glass-transition temperature, T_g, °C	−84	4,9–12
density at 25°C, g/cm^3		
amorphous	0.975	9
crystalline	1.07–1.08	13
300% modulus, MPa[b,c]	1.6–14.3[d]	14
tensile strength, MPa[b,e]	29.0	15
elongation, %[e]	820	15
modulus of elasticity, MPa[b]	97.0	15
Shore A hardness	95	16–18
thermal expansion coefficient[f], K^{-1}	$(4–7) \times 10^{-4}$	19,20
compressibility[g], kPa^{-1}[b]	$(4–10) \times 10^{-7}$	19,20
internal pressure, P_i, MPa[b]	281	19,20
heat capacity, C_p at T_g, J/(mol·K)[h]		
rapidly cooled	19.4	21
annealed	15.8	21
coefficient of expansion[i], cm^3/(g·K)	7.3×10^{-4}	9
refractive index at 20°C	1.48	16–18
dielectric constant at 25°C	5.0	16–18
solubility parameter, δ^p, (J/cm^3)$^{1/2}$[j]	17.3–17.6	22
unit cell (oriented)		
monoclinic	$C_{2/c}$–$C^6{}_{2n}$	23,24
	$C_{2/c}$	25
a, nm	0.548–0.561	23–25
b, nm	0.873–0.892	23–25
c, nm	1.297–1.225	23–25
β, degrees	134.2–134.5	23–25

[a] The melting temperature most often reported for PTHF (see also Tables 2 and 3 for oligomeric glycols) is about 43°C, although these higher values have been observed after annealing.
[b] To convert MPa to psi, multiply by 145.
[c] Low to high molecular weight.
[d] Varies with the molecular weight.
[e] High molecular weight.
[f] $\alpha = (1/V)(\delta V/\delta T)_P$.
[g] $\beta = (1/V)(\delta V/\delta T)_T$.
[h] To convert J to cal, divide by 4.184.
[i] (dV/dT).
[j] To convert (J/cm^3)$^{1/2}$ to (cal/cm^3)$^{1/2}$, divide by 2.045.

of solvents (39–45),where $[\eta]$ is the intrinsic viscosity, M is molecular weight, and K and α are constants; many of the constants have been summarized and tabulated (6).

The phase structure of PTME has been studied by ^{13}C-nmr (46–48); the effects of chain entanglement (49, 50) and the PTME chain dimensions in model polyurethanes have been measured by small-angle neutron scattering using perdeuterated PTMEG (51, 52). Molecular interactions and cohesive energy densities of PTMEG have been determined (53), molecular orientation has been measured by x-ray diffraction (54), and molecular motion of PTMEG in solution and in melts has been studied by using coupled spin relaxation ^{13}C-nmr (47, 48, 55). Thermal properties (56, 57), dielectric relaxation (58), and pressure–volume–temperature data have been measured, as well as surface tension (59). Plastic deformation of PTMEG has been determined, the influence of molecular weight distribution on crystallinity (60) and on equilibrium melting points has been studied (61), and thermal properties of phthalate end-capped PTMEG have been measured (62). Thermal crystallization of polytetrahydrofuran chains in cross-linked networks and the influence of chain length and polydispersity on crystallization has been examined (63). Among other published reports are the segmental adsorption energies of PTMEG on silica and alumina surfaces (64) and measurements of the crystallite core size (65).

Number-average molecular weights, M_n, of THF polymers have been determined by standard techniques. For polymers of low molecular weight, M_n has been calculated primarily from data obtained by end-group analysis. Depending on the nature of the end group, the methods used include titration (39), nmr (6, 31, 66, 67), ir (39), uv (39, 68, 69), elemental analysis (38, 70), liquid scintillation counting of C-labeled end groups (71), and fluorescence spectroscopy (70). Ebulliometry and osmometry have also been used (39, 71, 72). For polymers with $M_n > 15,000$, osmometry has been used frequently, with toluene as the most common solvent (39, 45, 72–74).

Weight-average molecular weights of high molecular weight THF polymers have been determined by light scattering in a variety of solvents (42–44, 75).Refractive index increments, dn/dc, and refractive indexes, n_D, for typical solvents have been calculated (42–45, 75–78). Molecular weight distribution of THF polymers have been determined from$M_\mathrm{w}/M_\mathrm{n}$ ratios derived from light scattering and osmometry (78), turbidimetric titration (78), sedimentation velocity in a theta-solvent (42, 79), and gel-permeation chromatography (gpc) (80–83). THF is used as the preferred solvent for measurements of the molecular weight distribution by gpc. Usual detectors are differential refractometers or viscometers (84, 85). High pressure liquid chromatography (hplc) with gradient elution separates PTMEG into individual oligomer fractions and gives information about molecular weights and molecular weight distributions without requiring calibration standards (86).

1.2. Chemical Properties

The most important tetrahydrofuran polymers are the hydroxy-terminated polymers, that is, the α,ω-poly(tetramethylene ether) glycols used commercially to manufacture polyurethanes and polyesters (see Urethane polymers; Polyesters, thermoplastic).

1.2.1. End-Group Reactions

PTME glycols are normally the primary THF polymerization products, but THF polymers can be prepared with other end groups, either by direct polymerization of THF, or by chemical transformation of the hydroxy groups of the preformed polymer. For example, polymerization of THF in presence of carboxylic acid anhydrides results in PTME chains with the corresponding ester end groups, such as acetate, acrylate, or methacrylate groups (87–89). Such diesters can also be prepared by conventional esterification of the polymeric diols (90–93). Diols are also the starting materials for a number of other reported PTME derivatives, such as dialkylsulfonates (94), dithiols via disulfonates (95) or dihalides (96), alkyl ethers via alkylsulfates (97), and unsaturated alkenyl ethers such as diallyl ethers via alkenyl chlorides or sulfones (98, 99). Unsaturated ether end groups have also been introduced by catalytic vinylation of PTMEG with acetylene (100). Such unsaturated polyether macromers are claimed as comonomers for olefin polymerizations (99). Among other PTME derivatives are diglycidyl ethers (101), dialdehydes (102), and diacids (103, 104). Reaction of PTME diols with difunctional reagents results in coupling and formation of longer PTME chains with formaldehyde (105), short-chain diols (106), or carbonate links (107).

A number of different routes have been described for the preparation and manufacture of amine-terminated tetrahydrofuran polymers. The simplest route to PTMEG diamines appears to be esterification with *p*-aminobenzoic acid. Such a product is commercially available under the tradename Versalink (Air Products Corporation). Amines have also been prepared by reductive amination of the corresponding polymer glycols

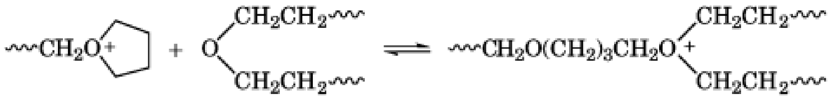
(108, 109) or diacetates (110). PTME diamines can be prepared by the addition of acrylonitrile to the hydroxy groups, followed by hydrogenation. The resulting diamines are bis(1,3-aminopropyl)poly(tetramethylene oxides) [72088-96-1]. Amine-terminated PTMEs have also been prepared from PTMEG disulfonates (94) and alkylene diamines (111). The resulting polymer is a mixture of primary, secondary, and tertiary amines. PTME diamines are claimed by reacting PTMEG with diisocyanates, such as methylene-bis(phenylene isocyanate) (MDI) or toluene diisocyanate (TDI), followed by hydrolysis (112). Finally, PTME diamines can also be prepared directly by polymerizing THF with triflic anhydride, $(CF_3SO_2)_2O$, and quenching the resulting dioxonium ions with hexamethylenetetramine. Exclusive formation of primary amines is claimed (113), but quenching even with an excess of ammonia results in a mixture of primary and secondary amines (114–116).A similar method has been used to put a variety of different end groups on PTME (116), for instance dimethylamino groups (117) or amino phenoxy groups (118). PTME with aminophenoxy end groups has also been prepared by hydrogenation of the corresponding nitro compounds (119). The basicity of different aromatic PTME diamines has been studied (120). In most cases these reactions do not result in complete amination of the PTME chain. Nevertheless, PTME diamines have been chain-extended with diisocyanates to give polyureas in fast reactions, or with common epoxy resins to give unusual elastomeric composites (121).

