

TITLE

POLYMERIZATION OF CYCLIC ETHERS  
USING SELECTED METAL COMPOUND CATALYSTS

FIELD OF THE INVENTION

5        This invention concerns the polymerization of  
oxiranes, oxetanes, oxepanes, 1,3-dioxolanes,  
1,3,5-trioranes, and tetrahydrofurans to linear  
polyethers catalyzed by selected metal compounds  
together with selected accelerators.

10        BACKGROUND OF THE INVENTION

Cyclic ethers are polymerized by various means to  
give products of widespread utility. For instance,  
ethylene oxide is polymerized to polyethylene oxide  
which is useful, in lower molecular weight grades, for  
15 ceramics (as a binder), cosmetics, lubricants,  
polyurethanes; and in higher molecular weight grades,  
for packaging film, denture adhesives, lubricants,  
flocculation and for other articles and products.  
Tetrahydrofuran (THF) is polymerized to poly(tetra-  
20 methylene ether) glycol which is useful in the  
preparation of Spandex fibers; polyurethane resins which  
are useful in elastomeric parts; and thermoplastic  
elastomers which are useful for molding various  
mechanical parts. Therefore, improved methods of making  
25 these polymers are sought.

U.S. Patent 3,842,019 describes the polymerization  
of oxiranes and other small ring compounds by a presumed  
cationic mechanism, using as the catalyst the  
decomposition products of metal perfluoroalkyl-  
30 sulfonates. These catalysts are described as "latent",  
that is no reaction occurs until the metal salt is  
decomposed. The reactions reported are relatively slow,  
even at elevated temperatures.

U.S. Patents 5,084,586 and 5,124,417 describe the  
35 cationic polymerization of various monomers, including



cyclic ethers, using onium cations, whose corresponding anions are fluororalkylsulfatometallates. Onium ion catalyzed cationic polymerizations are known, and there is no mention in these patents of the use of metal salts not containing onium ions, such as metal triflates, as catalysts for the polymerization of cyclic ethers.

J. S. Hrkach, et al., *Macromolecules*, vol. 23, p. 4042-4046 (1990) describe the polymerization of tetrahydrofuran using trimethylsilyl trifluoromethanesulfonate as the initiator. No mention is made of any other triflates as catalysts for this polymerization.

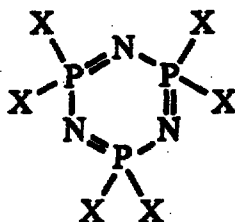
G. A. Olah, et al., *J. Appl. Polym. Sci.*, Vol. 45, 1355-1360 (1992) describe the use of boron, aluminum and gallium trisulfate to catalyze the polymerization of THF.

S. L. Borkowsky, et al., *Organometal.*, Vol. 10, p. 1268-1274 (1991) report that certain zirconium complexes can initiate the polymerization of tetrahydrofuran. No mention is made of zirconium perfluoroalkylsulfonates, or of copolymers.

I. Yamashita, et al., *Kogyo Kagaku Zasshi*, vol. 71, p. 1061-1064 (1968) describes the polymerization of tetrahydrofuran using a catalyst system consisting of a Lewis acid such as ferric chloride and a phosphorous compound such as triphenyl phosphite. The use of metal perfluoroalkylsulfonates is not mentioned.

#### SUMMARY OF THE INVENTION

This invention concerns a process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes with a compound of the formula  $MZ_s \cdot Q_t$ , and an accelerator which is a compound of the formula

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wherein:

$R^1$  is hydrogen, hydrocarbyl or substituted hydrocarbyl;

$R^2$  is hydrogen, hydrocarbyl or substituted hydrocarbyl;

each  $R^3$  is independently hydrocarbyl or substituted hydrocarbyl;

each X is independently chlorine, bromine or iodine;

M is a metal selected from the group consisting of

strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, cobalt, vanadium, niobium, tungsten, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula  $^{-}SO_3R^5$ , wherein  $R^5$  is perfluoroalkyl containing 1 to 12 carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;



- s is 1 when M is silver;  
s is 2 when M is strontium, barium, cobalt, rhodium,  
iridium, palladium, platinum, chromium, zinc,  
cadmium or mercury;  
5 s is 3 when M is scandium, yttrium, a rare earth  
metal, arsenic, antimony, bismuth, gold, iron,  
ruthenium, osmium, aluminum, gallium, indium or  
thulium;  
s is 4 when M is titanium, zirconium, hafnium,  
10 molybdenum, germanium, tin, or lead;  
s is 5 when M is rhenium, vanadium, niobium or  
tantalum;  
s is 6 when M is tungsten;  
Q is a neutral ligand;  
15 t is 0 or an integer of 1 to 6; and  
provided that each oxo group present counts as two of s.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

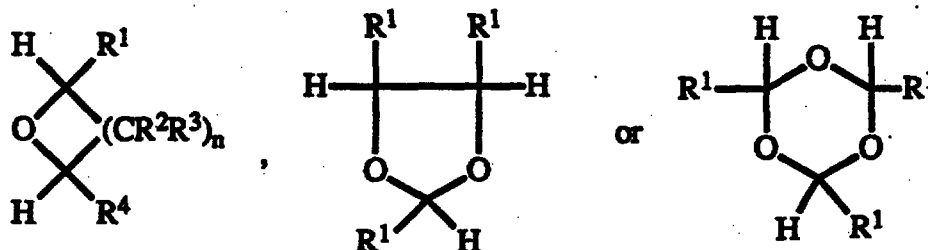
In the polymerization process described herein one  
or more cyclic ethers, oxiranes, oxetanes, 1,3-dioxo-  
20 lanes, 1,3,5-trioxanes, or tetrahydrofurans are  
polymerized to form a polyether. Oxirane (more commonly  
called epoxide) is herein given its usual structure, a  
saturated three membered ring containing two carbon  
atoms and one oxygen atom. Oxetane is also given its  
25 common meaning, a saturated four membered ring  
containing three carbon atoms and one oxygen atom. The  
term oxepane means a saturated seven membered ring  
containing six carbon atoms and one oxygen atoms. The  
term 1,3-dioxolane means a saturated five membered ring  
30 which contains two oxygen atoms separated by 1 carbon  
atom. The term 1,3,5-trioxane means a six membered ring  
containing 3 oxygen atoms in which the oxygen atoms and  
carbons atoms are alternated. All of these terms  
include compounds containing those ring systems which  
35 are substituted with hydrocarbyl or hydrocarbylene



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groups containing 1 to 20 carbon atoms. The hydrocarbylene groups may form carbocyclic rings, which include bicyclic, tricyclic, etc., systems. By a hydrocarbylene group herein is meant a divalent radical containing carbon and hydrogen which is part of a carbocyclic ring.

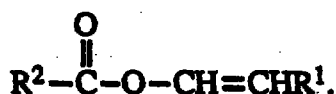
Preferred cyclic ethers have the formula



wherein  $n$  is 2 or 4 and each  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms. Some of these cyclic ethers polymerize to give repeat units of the formula  $-\text{CHR}^1(\text{CR}^2\text{R}^3)_n\text{CHR}^4\text{O}-$ . In a more preferred cyclic ether all of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrogen. In another more preferred cyclic ether where  $n=2$ ,  $R^1$ , one of  $R^2$ , both of  $R^3$  and  $R^4$  are hydrogen, and the remaining  $R^2$  is alkyl containing 1-4 carbon atoms, especially preferably the remaining  $R^2$  is methyl. By hydrocarbyl herein is meant a univalent radical containing carbon and hydrogen.

The polymerization is run in the presence of an accelerator. Suitable accelerators include selected vinyl esters and selected phosphorous compounds.

The vinyl ester accelerators have the formula



In a preferred vinyl ester  $R^1$  is hydrogen or alkyl, more preferably hydrogen or  $n$ -alkyl. In another preferred vinyl ester  $R^2$  is alkyl, phenyl, or substituted phenyl, more preferably  $n$ -alkyl. In an



especially preferred vinyl ester  $R^1$  is hydrogen and  $R^2$  is methyl.

In the accelerators which are phosphorous compounds it is preferred if each  $R^3$  is independently alkyl, phenyl, or substituted phenyl, more preferably n-alkyl containing 1, 2, 3 or 4 carbon atoms or phenyl. It is also preferred if X is chlorine.