Commercially, the most important reaction of PTME glycols is the reaction with diisocyanates. Reaction with an excess of diisocyanate yields a prepolymer having isocyanate end groups, which can further react with short-chain diols or amines to give high molecular weight polyurethanes or polyurethane ureas (122, 123). Some of these prepolymers are also available commercially. Typical examples are Adiprene and Vibrathane from Uniroyal, Airthane from Air Products Corporation, Conathane from Conap, and Hyprene from Mitsui Toatsu. These prepolymers can be chain-extended (cured) to high molecular weight polyurethanes with aliphatic diols or to polyureas with diamines, or they can be cross-linked by reaction with moisture (124). High molecular weight, fully cured PTMEG polyurethanes are also commercially available as thermoplastic polyurethanes (TPUs). Examples are certain grades of Pellethane (Dow Chemical Corporation), Estane (BF Goodrich), and Texin (Bayer/Miles Corporation). Thermoplastic polyesters based on PTMEG are other types of important commercial elastomer. They are generally based on PTMEG soft segments and terephthalate hard segments with aliphatic short-chain diols, such as ethylene glycol, 1,4-butandiol, or cycloaliphatic diols (123–139). Examples of such polyester elastomers are Hytrel (Du Pont), Pelprene (Toyobo), Ecdel (Eastman Chemicals), Lomod (General Electric), and Arnitel (DSM). PTME is also the soft segment in an elastomeric polyamide, which contains nylon-type hard segments (Pebax, by Elf Atochem). The chemical and physical properties of thermoplastic elastomers have been reviewed (140).

1.2.2. Main-Chain Reactions

The backbone of PTME (PTHF) consists of a series of linear aliphatic ether sequences. Like monomeric ethers, it is subject to oxidation to hydroperoxides and subsequent thermal degradation. The addition of common antioxidants, such as amines or hindered phenols, inhibits these reactions and thereby imparts adequate stability to the polymer (141, 142). In vacuum in the absence of acidic impurities, temperatures of over 200°C are needed to degrade the polymer completely. THF polymers are also subject to degradation by ionizing radiation. They undergo both chain scission and cross-linking with evolution of hydrogen and traces of other gases (143). The ratio of main-chain scission to cross-linking was found to be 0.37. PTHF is quite stable to attack by bases but can be degraded by strong acids. Because the synthesis of PTHF often involves the use of strong acid initiators, it is important to remove these before storage.

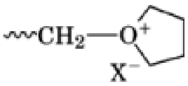
The PTHF chain is also subject to attack and reaction during the polymerization process. These are reactions of the active end group of the growing polymer chain in the polymerizing mixture and an oxygen atom in the main chain. The nucleophilicity of the oxygen atom decreases when it is transformed from a monomeric THF oxygen to a polymeric ether oxygen, but detectable reactivity remains. These polymeric oxygen atoms can react with the THF oxonium ion to produce a branched ion. Further reaction with THF can occur at any of the three carbon atoms α to the acyclic polymeric oxonium ion. The result is a randomization of the molecular weight distribution of PTHF. This process ensures a polydispersity M_w/M_n of about 2.0 for high conversion polymerizations. Under certain conditions, lower polydispersity may be achieved by limiting polymerization to low conversions or, especially for low molecular weight (500–3000) materials, by post-treatments designed to remove short-chain fractions (86). Depropagation with expulsion of monomer occurs on intramolecular reaction of the penultimate oxygen atom with the acyclic carbon atom α to the oxonium ion. If the oxygen atom that reacts is a few monomer units removed from the active end, intramolecular reaction with polymer oxygen atom results in a macrocyclic oxonium ion (144). Further reaction with THF may lead to the formation of macrocycles. The proportions of cyclic oligomers depend on the initiator and the polymerization conditions. The concentration of the macrocycles generally is less than 1% of the total product formed at 25°C.



1.2.3. Polymerization

The THF ring contains an oxygen atom with two unshared pairs of electrons. THF is therefore a nucleophilic monomer having little steric interference toward potential electron acceptors. The free energy of polymerization is only about -4.2 kJ/mol (-1 kcal/mol) at ambient temperatures. Consequently, a polymerization characterized by modest rates and heats of polymerization is not surprising. Simply substituted tetrahydrofurans, in general, do not polymerize, although oligomers have been reported for monomethyl derivatives (6). Copolymerization of these substituted THFs is possible and has been realized. Purity of reagents, dryness of apparatus, choice of initiator, atmosphere, monomer concentration, and solvent greatly influence the course of the polymerization.

Cationic ring-opening polymerization is the only polymerization mechanism available to tetrahydrofuran (5, 6, 8). The propagating species is a tertiary oxonium ion associated with a negatively charged counterion:



For continuing polymerization to occur, the ion pair must display reasonable stability. Strongly nucleophilic anions, such as Cl^-, are not suitable, because the ion pair is unstable with respect to THF and the alkyl halide. A counterion of relatively low nucleophilicity is required to achieve a controlled and continuing polymerization. Examples of anions of suitably low nucleophilicity are complex ions such as $SbF^-{}_6$, $AsF^-{}_6$, $PF^-{}_6$, $SbCl^-{}_6$, $BF^-{}_4$, or other anions that can reversibly collapse to a covalent ester species: $CF^3SO^-{}_3$, $FSO^-{}_3$, and $ClO^-{}_4$. In order to achieve reproducible and predictable results in the cationic polymerization of THF, it is necessary to use pure, dry reagents and dry conditions. High vacuum techniques are required for theoretical studies. Careful work in an inert atmosphere, such as dry nitrogen, is satisfactory for many purposes, including commercial synthesis.

The polymerization of THF is an equilibrium polymerization. It fits the equation that relates the enthalpy of polymerization, ΔH_p, and entropy of polymerization at 1 M, $\Delta S^0{}_p$, to the equilibrium monomer concentration, $[M]_e$, as a function of the absolute temperature, T, where R is the gas constant (6, 145).

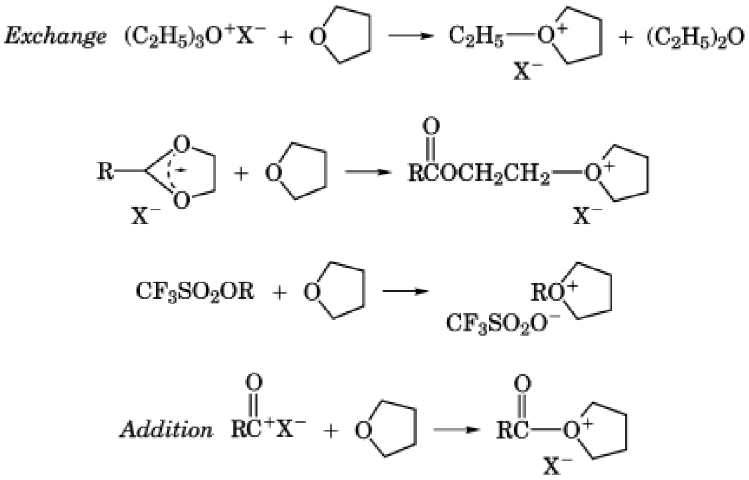
$$\ln [M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p^0}{R} \qquad (1)$$

Thus, to obtain significant conversions to polymer, it is essential both to choose the polymerization temperature carefully and to limit the amount of solvent. The polymerization of bulk THF has a relatively low ceiling temperature, T_c, of $83 \pm 2°C$. At T_c or above, no polymer is formed. At temperatures belowT_c, there is an equilibrium monomer concentration below which no further polymerization occurs. As indicated by equation 1, the conversion to PTHF at any given temperature depends on the monomer concentration and is independent of polymer concentration. Thus the use of a solvent (inert diluent) reduces the conversion to polymer at that temperature. When a solvent is used, the M_e characteristic of a given temperature and the monomer–solvent mixture can be achieved only at the expense of polymer conversion (146–148). The T_c of a system diluted by solvent is substantially lower than that observed for bulk monomer and drops in direct proportion to the amount of solvent employed. For example, in THF polymerization carried to equilibrium conversion at 30°C, polymerization in bulk monomer gives 72% polymer, whereas polymerization in a solution containing THF/CH_2Cl_2 in a 5/3 ratio by volume gives only 27% polymer. Largely because of these considerations, THF polymerizations are generally carried out near or below room temperature, especially if an inert diluent is used. Below ca $-20°C$, the rate of polymerization of THF becomes prohibitively slow unless the initiator concentration is raised substantially. The enthalpy and entropy data on THF polymerization have been obtained from data relating M_e with temperature. Values reported for the enthalpy of polymerization fall in the range of -18.0 to -23.4 kJ/mol (-4.3 to -5.6 kcal/mol); for the entropy of polymerization, -71 to -87 J/(mol·K) (-17 to -21 cal/(mol·K)) (13). The values are somewhat dependent on the counterion and solvent. The reasons for these differences are related to structural factors and to solvation (149).

It is possible to balance all of these thermodynamic, kinetic, and mechanistic considerations and to prepare well-defined PTHF. Living oxonium ion polymerizations, ie, polymerizations that are free from transfer and termination reactions, are possible. PTHF of any desired molecular weight and with controlled end groups can be prepared.

1.2.3.1. Initiation. The basic requirement for polymerization is that a THF tertiary oxonium ion must be formed by some mechanism. If a suitable counterion is present, polymerization follows. The requisite tertiary oxonium ion can be formed in any of several ways.