By substituted hydrocarbyl (or substituted in substituted phenyl) is meant that the moiety may contain inert substituents (functional groups). By inert is meant that they don't react with any of the starting materials or products nor interfere with the polymerization. Such substituents include (linear) ether, alkyl, aryl, and halo.

An important consideration in the preparation of polyethers is the number average molecular weight ( $M_n$ ) of the polyether and its molecular weight distribution. When the polyether is to be used as a monomer in the preparation of another polymer (usually in the diol form), it is often preferred that the  $M_n$  of the polyether be in the range of about 400 to about 20,000, preferably about 500 to about 5,000.

The catalyst may be yttrium or a rare earth compound of the formula  $MZ_3$  where M is a trivalent ion of yttrium, or one of the rare earths, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

Preferred metals, M, are strontium, scandium yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin and bismuth. More preferred metals are yttrium, the rare earth metals, and scandium. Especially preferred metals are yttrium,

ytterbium, dysprosium, erbium, neodymium, lanthanum, and scandium. Another preferred metal is "mischmetall" (sometimes also called "didymium"), which is a mixture of rare earth metals as obtained from the ore.

5 It is currently believed monovalent anions that are relatively nonnucleophilic are useful as Z. Examples of such anions are tetraphenylborate,  $^{-}\text{SO}_3\text{R}^5$ , wherein  $\text{R}^5$  is perfluoroalkyl, or wherein  $\text{R}^5$  is part of a fluorinated polymer wherein the carbon atoms alpha and beta to a  
10 sulfonate group are together bonded to at least 4 fluorine atoms (as in  $^{-}\text{CF}_2\text{CF}_2\text{SO}_3^{-}$ ). It is preferred if  $\text{R}^5$  is perfluoroalkyl. In a particularly preferred embodiment,  $\text{R}^5$  is trifluoromethyl, and the anion is herein called "triflate".

15 Generally speaking, any metallic compound in which the correct metal in the correct oxidation state (see - above) is present and bonded to a triflate or similar anion will be a catalyst. Such a compound must of course be reasonably stable during the polymerization or  
20 decompose to another compound which is still a triflate (or similar anion) compound of the metal in the correct oxidation state. It has been found that, in general, the greater the number of triflate groups bonded to the metal cation, the more active the metal compound will be  
25 as a catalyst. It is preferred if half or more of the anions (Z) bound to each metal cation is triflate or a similar anion.

The metal catalysts may optionally contain one or more neutral ligands coordinated to the metal. By a  
30 neutral ligand is meant a neutral compound that can coordinate with the catalysts, usually the metal cation. Neutral ligands include water, and ethers such as dimethyl ether and tetrahydrofuran.

The metals catalysts may contain other anions than  
35 triflate and similar anions, and tetrafluoroborate,



although at least one of triflate or tetrafluoroborate anions must be present. Some other useful anions are alkoxide, particularly lower alkoxide containing 1-4 carbon atoms, acetylacetonate, cyclopentadieneide, pentamethylcyclopentadieneide, t-butylacetylacetonate, and halide. It is preferred if all of the anions are triflate.

In general, the higher the molar ratio of metal compound to cyclic ether monomer originally present, the lower the molecular weight of the resulting polyether will be. Similarly, the higher the ratio of accelerator (if present) to monomer originally present, the lower the molecular weight of the polyether will be. It is currently believed that the effects of these two ratios are cumulative.

The polymerization may be run at a temperature of about  $-80^{\circ}\text{C}$  to about  $130^{\circ}\text{C}$ . If this temperature is above the boiling point of the cyclic ether monomer, a pressure vessel may be used. A preferred temperature is ambient to the boiling point of the monomer, or  $110^{\circ}\text{C}$ , whichever is lower. An inert solvent such as di-n-butyl ether, diethyl ether or toluene may be used, but it is preferred if solvents are not present. Protic compounds such as water, methanol and ethanol should preferably not be present, and it is convenient to exclude them by drying the starting materials and keeping the process under an inert dry gas such as nitrogen. As in most chemical processes, the ingredients should be mixed at least initially. Continued agitation is preferred to assure that the process materials remain well mixed, and to avoid overheating. The polymerization is mildly exothermic. If the polymerization temperature goes up appreciably, refluxing of the monomer may be used to help cool the process.