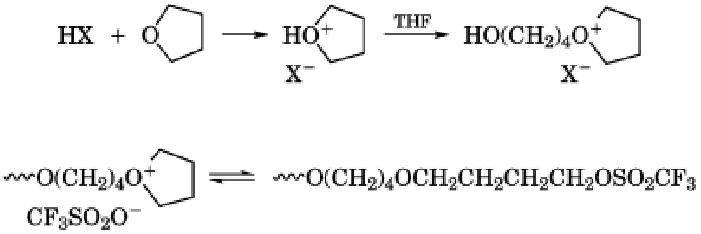
Direct alkylation or acylation of the oxygen of THF by exchange or addition occurs with the use of trialkyloxonium salts, carboxonium salts, super-acid esters or anhydrides, acylium salts, and sometimes carbenium salts.



The first three equations illustrate exchange reactions in which an alkyl group is exchanged from the initiator to the THF molecule and the last equation illustrates the addition mechanism.

Often the requisite THF oxonium ion is generated *in situ* by using a combination of reagents based on the Meerwein syntheses of trialkyl oxonium salts (150). These combinations include epichlorohydrin or a reactive halide with a Lewis acid, a reactive halide with a metal salt, or sometimes just a Lewis acid alone. The epoxide portion is often referred to as a promoter.

A protonic acid derived from a suitable or desired anion would seem to be an ideal initiator, especially if the desired end product is a poly(tetramethylene oxide) glycol. There are, however, a number of drawbacks. The protonated THF, ie, the secondary oxonium ion, is less reactive than the propagating tertiary oxonium ion. This results in a slow initiation process. Also, in the case of several of the readily available acids, eg, CF_3SO_3H, FSO_3H, $HClO_4$, and H_2SO_4, there is an ion–ester equilibrium with the counterion, which further reduces the concentration of the much more reactive ionic species. The reaction is illustrated for $CF_3SO^-_3$ counterion as follows:

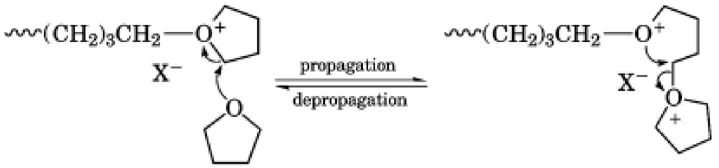


The reverse reaction (ion formation) can occur in two ways: internally, by attack of the penultimate polymer oxygen atom, or externally, by attack of a monomer oxygen atom (chain growth). The external process is about 10 times slower than the internal process in bulk THF (1). Since ion formation is a slow process compared to ion chain growth, chain growth by external attack of monomer on covalent ester makes a negligible contribution to the polymerization process.

The hydroxyl end group is a reactive functional group, the interaction of which with the propagating tertiary oxonium ion can lead to chain coupling and a rapid increase of molecular weight. In these cases chain length and molecular weight are not simple functions of initiator concentration. Covalent coupling is more important with nonhydrolyzable anions, such as $CF_3SO^-_3$, than with hydrolyzable anions, such as FSO^-_3 or $ClSO^-_3$. Long reaction time with the latter anions results in equilibration closer to the predicted molecular weight (1, 6).

Protonic initiation is also the end result of a large number of other initiating systems. Strong acids are generated *in situ* by a variety of different chemistries (6). These include initiation by carbenium ions, eg, trityl or diazonium salts (151); by an electric current in the presence of a quartenary ammonium salt (152); by halonium, triaryl sulfonium, and triaryl selenonium salts with uv irradiation (153–155); by mercuric perchlorate, nitrosyl hexafluorophosphate, or nitryl hexafluorophosphate (156); and by interaction of free radicals with certain metal salts (157). Reports of "new" initiating systems are often the result of such secondary reactions. Other reports suggest standard polymerization processes with perhaps novel anions. These latter include $(Tf)_4Al^-$ (158); heteropoly acids, eg, tungstophosphate anion (159, 160); transition-metal-based systems, eg, Pt (161) or rare earths (162); and numerous systems based on triflic acid (158, 163–166). Coordination polymerization of THF may be in a different class (167).

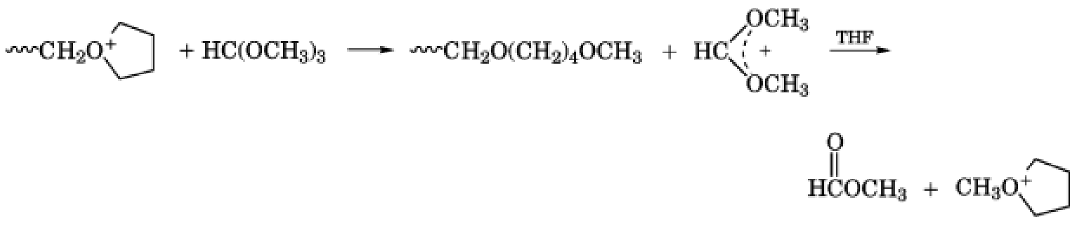
1.2.3.2. Propagation. The tertiary THF oxonium ion undergoes propagation by an S_N2 mechanism as a result of a bimolecular collision with THF monomer. Only collisions at the ring α-carbon atoms of the oxonium ion result in chain growth. Depropagation results from an intramolecular nucleophilic attack of the penultimate chain oxygen atom at the exocyclic α-carbon atom of the oxonium ion, followed by expulsion of a monomer molecule.



Studies have shown that, in marked contrast to carbanionic polymerization, the reactivity of the free oxonium ion is of the same order of magnitude as that of its ion pair with the counterion (6). On the other hand, in the case of those counterions that can undergo an equilibrium with the corresponding covalent ester species, the reactivity of the ionic species is so much greater than that of the ester that chain growth by external attack of monomer on covalent ester makes a negligible contribution to the polymerization process. The relative concentration of the two species depends on the dielectric constant of the polymerization medium, ie, on the choice of solvent.

1.2.3.3. Termination. THF can be polymerized in the virtual absence of termination and transfer reactions. Under these conditions a living polymerization results and the number-average molecular weight of the polymer produced can be calculated from the number of active sites introduced and the amount of polymer produced at equilibrium. For many initiators, the number of active sites corresponds directly to the number of moles of initiator used. In other cases, a number of methods are available that allows analytical determination of the number of active sites (6). In order to eliminate all termination and transfer reactions, it is necessary to carry out the polymerization while carefully avoiding any adventitious impurities such as air or water. This is generally most easily accomplished by working under high vacuum. In living polymerizations, the head group of the polymer is generally determined by the initiator, whereas the end group is a function of the method of termination chosen. Any strong nucleophile can be used for chain termination. For example, water leads to hydroxyl end groups; ammonia gives amine end groups. Some counterions, such as the halides, are strong enough nucleophiles to prevent polymerization. They can be used to terminate a polymerization by addition at the desired time. Some counterions, such as BF_4^- or $SbCl_6^-$, are weak nucleophiles and their use results in slow chain termination during the course of the polymerization, especially if used at room temperature or above. In the case of $SbCl_6^-$, the $SbCl_5$ that forms upon termination can itself initiate a new active center. The net result is one of chain transfer. Termination by some nucleophiles allows the determination of the number of active sites that were present at the time of termination. Thus, the use of sodium phenoxide is followed by a uv analysis of phenoxide end groups (69), and triphenylphosphine permits analysis with ^{31}P-nmr (31, 66). Mercaptans or sulfides are also effective terminating agents. If a polymerizable cyclic sulfide is employed, a block polymer of PTHF and the cyclic sulfide results (168). No further polymerization of the THF occurs. The cyclic ether polymerization is effectively terminated because sulfur is a much stronger nucleophile than oxygen.

1.2.3.4. Chain Transfer. A number of materials act as true transfer agents in THF polymerization; notable examples are dialkyl ethers and orthoformates. In low concentrations, water behaves as a transfer agent, and hydroxyl end groups are produced. The oxygen of dialkyl ethers are rather poor nucleophiles compared to THF and are therefore not very effective as transfer agents. On the other hand, orthoformates are effective transfer agents and can be used to produce alkoxy-ended PTHFs of any desired molecular weight (169).



Acetic and other acid anhydrides were at first thought to behave as transfer agents. Acetate end groups and low molecular weight polymers can be obtained, but proton initiation and rather long reaction times are required, and suggest a more complex process (1, 170, 171). Transfer to polymer ether oxygen does occur. Depropagation is an example. Back-biting and formation of cyclic oligomers exemplify intramolecular transfer to polymer ether oxygen. The analogous intermolecular reaction can also occur.

1.2.3.5. Kinetics. Details of the kinetics of polymerization of THF have been reviewed (6, 148). There are five main conclusions. (*1*) Macroions are the principal propagating species in all systems. (*2*) With stable complex anions, such as $\mathrm{PF^-}_6$, $\mathrm{SbF^-}_6$, and $\mathrm{AsF^-}_6$, the polymerization is living under normal polymerization conditions. When initiation is fast, kinetics of polymerizations in bulk can be closely approximated by equation **2**, wherek_{p} is the specific rate constant of propagation; t is time; $[I]_0$ is the initiator concentration at $t = 0$; and $[M]_0$, $[M]_e$, and $[M]_t$ are the monomer concentrations at $t = 0$, at equilibrium, and at time t, respectively.

$$k_p t = \left[\frac{1}{[I]_0}\right]\left[\ln\frac{[M]_0 - [M]_e}{[M]_t - [M]_e}\right] \qquad (2)$$

The rate of ion propagation, k_{ip}, is independent of the counterion and has been found to be about 46×10^{-2} in all cases for $\mathrm{CF_3SO^-}_3$, $\mathrm{AsF^-}_6$, $\mathrm{SbF^-}_6$, $\mathrm{SbCl^-}_6$, $\mathrm{PF^-}_6$, and $\mathrm{BF^-}_4$ counterions. Conditions were the same for all counterions, ie, 8.0 M of monomer in $\mathrm{CCl_4}$ solvent and 25°C polymerization temperature. With less stable counterions such as $\mathrm{SbCl^-}_6$ and $\mathrm{BF^-}_4$ at most temperatures, the influence of transfer and termination reactions must be taken into account (71).

(*3*) PTHF does not behave ideally in solution and the equilibrium monomer concentration varies with both solvent and temperature. Kinetics of THF polymerizations fit equation 2, provided that the equilibrium monomer concentration is determined for the conditions used.

(*4*) For counterions that can form esters with the growing oxonium ions, the kinetics of propagation are dominated by the rate of propagation of the macroions. For any given counterion, the proportion of macroions compared to macroesters varies with the solvent–monomer mixture and must be determined independently before a kinetic analysis can be made. The macroesters can be considered to be in a state of temporary termination. When the proportion of macroions is known and initiation is sufficiently fast, equation 2 is satisfied.

(*5*) When the initiation is slow, the number of growing centers as a function of time must be determined in a separate step before the kinetic analysis can be carried out. Several different methods are available (6, 31, 66, 69–71).

1.3. Copolymerization

THF copolymerizations are of interest for several reasons. Random copolymerization provides a way of reducing the melting temperature of THF polymers to room temperature and below. The crystallization tendency of THF segments in products is thereby reduced and mechanical properties of the products are often improved. Copolymers also provide a way of introducing unsaturated units for vulcanization purposes (172) or active groups such as -$\mathrm{CH_2N_2}$, -$\mathrm{NO_2}$, and -$\mathrm{CH_2OCH_2C(NO_2)_2CH_3}$ units for energetic polymers (173).

Many copolymerization studies have been made. A detailed discussion and critique of the results has been published (1) and the breadth of the comonomers studied has been summarized (6). Among the comonomers used are oxiranes, oxetanes, 1,3-dioxolane, substituted tetrahydrofurans, 1,4-dioxane, ϵ-caprolactone, and cyclopentadiene. Random copolymerization with cyclic sulfides and most vinyl compounds does not occur. Some monomers that do not homopolymerize do copolymerize. In addition to chemical functionality, relative basicity, ring strain, and ring size all seem to be important factors in determining the reactivity of different monomers in copolymerizations. Many attempts have been made to apply the usual copolymer equation (174) and associated methods of analyses (175, 176) to determine relative reactivity ratios for the comonomers. Numbers are readily obtained, but often they are meaningless because some of the assumptions on which the derivation of the equation is based are not obeyed, especially at low concentrations of THF and polymerization temperatures near room temperature. In particular, THF polymerizations have a significant rate of reversibility, which markedly affects the composition of the polymer obtained and sometimes makes THF appear less reactive than it is. Also, THF oxonium ion copolymerizations are sometimes complicated by the possibility of interconversion of active species without propagation, by redistribution of molecular weights of initially formed copolymers, and by significant effects of the penultimate or even antipenultimate monomer unit in copolymer chains. Other theoretical treatments have been published (177–179) to account for some of these factors, especially reversibility, but the solutions are more complex, and more constants need to be determined or assigned than for the original copolymer equation.

1.3.0.6. Block, Graft, and Star Copolymers. A host of copolymers of these types have been prepared. They include block copolymers from ϵ-caprolactam and PTMEG as well as block copolymers from PTHF and other cationically polymerizable heterocycles, including 3,3-bis(chloromethyl)oxetane (180), 7-oxabicyclo[2.2.1]heptane, 1,3-dioxolane, pivalolactone, and ethylene oxide. Block copolymers from polystyrene and PTHF have been prepared, including AB, ABA, and $(AB)_n$ copolymers, where A and B can be either polystyrene or PTHF (6, 180–183). One-, two-, three-, and four-arm stars have been prepared with PTHF arms (184). Graft copolymers with PTHF branches have been made from a variety of hydrocarbon backbones (11, 185–188),and graft copolymers with poly(vinyl chloride) branches have been prepared from PTHF backbones (118). The properties determined for some of these copolymers are sometimes unusual, but as of 1996 none had achieved commercial importance.

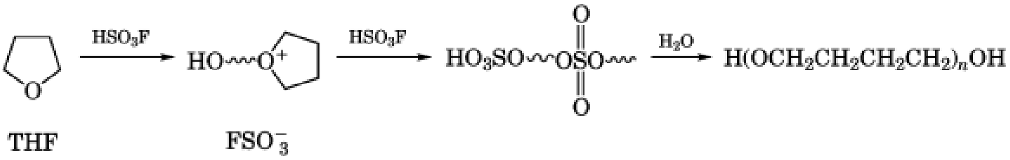
In addition to the primary application of PTMEG in polyurethanes, polyureas, and polyesters, a considerable number of reports of other block and graft polymers highlighting PTME units have appeared. Methods have been developed that allow the conversion of a cationically polymerizing system to an anionic one or vice versa (6, 182).

Cationic polymerization followed by carefully defined free-radical polymerization has also been designed for preparing novel block polymers. The latter often involves the preparation of PTHF containing an azo or peroxy linkage, which is then used to initiate free-radical polymerization of standard vinyl or acrylate monomers (189–191). The preparation of PTHF block and graft polymers has been reviewed (192, 193). Thus, THF has been grafted from cellulose derivatives (194), from silane polymers (195), from ethylene propylene diene monomer (EPDM) rubber (185, 196), from butyl rubber (185, 197), and from poly(phenylmethylsilylene) (198). Newer block systems that have been prepared include blocks with azetidine (199), with *p*-chlorostyrene (200), with oxazolines (201, 202), with polyether sulfones (203), and with methyl methacrylate (MMA) and styrene (204). Availability of various block and graft THF polymers has also led to their use as compatibilizers in blending studies (205).

1.4. Manufacture and Processing

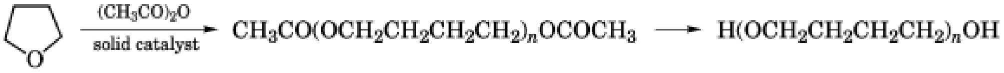
THF can be polymerized by many strongly acidic catalysts, but not all of them produce the required bifunctional polyether glycol with a minimum of by-products. Several large-scale commercial polymerization processes are based on fluorosulfonic acid, $HFSO_3$, catalysis, which meets all these requirements. The catalyst is added to

THF at low temperatures and an exothermic polymerization occurs readily. The polymerization products are poly(tetramethylene ether) chains with sulfate ester groups (8).



In a subsequent product work-up, the sulfates are hydrolyzed and the acid is removed by water extraction (206, 207). In the extraction step, most water-soluble short polyether chains are also removed, and the molecular weight distribution becomes narrower, from close to the theoretical M_w/M_n value of 2 to 1.6 or less, depending on the particular molecular weight (86, 208). The lower molecular weight grades become narrower than the higher molecular weight grades because they contain a larger concentration of short, water-soluble chains which are partly removed in this step. After neutralization and vacuum drying, the product is filtered hot and loaded into drums or tank trucks under nitrogen.

Many other polymerization processes have been patented, but only some of them appear to be developed or under development in 1996. One large-scale process uses an acid montmorrillonite clay and acetic anhydride (209); another process uses strong perfluorosulfonic acid resin catalysts (170, 210). The polymerization product in these processes is a poly(tetramethylene ether) with acetate end groups, which have to be removed by alkaline hydrolysis (211) or hydrogenolysis (212). If necessary, the product is then neutralized, eg, with phosphoric acid (213), and the salts removed by filtration. Instead of montmorrillonite clay, other acidic catalysts can be used, such as Fuller's earth or zeolites (214–216).



The primary polymerization product in these processes has a relatively wide molecular weight distribution, and a separate step is often used to narrow the polydispersity. Such a narrowing step may consist of high vacuum stripping to remove volatile polymer chains, often followed by a solvent fractionation step (35, 36), sometimes a solvent fractionation step alone (37, 38), or a fractional precipitation from organic solvent (32). The molecular weight distribution can also be narrowed by depolymerization at elevated temperatures in the presence of a depolymerization catalyst (217–220).