The polymerization process can be performed in a variety of ways known to those skilled in the art. It can be done by batch, semi-batch and continuous processes. Continuous processes include continuous stirred tank reactor(s) with one or more stages, and/or plug flow reactors. Other variations will be evident to those skilled in this art.

In the polymerization process disclosed herein the catalyst may be recovered and reused. It may be recovered from the polymerization process by extracting the polymer formed with water. The recovered catalyst may be used again in the polymerization. The aqueous washings may be concentrated by removal of the water (as by evaporation) and the solid catalyst recovered.

#### EXAMPLES

In the following non-limiting Examples, the following abbreviations are used:

GPC - gel permeation chromatography  
Mn - number average molecular weight  
Mw - weight average molecular weight  
PD - polydispersity, Mw/Mn  
PS - polystyrene  
RB - round-bottomed  
STD - standard  
THF - tetrahydrofuran

#### EXAMPLE 1

##### Polymerization of THF with Diethyl Chlorophosphite and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (1.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water,

THF and ether. The resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum affording 12.63 g of polymer. GPC analysis (PS STD.):  $M_n = 10200$ ,  $M_w = 20100$ ,  $PD = 1.96$ .

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EXAMPLE 2Polymerization of THF with  
Diphenylphosphinic Acid and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) and diphenylphosphinic acid (1.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) was added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The resulting white mixture was filtered through Celite. The resulting filtrate was washed with water, concentrated at reduced pressure and dried under vacuum affording 8.22 g of polymer. GPC analysis (PS STD.):  $M_n = 50900$ ,  $M_w = 112000$ ,  $PD = 2.21$ .

20

EXAMPLE 3Polymerization of THF with  
Diethyl Chlorophosphite and Erbium Triflate

In a dry box, erbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphite (2.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 9.68 g of polymer. GPC analysis (PS STD.):  $M_n = 10800$ ,  $M_w = 19600$ ,  $PD = 1.82$ .

EXAMPLE 4Polymerization of THF withDiethyl Chlorophosphite and Neodymium Triflate

In a dry box, neodymium triflate (2.00 g) was  
5 weighed in an oven dried 100 mL RB flask equipped with a  
stirring bar. The flask was sealed with a rubber septum  
and removed from the dry box. After the attachment of a  
nitrogen bleed, THF (20.0 mL) and diethyl chlorophos-  
phite (2.00 mL) were added. After 17 hours the  
10 polymerization was terminated via the addition of water,  
THF and ether. The separated organic phase was again  
washed with water. The organic phase was concentrated  
at reduced pressure and then dried under vacuum  
affording 4.73 g of polymer. GPC analysis (PS STD.):  
15 Mn = 12200, Mw = 22600, PD = 1.85.

EXAMPLE 5Polymerization of THF withDiethyl Chlorophosphite and Dysprosium Triflate

In a dry box, dysprosium triflate (2.00 g) was  
20 weighed in an oven dried 100 mL RB flask equipped with a  
stirring bar. The flask was sealed with a rubber septum  
and removed from the dry box. After the attachment of a  
nitrogen bleed, THF (20.0 mL) and diethyl chlorophos-  
phite (2.00 mL) were added. After 17 hours the  
25 polymerization was terminated via the addition of water,  
THF and ether. The separated organic phase was again  
washed with water. The organic phase was concentrated  
at reduced pressure and then dried under vacuum  
affording 9.80 g of polymer. GPC analysis (PS STD.):  
30 Mn = 14100, Mw = 27900, PD = 1.98.

EXAMPLE 6Polymerization of THF withDiethyl Chlorophosphite and Tin Triflate

In a dry box, tin triflate (2.00 g) was weighed in  
35 an oven dried 100 mL RB flask equipped with a stirring

bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphate (2.00 mL) were added. After 17 hours the  
5 polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 14.93 g of polymer. GPC analysis (PS STD.):  
10 Mn = 2680, Mw = 5520, PD = 2.06.

#### EXAMPLE 7

##### Polymerization of THF with Diethyl Chlorophosphate and Bismuth Triflate

In a dry box, bismuth triflate (2.00 g) was weighed  
15 in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphate (2.00 mL) were added. After 17 hours the  
20 polymerization was terminated via the addition of water, THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 7.99 g of polymer. GPC analysis (PS STD.):  
25 Mn = 3050, Mw = 6600, PD = 2.16.

#### EXAMPLE 8

##### Polymerization of THF with Diethyl Chlorophosphate and Lanthanum Triflate

In a dry box, lanthanum triflate (2.00 g) was  
30 weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and diethyl chlorophosphate (2.00 mL) were added. After 15 hours the  
35 polymerization was terminated via the addition of water,

THF and ether. The separated organic phase was again washed with water. The organic phase was concentrated at reduced pressure and then dried under vacuum affording 7.03 g of polymer. GPC analysis (PS STD.):

5 Mn = 14500, Mw = 30300, PD = 2.08.

#### EXAMPLE 10

##### Polymerization of THF with Phosphonitrilic Trimer and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) and  
10 phosphonitrilic trimer (1.00 g) were weighed in an oven  
dried 100 mL RB flask equipped with a stirring bar. The  
flask was sealed with a rubber septum and removed from  
the dry box. After the attachment of a nitrogen bleed,  
THF (20.0 mL) was added. After 16 hours the  
15 polymerization was terminated via the addition of water,  
THF and ether. The separated organic phase was again  
washed with water. The organic phase was concentrated  
at reduced pressure and then dried under vacuum  
affording 7.78 g of polymer. GPC analysis (PS STD.):  
20 Mn = 6710, Mw = 28500, PD = 4.25.

#### EXAMPLE 11

##### Polymerization of THF with Vinyl Acetate and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) was  
25 weighed in an oven dried 100 mL RB flask equipped with a  
stirring bar. The flask was sealed with a rubber septum  
and removed from the dry box. After the attachment of a  
nitrogen bleed, THF (20.0 mL) and vinyl acetate  
(1.00 mL) were added. After 17 hours the polymerization  
30 was terminated via the addition of water, THF and ether.  
The resulting organic phase was separated, washed with  
water, concentrated at reduced pressure and then dried  
under vacuum affording 7.66 g of polymer. GPC analysis  
(PS STD.): Mn = 184000, Mw = 335000, PD = 1.82.

EXAMPLE 12Polymerization of THF with  
Vinyl 2-Ethylhexanoate and Ytterbium Triflate

In a dry box, ytterbium triflate (2.00 g) was added  
 5 to each of four 100 mL RB flasks equipped with stirring  
 bars. The flasks were sealed with rubber septa and  
 removed from the dry box. After the attachment of  
 nitrogen bleeds THF (20.0 mL) was added to each flask.  
 Vinyl 2-ethylhexanoate (1.0, 2.0, 3.0 and 4.0 mL) was  
 10 added to each flask. After 17 hours the polymerizations  
 were terminated via the addition of water, THF and  
 ether. The separated organic phases were again washed  
 with water, separated, concentrated at reduced pressure  
 and then dried under vacuum. Polymer yields and GPC  
 15 analyses:

| <u>Vinyl 2-Ethyl-<br/>hexanoate (mL)</u> | <u>Polymer Yield<br/>(g)</u> | <u>Mn<br/>(PS STD.)</u> | <u>Mw</u> | <u>PD</u> |
|------------------------------------------|------------------------------|-------------------------|-----------|-----------|
| 1.0                                      | 1.47                         | 435000                  | 774000    | 1.78      |
| 2.0                                      | 1.85                         | 429000                  | 681000    | 1.59      |
| 3.0                                      | 2.28                         | 410000                  | 622000    | 1.52      |
| 4.0                                      | 3.07                         | 253000                  | 543000    | 2.15      |

EXAMPLE 13
Polymerization of THF with Vinyl Acetate  
 and Bis(*n*-cyclopentadienyl)tetrahydrofuran-  
 bis(trifluoromethanesulfonato)zirconium  
 20 (Cp<sub>2</sub>Zr[(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>](THF))

In a dry box, bis(*n*-cyclopentadienyl)tetrahydro-  
 furan-bis(trifluoromethanesulfonato)zirconium  
 (Cp<sub>2</sub>Zr[(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>](THF)) (2.00 g) was weighed in an oven  
 dried 100 mL RB flask equipped with a stirring bar. The  
 25 flask was sealed with a rubber septum and removed from  
 the dry box. After the attachment of a nitrogen bleed,  
 THF (20.0 mL) and vinyl acetate (2.00 mL) were added.  
 After 17 hours the polymerization was terminated via the

addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 12.17 g of polymer. GPC analysis (PS STD.): Mn = 60100, Mw = 126000, PD = 2.10.