A more recent catalyst system introduced by Asahi Chemical Industries (221) involves the use of heteropoly acids (HPA) such as phosphomolybdic acid or phosphotungstic acids (222, 223). These catalysts appear to work in the presence of small amounts of water (224) and lead directly to the polymeric glycols (59). In the presence of alcohols instead of water, the products are PTMEG monoalkyl ethers (225). The process is carried out by mixing two liquid phases: a THF phase and an aqueous heteropoly acid phase. Control of water concentration is critical for control of molecular weight and conversion (226). Asahi is operating a small PTMEG plant based on this technology.

A number of papers and patents describe polymerization processes to poly(tetramethylene ether) glycols having a narrow molecular weight distribution (M_w/M_n = 1.2–1.4). In principle, this can be achieved by having all chains grow quickly at one time, either by high temperature initiation (33) followed by low temperature propagation, or by a temperature-cycling process, which can give product of narrow distribution (227). On a larger scale, temperature-cycling processes to narrow distribution PTMEG can be carried out with advantage in pipeline reactors. PTMEG of narrow molecular weight distribution can also be obtained by rapid initiation with an active catalyst system, such as fluorosulfonic acid/acetic anhydride or perchloric acid/acetic anhydride

(228–230). If such polymerizations are quenched after short polymerization times, products with narrower than normal distributions can be obtained. Rapid initiation and chain growth can also be achieved by initiation with fluorosulfonic acid anhydride $(FSO_2)_2O$ or trifluoromethane sulfonic anhydride $(CF_3SO_2)_2O$ (231, 232). In these cases, chain growth occurs at both chain ends simultaneously, and short polymerization times can lead to products having narrow molecular weight distribution.

Many patents claim PTMEG of narrow polydispersity by using special catalyst blends or polymerization conditions (233–239). Whereas some of these processes may lead to a certain narrowing of the polydispersity, others give product with marginal narrowing. Polyurethanes made from PTMEG of narrow molecular weight distribution are claimed to have some improved properties, but other properties are adversely affected (240).

Other THF polymerization processes that have been disclosed in papers and patents, but which do not appear to be in commercial use in the 1990s, include catalysis by boron trifluoride complexes in combination with other cocatalysts (241–245), modified montmorrillonite clay (246–248) or modified metal oxide composites (249), rare-earth catalysts (250), triflate salts (164), and sulfuric acid or fuming sulfuric acid with cocatalysts (237, 251–255).

A number of patents claim THF copolymers by direct copolymerization of THF and other cyclic ethers (168, 256–259). Although samples of THF copolyethers are available occasionally, none had any industrial importance as of 1996.

1.5. Storage and Handling

PTMEG is normally available in 20-kg steel pails, 200-kg steel drums, and in stainless steel tank cars or tank trucks, which are insulated and equipped with heating coils. Shipping temperature for tank trucks is normally 80°C (175°F) to maintain the product in liquid state. If subjected to low temperatures, it has to be reheated and melted, eg, with low pressure steam (350 kPa ≈ 50 psig). Product transfer from tank trucks requires special precaution; the procedure has been described in detail in product bulletins (260). Drums should be stored in a warm room to prevent freezing. Frozen drums can be thawed by loosening the bung and storing for 1 day at 70°C (160°F). The content should be mixed thoroughly before use, because fractionation and stratification by molecular weight may occur during freezing. Centrifugal or gear pumps, and butyl rubber- or neoprene-lined hose or stainless steel flexible hose, are used for product transfer. All piping should be heat-traced (260).

PTMEG is a polymeric ether susceptible to both thermal and oxidative degradation. It usually contains 300–1000 ppm of an antioxidant such as 2,6-di-*tert*-butyl-4-hydroxytoluene (BHT) to prevent oxidation under normal storage and handling conditions. Thermal decomposition in an inert atmosphere starts at 210–220°C (410–430°F) with the formation of highly flammable THF. In the presence of acidic impurities, the decomposition temperature can be significantly reduced; contact with acids should therefore be avoided, and storage temperatures have to be controlled to prevent decomposition to THF (261).

Oxidative degradation occurs when PTMEG is heated in contact with air (262). Under these conditions, decomposition can start at temperatures as low as 100°C, along with evolution of THF and formation of aldehydes and ketones. Degradation occurs particularly readily when PTMEG is in contact with high surface area materials, eg, pipe insulation. In such cases the heat of oxidative degradation is normally sufficient to sustain the degradation reaction, and spontaneous combustion can occur. Contaminated fibrous insulation should therefore immediately be cooled and discarded. PTMEG is also hygroscopic and should be stored in completely enclosed tanks under a dry nitrogen blanket. Mild steel tanks, tanks lined with phenolic resin, or stainless steel (type 304) tanks are usually satisfactory. The storage tank must be provided with external or internal heating to maintain a temperature of about 50°C. The storage tanks should be pressure-tested and equipped with a vacuum pressure-relief conservation vent and an emergency vent. Vents should be heat-traced and insulated to prevent plugging by solidified polymer. New equipment should be cleaned and dried carefully to avoid contamination. If necessary, PTMEG can be dried, eg, by removing water by azeotropic distillation with toluene, by heating (120°C) under reduced pressure (263), or by sparging the hot polyglycol with dry nitrogen.

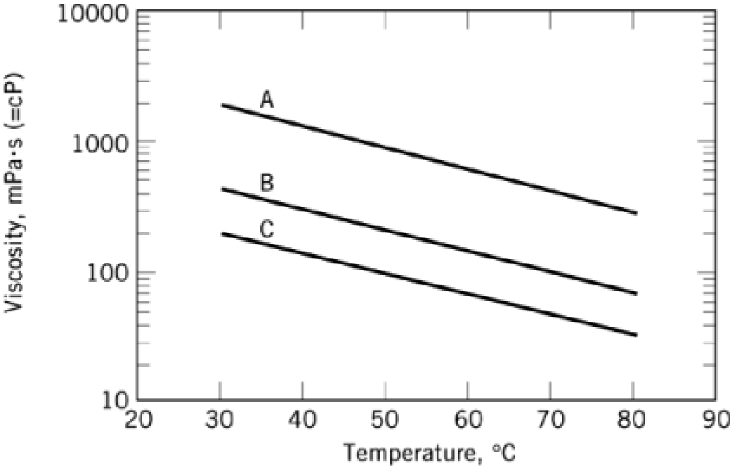


Fig. 1. Viscosities (Brookfield) of poly(tetramethylene ether) glycol of the following molecular weights: A, 2000 (Terathane 2000); B, 1000 (Terathane 1000); and C, 650 (Terathane 650).

PTMEG is not regulated as a hazardous material by the U.S. Department of Transportation. Liquid spills may be absorbed with a material such as vermiculite and handled as nontoxic waste. Larger spills, if fluid, may be pumped into drums or, if solid, shoveled into drums for later recovery or disposal by burning under controlled conditions. PTMEG has a flash point above 150°C, and little fire hazard exists under normal conditions. When handled above 150°C, particularly when in contact with high surface area material, ignition may occur by flames, sparks, or hot surfaces. PTMEG fires can be extinguished with water spray, foam, dry chemical, or CO_2 extinguishers (263).

1.6. Specifications, Standards, and Analysis

The standard commercial molecular weight grades for polytetramethylene ether glycol are 650, 1000, 1800, and 2000, but other molecular weight grades, such as 1400 and 2900, are available for special applications. Commercial poly(tetramethylene ether) glycols are waxy, white solids that melt over a temperature range near room temperature to clear, colorless, viscous liquids. The viscosities of PTMEG 650, 1000, and 2000, up to a temperature of 80°C, are shown in Figure 1, and the corresponding densities in Figure 2.

There are no generally accepted specifications; manufacturers set their own specifications for hydroxyl number range, melt viscosity, water content, etc. Typical properties of Du Pont Terathane PTMEG are listed in Table 2, and selected thermal properties are given in Table 3 (260). For all grades, water content is <0.015 wt %; ash, <0.001 wt %; iron, <1 ppm; peroxide, <5 ppm as H_2O_2; and flash point TOC is >163°C.