#### EXAMPLE 14

##### Polymerization of THF with Vinyl Acetate and Yttrium Triflate

In a dry box, yttrium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and vinyl acetate (3.00 mL) were added. After 19.5 hours the polymerization was terminated via the addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 3.15 g of polymer. GPC analysis (PS STD.): Mn = 100000, Mw = 194000, PD = 1.94.

#### EXAMPLE 15

##### Polymerization of THF with Vinyl Acetate and Erbium Triflate

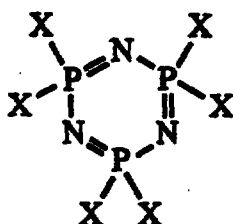
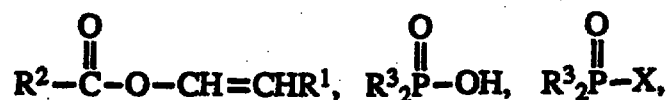
In a dry box, erbium triflate (2.00 g) was weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum and removed from the dry box. After the attachment of a nitrogen bleed, THF (20.0 mL) and vinyl acetate (3.00 mL) were added. After 17 hours the polymerization was terminated via the addition of water, THF and ether. The resulting organic phase was separated, washed with water, concentrated at reduced pressure and then dried under vacuum affording 0.54 g of polymer. GPC analysis (PS STD.): Mn = 222000, Mw = 396000, PD = 1.76.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous  
5 modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than the foregoing specification, as indicating the scope of the invention.



## WHAT IS CLAIMED IS:

1. A process for the polymerization of cyclic ethers, comprising, contacting one or more oxiranes, oxetanes, tetrahydrofurans, oxepanes, 1,3-dioxolanes or  
5 1,3,5-trioxanes with a compound of the formula  $MZ_s \cdot Q_t$ , and an accelerator which is a compound of the formula



wherein:

- $R^1$  is hydrogen, hydrocarbyl or substituted hydrocarbyl;  
10  $R^2$  is hydrogen, hydrocarbyl or substituted hydrocarbyl;  
each  $R^3$  is independently hydrocarbyl or substituted hydrocarbyl;  
each  $X$  is independently chlorine, bromine or iodine;  
15  $M$  is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, cobalt, vanadium, niobium, tungsten, ruthenium,  
20 osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;  
at least one of  $Z$  is an anion of the formula  $^{-}SO_3R^5$ ,  
25 wherein  $R^5$  is perfluoroalkyl containing 1 to 12



carbon atoms or part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least four fluorine atoms, or tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

s is 1 when M is silver;

s is 2 when M is strontium, barium, cobalt, rhodium, iridium, palladium, platinum, chromium, zinc, cadmium or mercury;

s is 3 when M is scandium, yttrium, a rare earth metal, arsenic, antimony, bismuth, gold, iron, ruthenium, osmium, aluminum, gallium, indium or thulium;

s is 4 when M is titanium, zirconium, hafnium, molybdenum, germanium, tin, or lead;

s is 5 when M is rhenium, vanadium, niobium or tantalum;

s is 6 when M is tungsten;

Q is a neutral ligand;

t is 0 or an integer of 1 to 6;

and provided that each oxo group present as part of Z is considered to account for two of s.

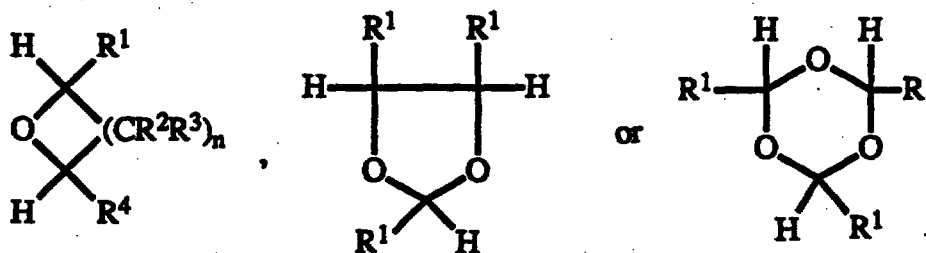
2. The process as recited in Claim 1 wherein said cyclic ether is one or more of said tetrahydrofurans, oxepanes, 1,3-dioxolanes or 1,3,5-trioxanes.