1.6.1. *Analytical and Test Methods*

General analytical procedures are applicable in most cases, although a number of specific test methods have been developed for the analysis of polyether glycols. One of the most important tests is the determination of the hydroxyl number, ie, the number of milligrams of KOH (formula weight $= 56.1$) equivalent to the hydroxyl content of 1 g of the polymer diol sample (264). Because all the PTME chains are strictly difunctional, the number-average molecular weight is calculated from the hydroxyl number according to the following relation:

$$\text{molecular weight} = 56.1 \times 1000 \times 2/\text{hydroxyl number}$$

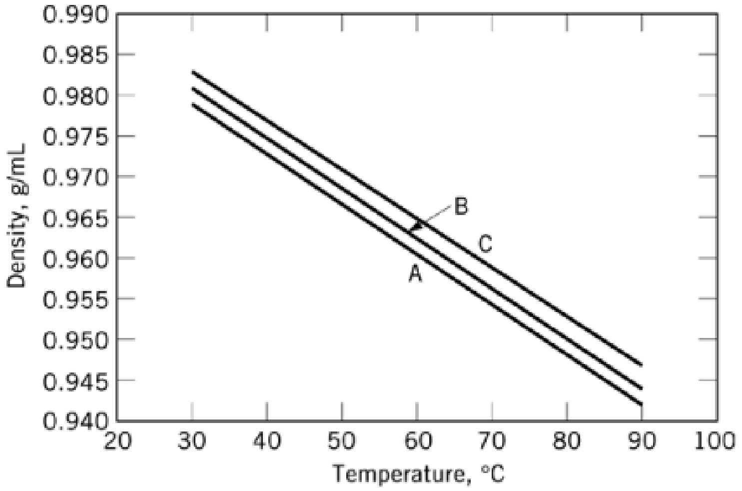


Fig. 2. Densities of poly(tetramethylene ether) glycols of the following molecular weights: A, 2000 (Terathane 2000); B, 1000 (Terathane 1000); and C, 650 (Terathane 650).

Table 2. Properties[a] of Terathane Polyether Glycols

Property	Terathane 650	Terathane 1000	Terathane 1400	Terathane 2000
molecular weight	625–675	950–1050	1350–1450	1900–2100
hydroxyl number	166–180	107–118	77–83	53–59
viscosity at 40°C, mPa·s (= cP)	100–200	260–320	525–600	950–1450
density at 40°C, g/mL	0.978	0.974	0.973	0.972
melting point, °C	11–19	25–33	27–35	28–40
color, APHA[b]	<20	<10	<10	<10
refractive index, n_D^{25}	1.462	1.463–1.465	1.464	1.464
alkalinity number, meq·KOH/kg × 30	−2.0 to 1.0	−2.0 to 1.0	−2.0 to 1.0	−3.0 to 1.0
heat of fusion, kJ/kg[c]		90.4		∼109

[a] Property values = specifications unless otherwise noted.
[b] Color specification is <40 for Terathane 1000, 1400, and 2000; <50 for Terathane 650.
[c] To convert kJ to kcal, divide by 4.184.

Hydroxyl number and molecular weight are normally determined by end-group analysis, by titration with acetic, phthalic, or pyromellitic anhydride (264). For lower molecular weights (higher hydroxyl numbers), ^{19}F- and ^{13}C-nmr methods have been developed (265). Molecular weight determinations based on colligative properties, eg, vapor-phase osmometry, or on molecular size, eg, size exclusion chromatography, are less useful because they do not measure the hydroxyl content.

Other important tests are for acid and alkalinity number and for water content (266), because water content and alkalinity of the polyether glycol can influence the reaction with isocyanates. The standard ASTM test for acid and alkalinity number, ASTM D4662 (267), is not sensitive enough for the low acidity and alkalinity numbers of PTMEG, and special methods have been developed. A useful alkalinity number (AN) has been defined as milliequivalents KOH per 30 kg of PTMEG, as titrated in methanol solution with 0.005 *N* HCl (268). Other useful nonstandard tests are for heavy metals, sulfated ash, and peroxide. The peroxides formed initially in oxidations are quickly transformed into carbonyl groups, which are detectable by infrared

Table 3. Selected Thermal Properties of Poly(Tetramethylene Ether) Glycols[a]

Property	Value
heat of fusion, kJ/kg[b]	90.4
	109[c]
heat of combustion, MJ/kg[b]	35
	35[c]
thermal conductivity, W/(m^2·K)	
at 20°C	0.62
at 60°C	0.57
specific heat, J/(g·K)[b]	0.52
	0.55[d]
	0.50[c]
enthalpy of combustion[e], MJ/(kg·mol)	−29.8

[a] Molecular weight = 100 unless otherwise noted; Ref. 260.
[b] To convert J to cal, divide by 4.184.
[c] Molecular weight = 2000.
[d] Molecular weight = 650.
[e] Liquid at 25°C to all gases, calculated.

spectroscopy. On oxidation, a small C—O peak develops at 1726 cm^{-1} and can be detected in thick (0.5-mm) films. A relative ratio of this peak against an internal standard peak at 2075 C—O is sometimes defined as the carbonyl ratio.

APHA color (269) is usually one of the specifications of PTMEG, sometimes viscosity is another (270). Melt viscosity at 40°C is often used as a rough measure of the molecular weight distribution within a narrow molecular weight range. Sometimes an empirical molecular weight ratio, MWR = M'_v/M_n, is used, where M'_v is a melt-viscosity-average molecular weight defined by the equation $\overline{M}'_v$ = antilog, (0.493 log $\eta + 3.5576$, where η is the viscosity in Pa·s at 40°C (240). Commercially available PTMEG-grades usually have a molecular weight ratio in the range of 2.0–2.1. The molecular weight distribution is generally characterized by the dispersity index or polydispersity MWD = M_w/M_n. This ratio is lower than the ratio M'_v/M_n. For a commercial-grade PTMEG 1000, it is approximately 1.6. The molecular weight distribution can be determined by size exclusion/gel-permeation chromatography (gpc).

The normally used polystyrene or poly(methyl methacrylate) standards may give erroneous gpc results, and primary PTMEG standards have to be used for calibration. Such primary standards can be defined by high performance liquid chromatography (hplc), which effectively separates every molecular weight fraction. Molecular weight and molecular weight distribution can be calculated directly from such a chromatogram, and no calibration is required (86). A bargraph of Terathane 1000, based on an hplc chromatogram, is shown in Figure 3.

The most important general test methods are issued as ASTM Test Methods and are periodically updated by the Polyurethane Raw Materials Analysis Committee (PURMAC) of the Society for the Plastics Industry (SPI). PURMAC has collected all pertinent analytical methods in a manual (271).

1.7. Health and Safety Factors

Poly(tetramethylene ether) glycols were found to have low oral toxicity in animal tests. The approximate lethal oral dose, LD_{50}, for Terathane 1000 has been found to be greater than 11,000 mg/kg (272). No adverse effects on inhalation have been observed. The polymer glycols are mild skin and eye irritants, and contact with skin, eyes,

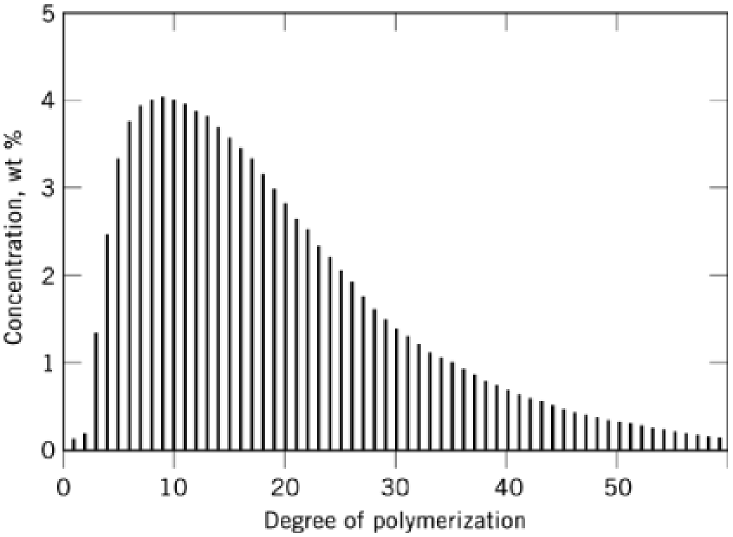


Fig. 3. Graph based on an hplc chromatogram of a commercial PTMEG of molecular weight $M_n=1000$. The bars represent the weight percentage of the individual oligomer fractions. The degree of polymerization is the number of repeating monomer units per polymer chain.

and clothing should be avoided. Goggles and gloves are recommended. In case of contact with the skin, wash thoroughly with water and soap. If swallowed, no specific intervention is indicated, because the compounds are not hazardous. However, a physician should be consulted (260).

Tests with bacterial or mammalian cell cultures demonstrated no mutagenic activity. PTMEG is not listed as a carcinogen by the Occupational Safety and Health Administration (OSHA), International Agency for Research on Cancer (IARC), National Toxicology Program (NTP), or American Conference of Governmental Industrial Hygienists (ACGIH), and exposure limits have not been established by either OSHA or ACGIH. Poly(tetramethylene ether) glycols are cleared as indirect food additives under 21 CFR 175.105 (adhesives) and 21 CFR 177.1680 (polyurethane resins). In addition, elastomers made from PTMEG may be acceptable under 21 CFR 177.1590 (polyester elastomers) and 21 CFR 177.2600 (rubber articles for repeated use).

Various medical devices based on Terathane have been approved by the U.S. FDA, including those used within the body. Formulators are cautioned, however, that FDA approval is not given generically for these devices; it must be applied for separately by each manufacturer for each device. Additional data on safety of PTMEG may be found in the material safety and data sheets provided by the manufacturers.