3. The process as recited in Claim 2 wherein M is a metal selected from the group consisting of strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold, zinc, cadmium, mercury, germanium, tin, lead, arsenic, antimony and bismuth.





4. The process as recited in Claim 3 wherein said cyclic ether comprises the formula



wherein:

each  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms; and  $n$  is 2 or 4.

5. The process as recited in Claim 4 wherein  $n$  is 2 and  $R^1$ ,  $R^4$  and all of  $R^2$  and  $R^3$  are hydrogen.

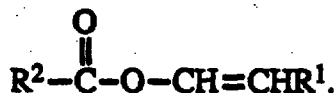
6. The process as recited in Claim 4 wherein  $n$  is 2 and  $R^1$  and  $R^4$  are each hydrogen, one of  $R^2$  is hydrogen, the other  $R^2$  is methyl, and both  $R^3$  are hydrogen.

7. The process as recited in Claim 3 wherein  $R^5$  is trifluoromethyl or perfluoroalkyl.

8. The process as recited in Claim 5 wherein  $M$  is strontium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, rhenium, iron, ruthenium, palladium, copper, gold, zinc, tin, bismuth or mischmetall.

9. The process as recited in Claim 1 carried out at a temperature of about  $-80^\circ\text{C}$  to about  $130^\circ\text{C}$ .

10. The process as recited in Claim 1 wherein said accelerator is a compound of the formula



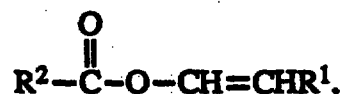
11. The process as recited in Claim 10 wherein  $R^1$  is hydrogen or alkyl, and  $R^2$  is alkyl, phenyl, or substituted phenyl.





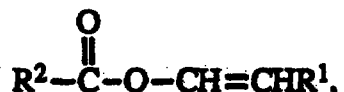
12. The process as recited in Claim 10 wherein R<sup>1</sup> is hydrogen and R<sup>2</sup> is methyl.

13. The process as recited in Claim 5 wherein said accelerator is



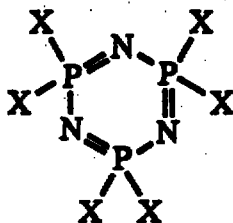
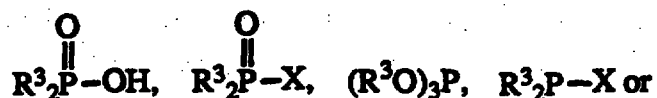
5 and R<sup>1</sup> is hydrogen or alkyl, and R<sup>2</sup> is alkyl, phenyl, or substituted phenyl.

14. The process as recited in Claim 5 wherein said accelerator is



and R<sup>1</sup> is hydrogen and R<sup>2</sup> is methyl.

10 15. The process as recited in Claim 1 wherein said accelerator is

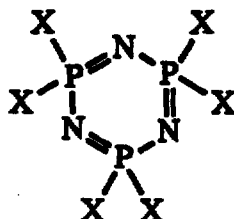
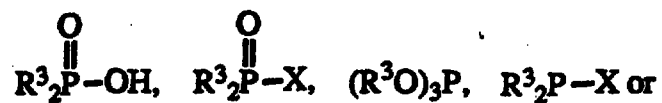


16. The process as recited in Claim 15 wherein each R<sup>3</sup> is independently alkyl, phenyl, or substituted phenyl, and X is chlorine.

15 17. The process as recited in Claim 15 wherein each R<sup>3</sup> is n-alkyl containing 1, 2, 3 or 4 carbon atoms or phenyl.



18. The process as recited in Claim 5 wherein said accelerator is



and each  $R^3$  is independently alkyl, phenyl, or substituted phenyl, and X is chlorine.

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This Sheet Has Been Replaced



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