1.8. Economic Aspects

Poly(tetramethylene ether) glycols of molecular weights 1000, 1800, and 2000 represent the bulk of commercially produced and used PTMEG. Polyglycols of molecular weights 650, 1400, and 2900 are produced only on a smaller scale. Other molecular weight grades are sometimes manufactured as specialty products. The 1996 prices range from about $3.50/kg to about $4.20/kg. Du Pont is the world capacity leader, with the largest PTMEG plants both in the United States and in Europe and a total capacity in 1993 of about 60,000 metric tons, 30,000 tons of which were produced each in the United States and in Europe. Du Pont has announced plans for construction of another PTMEG plant based on an internally developed catalyst system to come onstream in 1997 (273, 274). Du Pont has a large internal demand for PTMEG; the rest is sold on the merchant market under the trade name Terathane. BASF, the second largest producer of PTMEG, has an estimated capacity of

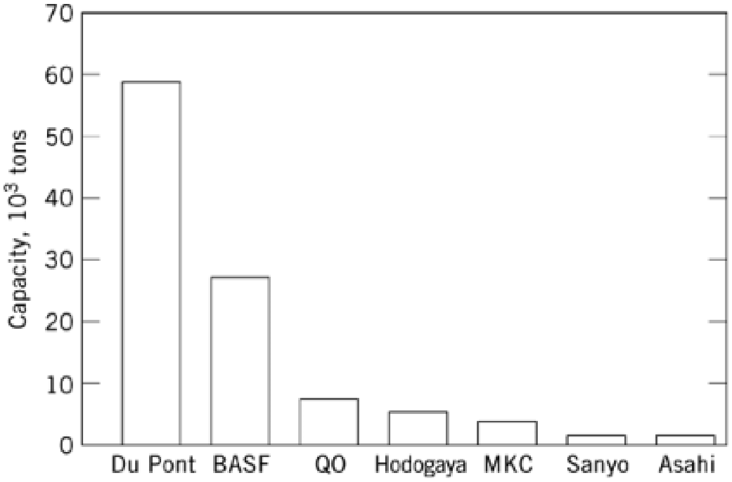


Fig. 4. Estimated world PTMEG capacity in 1993.

about 16,000 metric tons in the United States and 12,000 metric tons in Japan. Construction of a new PTMEG facility in Germany, with a projected capacity of 16,000 metric tons, has been announced (275). BASF also has a substantial internal demand. In 1993, QO Chemicals, a subsidiary of Great Lakes Chemicals, was the third largest producer of PTMEG, with a capacity of about 8000 metric tons. There are several manufacturers in Japan that produce PTMEG on a smaller scale, each one of them using a different process. The largest are Hodogaya, with about 6000 tons capacity, and Mitsubishi (MKC), with an estimated capacity of about 4000 tons. Sanyo and Asahi Chemicals each produce about 1000 t/yr. An estimated world capacity of PTMEG is shown in Figure 4.

1.9. Uses

The most important use area for poly(tetramethylene ether) glycols is polyurethane technology. Polyurethanes based on PTMEG have some outstanding properties that set them apart from polyurethanes based on other soft segments. They have excellent hydrolytic stability, high abrasion resistance, and excellent elastomeric properties, such as low hysteresis, high rebound, and high flexibility and impact resistance, even at low temperatures. Other benefits include strength, toughness, durability, low compression set, and high water vapor permeability. These premium properties warrant their use in areas where polyurethanes with soft segments based on polyesters or poly(propylene ether) glycols are inadequate (276).

The largest polyurethane end use areas are in spandex fibers for apparel, which in 1993 accounted for about 50% of the PTMEG market (277). Examples of PTMEG spandex fibers are Lycra (Du Pont), Dorlastan (Bayer), Opelon (Du Pont–TDC), Roica (Asahi), and Acelan (Taekwang). (see Fibers, elastomeric). Next are thermoplastic polyurethanes (TPUs) and castable polyurethanes, accounting for about 15 and 14% of the market, respectively. Thermoplastic polyurethanes are fully cured polyurethanes suitable for conventional thermoplastics processing, such as injection molding and extrusion. Examples of TPUs are Pellethane (Dow), Estane (BFGoodrich), and Texin (Miles/Bayer). Castable urethanes are made by mixing and casting reactive liquid components. End use areas of TPUs and castables include wheels, high speed rolls, automotive parts, bushings, specialty hose, cable sheathing and coating, and pipeline liners (278–280). PTMEG is also used in millable gums as rubber substitutes for specialty applications, under conditions where natural rubber would degrade or could not be used for other reasons. PTMEG-based polyurethanes can be manufactured as clear, colorless films, and as such find use in security glazing as glass laminates for aircraft and in bulletproof glass (281).

Elastomers based on PTMEG have excellent microbial and fungus resistance. Their hydrolytic stability make these elastomers prime candidates for use in ground-contact applications, for example, as jacketing material for buried cables. Because of their good biocompatibility, they have also found uses in medical applications, such as catheter tubing.

A smaller but rapidly growing area is the use of PTMEG in thermoplastic polyester elastomers. Formation of such polyesters involves the reaction of PTMEG with diacids or diesters. The diols become soft segments in the resulting elastomeric materials. Examples of elastomeric PTMEG polyesters include Hytrel (Du Pont) and Ecdel (Eastman Chemicals).

For a total of 80,000 t, the estimated world end use markets for PTMEG in 1993 were spandex fibers, 50%; TPU, 15%; castable polyurethane, 14%; other thermoplastic elastomers, 10%; and other uses, 11%. Most of the PTMEG-grades used commercially have molecular weights between 1000–2000. High molecular weight PTMEG ($M_w > 5000$) finds no significant commercial applications as of 1996.

2. Oxetane Polymers

2.1. Physical Properties

In contrast to THF, substituted oxetanes polymerize readily as a result of the added ring strain associated with the smaller ring size. A large number of polyoxetanes have been prepared and partially characterized (282). The properties of the polymers vary greatly with the symmetry, bulk, and polarity of the substituents on the chain (283). The polymers range from totally amorphous liquids to highly crystalline, high melting solids. The unsubstituted oxetane polymer (POX) has a melting temperature, T_m, of 35°C, not far above ambient temperature. A single methyl or azido substituent at either the second or the third position gives an amorphous polymer with stereoisomeric possibilities (282, 283). The 3,3-dimethyl derivative (PDMOX) is a crystalline polymer having a T_m of 47°C, whereas 3,3-bis(halomethyl)oxetane polymers have a T_m of 135, 180, 220, and 290°C for fluoro-, chloro-, bromo-, and iodo-derivatives, respectively (282). For the 3,3-dinitro derivative (PDNOX) and the 3,3-diazidomethyl derivative (PDAMO), the melting temperatures are 200–202°C and 75–78°C, respectively. As usual, the effect of copolymerization is to lower the T_m. For example, the random, high molecular weight copolymer of 3,3-bis(chloromethyl)oxetane [78-71-7] (BCMO) and THF is a tough, amorphous rubber (74).

Other crystallization parameters have been determined for some of the polymers. The dependence of the melting temperature on the crystallization temperature for the orthorhombic form of POX ($T_m = 323\text{K}$) and both monoclinic ($T_m = 348\text{K}$) and orthorhombic ($T_m = 329\text{K}$) modifications of PDMOX has been determined (284). The enthalpy of fusion, ΔH_m, for the same polymers has been determined by the polymer diluent method and by calorimetry at different levels of crystallinity (284). ΔH_m for POX was found to be 150.9 J/g (36.1 cal/g); for the dimethyl derivative, it ranged from 85.6 to 107.0 J/g (20.5–25.6 cal/g). Numerous crystal structure studies have been made (285–292). Isothermal crystallization rates of POX from the melt have been determined from 19 to $-50°\text{C}$ (293, 294). Similar studies have been made for PDMOX from 22 to 44°C (295, 296).

The glass-transition temperatures, T_g, of several polyoxetanes with alkyl substituents in position three were determined by differential scanning calorimetry (dsc). The results showed a regular increase of T_g according to the size of the substituents, except for the dibutyl derivative. Intramolecular interactions had a greater effect on T_g than intermolecular interactions (297, 298). The pressure dependence of the T_g of diazidomethyl oxetane–THF copolymers has been determined by high pressure ($\leq 850\text{ MPa} = 8.5\text{ kbar}$) differential thermal analysis (dta) and dielectric methods (299). Glass-transition temperature increases with increasing pressure. The results fit a modified Gibbs-DiMarzio theory. The effect of copolymer composition on T_g (300) and on dipole moments (301) has been studied over the whole composition range for DMOX–THF copolymer. The copolymers exhibit a T_g intermediate between those of the parent homopolymers.

Solubility parameters of 19.3, 16.2, and 16.2 $(J/cm^3)^{1/2}$ (7.9 $(cal/cm^3)^{1/2}$) have been determined for polyoxetane, poly(3,3-dimethyloxetane), and poly(3,3-diethyloxetane), respectively, by measuring solution viscosities (302). Heat capacities have been determined for POX and compared to those of other polyethers and polyethylene (303, 304). The thermal decomposition behavior of poly[3,3-bis(ethoxymethyl)oxetane] has been examined (305).

Extensive physical property measurements have been reported for only PBCMO (283, 306). This polymer was commercially available in the United States from Hercules, Inc. for about 15 years under the trade name Penton, but it is not currently (1996) produced for commercial sale. It has been studied extensively in the former USSR (307), where it was called Pentaplast, and also in Japan. The comparatively high heat distortion temperature, combined with a low water absorption value, makes PBCMO suitable for articles that require sterilization. It also has excellent electrical properties, a high degree of chemical resistance, and, because of the chlorine on the side chain, is self-extinguishing. PBCMO is resistant to most solvents, specifically to water, ketones, aldehydes, esters, aromatic hydrocarbons, weak organic bases such as aniline and ammonia, weak acids, and weak and strong alkalies. Like most polyethers, PBCMO is attacked by strong acids (306). Most other crystalline oxetane polymers are also insoluble in common organic solvents (286). The amorphous and low melting oxetane polymers, in contrast, are soluble in a wide variety of organic solvents.

Properties have been determined for a series of block copolymers based on poly[3,3-bis(ethoxymethyl)oxetane] and poly{[3,3-bis(methoxymethyl)oxetane]-*co*-tetrahydrofuran}. The block copolymers had properties suggestive of a thermoplastic elastomer (308). POX was a good main chain for a well-developed smectic liquid crystalline state when cyano- or fluorine-substituted biphenyls were used as mesogenic groups attached through a four-methylene spacer (309, 310). Other side-chain liquid crystalline polyoxetanes were observed with a spacer-separated azo moiety (311) and with laterally attached mesogenic groups (312).

2.2. Chemical Properties

The chemistry of polymerization of the oxetanes is much the same as for THF polymerization. The ring-opening polymerization of oxetanes is primarily accomplished by cationic polymerization methods (283, 313–318), but because of the added ring strain, other polymerization techniques, eg, insertion polymerization (319), anionic polymerization (320), and free-radical ring-opening polymerization (321), have been successful with certain special oxetanes. With appropriately substituted oxetanes, aluminum-based initiators (321) impose a degree of microstructural control on the substituted polyoxetane structure that is not obtainable with a pure cationic system. A polymer having largely the structure of poly(3-hydroxyoxetane) has been obtained from an anionic rearrangement polymerization of glycidol or its trimethylsilyl ether, both oxirane monomers (322). Polymerization-induced epitaxy can produce ultrathin films of highly oriented POX molecules on, for instance, graphite (323). Theoretical studies on the cationic polymerization mechanism of oxetanes have been made (324–326).

Other differences between THF and oxetane polymerizations are noteworthy. The added ring strain in the four-membered ring oxetane results in much faster polymerization rates and higher heats of polymerization than are observed for THF polymerization. At near ambient temperature and moderately high initiator concentrations, high conversions to PTHF usually require hours to achieve, whereas most oxetane polymerizations are near 100% conversion in seconds or minutes. Typical heat of polymerization values, ΔH_p, are 84.6, 80.9, 67.9, and 25 kJ/mol (20.2–6 kcal/mol) for BCMO, OX, DMOX, and THF, respectively (6, 282). Nominally, the polymerization of oxetanes is reversible. However, the formation of a four-membered ring under the usual polymerization conditions is energetically so disfavored that the depolymerization reaction can be ignored; the formation of cyclic oligomers becomes much more significant in oxetane polymerizations. The amount of cyclic oligomer formed depends on the particular oxetane, the polymerization conditions, and the initiating system, polymerization temperature, and solvent (327–331). Super acids and their esters have been found to be of little value in oxetane polymerizations. The equilibrium between ester and the oxonium ion in a BCMO polymerization, for example, is far toward the ester form, which is virtually unreactive to the cyclic ether and does not participate in the propagation reaction. Moreover, the active oxonium ion, when formed, collapses immediately to the corresponding ester (332). Thus a suitable mechanism for rapid polymer formation with this group of initiators does not exist for BCMO, and probably not for other oxetanes.

2.2.1. Kinetics

Results of the earliest studies of the kinetics of polymerization of OX and DMOX were reported in 1956 (327). Subsequent analyses led to the conclusion that all oxetane polymerizations, regardless of the initiator used, could be described by the kinetic expression $-d[M]/dt =_p [I]_0 \cdot [M]$, where k_p is the propagation rate constant; $[I]_0$ is the concentration of a fast, 100% efficient initiator or the concentration of active sites as measured directly; and $[M]$ is the monomer concentration (67, 133). Later studies revealed that not all systems are that simple. For example, under some conditions the rate of initiation with trialkyl oxonium ions is slow compared to the rate of polymerization; because a competing fast reaction of the growing oxonium ion with polymer oxygen forms a polymeric acyclic oxonium ion, this reaction effectively leads to dormant or sleeping ions by a process often referred to as temporary termination (334). Also, the formation of cyclic oligmers by competing reactions, when they occur, needs to be considered.

2.3. Manufacture and Processing

The only commercially important products in this area are the low molecular weight polyethers with hydroxyl end groups resulting from THF polymerization. As the next lower homologue, and having increased potential for functional or modifying ring substitution, oxetane offers an enticing extension of this chemistry. Indeed it is possible to control the rapid polymerizations and to prepare low molecular weight products with the necessary end-group functionality. Japanese patents (335, 336) describe the preparation of low molecular weight oxetane–THF copolymers using methods that appear similar to those used to prepare PTHF glycols. The preparation of polyoxetanes and oxetane–THF copolymers where the oxetane moieties are substituted with energetic groups, such as azido or nitro groups, has also been described (337–339). The latter polymerizations are similar to oxirane polymerizations occurring by the activated monomer mechanism (340, 341) and generally involve polymerization in the presence of relatively large amounts of organic diols, eg, 1,4-butanediol, or the use of preformed Lewis acid–diol mixtures as polymerization initiators (342–344). Low molecular weight glycols have also been obtained by degrading high molecular weight polymer (342, 345). PBCMO, the only oxetane polymer that was once commercialized, is no longer available. Some details about its processing can be found in the literature (283, 306). Macroglycols from oxetanes or from mixtures of oxetanes with other monomers have been converted to polyurethanes using technology similar to that for the conversion of macroglycols from THF.

2.3.1. Economic Aspects

Oxetanes are expensive monomers and are not readily available in commercial quantities. Commercial production of PBCMO has been discontinued; its end uses were not able to support its comparatively high selling price. Energetic polymers prepared from appropriately substituted oxetanes have opened a new market for their use to prepare solid rocket propellants and explosives. Should this specialty market result in the large-scale production of these oxetanes even at current (1996) high prices and/or in a cheap synthetic route to oxetanes, this economic picture could change.

2.3.2. Analytical and Test Methods

Most of the analytical and test methods described for THF and PTHF are applicable to OX and POX with only minor modifications (346). Infrared and nmr are useful aids in the characterization of oxetanes and their polymers. The oxetane ring shows absorption between 960 and 980 cm^{-1},regardless of substituents on the ring (282). Dinitro oxetane (DNOX) has its absorption at 1000 cm^{-1}. In addition, ^{1}H-nmr chemical shifts for CH_2 groups in OX and POX are typically at 4.0–4.8 δ and 3.5–4.7 δ, respectively (6, 347, 348); ^{13}C-nmr is especially useful for characterizing the microstructure of polyoxetanes.

2.4. Health and Safety Factors

Toxicity and hazards of handling oxetanes and their polymers are influenced markedly by their substituents. For many of the monomers, these factors are described in detail in material safety data sheets. Special monomers such as those designed to yield energetic polymers require special care in handling because they are sensitive explosives. Under no circumstances should an energetic monomer be distilled; rather, purification via column chromatography is suggested (348–350). Polymers derived from energetic monomers burn with a large amount of smoke. Special procedures have been developed for disposal of these energetic polymers.

2.5. Uses

A large number of uses have been explored worldwide for high performance PBCMO (283), but none of these uses were adequate in the marketplace to support its high price. The energetic polymers derived from appropriately substituted oxetanes were specifically designed to increase the energy content of explosives and solid fuels that use polymeric binders (349). In this the oxetanes have advantages over THF and the oxiranes, which may ultimately help the oxetanes find continuing demand. Substituted oxetanes homopolymerize and copolymerize well with THF. The technology developed for converting PTHFs to useful products is readily adaptable to polyoxetanes. The formation of cyclic oligomers can be essentially eliminated in oxetane polymerizations by proper choice of the initiating system, counterion, and temperature of polymerization. Research on these applications continues (351–356).

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