

TITLE
COPOLYMERIZATION OF TETRAHYDROFURANS
AND CYCLIC ANHYDRIDES
FIELD OF THE INVENTION

5 This invention concerns a process for the copolymerization of tetrahydrofurans with cyclic carboxylic anhydrides to form a poly(ester-ether), wherein the polymerization is catalyzed by selected metal perfluoroalkylsulfonates.

BACKGROUND

10 Copolymers of tetrahydrofuran and cyclic anhydrides are known in the art. These polymers were made with the use of a Lewis acid catalyst such as an organoaluminum compound or an onium compound, optionally in the
15 presence of a cocatalyst, see for example J. Habermeier, et al., J. Polym. Sci., Part C, p. 2131-2141 (1967). No mention is made in this paper of metal perfluoroalkylsulfonates as catalysts.

20 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.

25 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 perfluoroalkylsulfonates. These catalysts are described as "latent", that is no reaction occurs until the metal salt is
30 decomposed. The reactions reported are relatively slow, even at elevated temperatures.

35 U.S. Patents 5,084,586 and 5,124,417 describe the cationic polymerization of various monomers, including cyclic ethers, using onium cations, whose corresponding anions are fluororalkylsulfatometallates. Onium ion

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REPLACED SHEETS	SG
☒ Description : paged 123,647 to paged 123,647	
☒ Claim(s) : paged 123,647 to paged 123,647	
☐ Drawing(s) : paged 123,647 to paged 123,647	
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catalyzed cationic polymerizations are well 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.

German Patent Application 2,459,163 describes the polymerization of THF using a combination of ferric chloride and carboxylic anhydride as catalyst.

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

SUMMARY OF THE INVENTION

This invention concerns a process for the production of a poly(ester-ether), comprising, contacting one or more cyclic carboxylic anhydrides, one or more tetrahydrofurans, and a catalyst of the formula $MZ_s \cdot Q_t$, and an accelerator selected from the group consisting of carboxylic acids whose pKa in water is less than 6, carboxylic anhydrides and acyl halides, wherein:

M is a metal selected from the group consisting of cobalt, vanadium, niobium, tungsten, 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, aluminum, gallium, indium, thulium, germanium, tin, lead, arsenic, antimony and bismuth;

at least one of Z is an anion of the formula $^{-}OSO_2R^5$, 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

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tetraphenylborate, and the remainder of Z is oxo or one or more monovalent anions;

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;

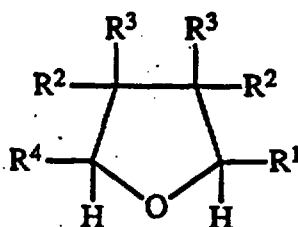
t is 0 or an integer of 1 to 6; and

provided that each oxo group present counts as two of s.

DETAILS OF THE INVENTION

In the instant process a tetrahydrofuran is copolymerized with a cyclic anhydride to yield a poly(ether-ester). By a tetrahydrofuran (THF) is meant the common meaning, a compound containing a saturated five membered ring in which one of the ring atoms is oxygen and the other four ring atoms are carbon.

Preferred tetrahydrofurans have the formula

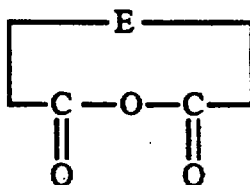


wherein each R^1 , R^2 , R^3 and R^4 is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms. In especially preferred THFs, R^1 , one of R^2 and all of R^3



and R^4 are hydrogen, and the remaining R^2 is alkyl containing 1-4 carbon atoms, particularly the remaining R^2 is methyl. In another especially preferred embodiment all of R^1 , R^2 , R^3 and R^4 are hydrogen.

- 5 By a cyclic carboxylic anhydride is meant the common meaning, a compound that can be represented by the formula



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- wherein E is a divalent organic radical which is bound to each valence of the carboxylic anhydride group through a carbon atom. In preferred embodiments, E is n-alkylene containing 1 to 4 carbon atoms or alkyl substituted n-alkylene wherein the n-alkylene group contains 1 to 4 carbon atoms, and E contains a total of 2 to 20 carbon atoms. Specific useful cyclic carboxylic anhydrides include, but are not limited to, succinic, maleic, phthalic, 5-methyl-5-nobornene-
15 dicarboxylic acid and 1,2-cyclohexanedicarboxylic acid anhydrides. Preferred cyclic carboxylic anhydrides include maleic, succinic, phthalic and 1,2-cyclohexanedicarboxylic acid anhydrides.

- 20 In the above formula E may be substituted with one or more additional carboxylic anhydride groupings. For instance, 1,2,4,5-benzenetetracarboxylic dianhydride may be used in the process. It is believed that, depending on the concentration of the dianhydride, the resulting copolymer may be branched or even crosslinked (higher
25 dianhydride levels).
30

It is believed that monovalent anions that are relatively nonnucleophilic are useful as Z. Examples of

such anions are tetraphenylborate, $^{-}\text{OSO}_2\text{R}^5$, wherein R^5 is perfluoroalkyl or wherein R^5 is part of a fluorinated polymer wherein the carbon atoms alpha and beta to the sulfonate group are together bonded to at least 4
 5 fluorine atoms (as in $^{-}\text{CF}_2\text{CF}_2\text{O}_2\text{SO}^{-}$). It is preferred if R^5 is perfluoroalkyl, and particularly preferred if R^5 is trifluoromethyl, so that $^{-}\text{OSO}_2\text{R}^5$ is trifluoromethanesulfonate, herein also called triflate.

The catalyst may be yttrium or rare earth compound
 10 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.

15 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
 20 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
 25 of rare earth metals as obtained from the ore.

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

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 depolymerization, see below), or 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 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 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. Useful compounds containing neutral ligands include bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)-zirconium and bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)hafnium.

The metal catalysts may contain other anions than 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.

It is believed that in the present process, the higher the ratio of metal catalyst compound to monomers,

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the lower the molecular weight of the resulting copolymer will be. It is also believed that the copolymer is a random copolymer, except that -O(O)CQC(O)- cannot be adjacent to itself. It is

5 further believed that simple monomers such as THF and, say, succinic or maleic anhydrides, have about an equal propensity to polymerize into the copolymer.

The temperature at which the polymerization process is run is not critical, about -80°C to about 110°C being
10 a convenient range, about 0°C to about 110°C is preferred, and about 25°C to about 65°C is especially preferred. At temperatures above the boiling point of the THF, a pressure vessel may be needed to contain that monomer.

15 It is preferred to run the polymerization neat, that is in the absence of solvent. However, inert solvents such as ethyl ether or toluene may be present if desired. Mild agitation to keep the process ingredients well mixed is preferred. The polymerization
20 is mildly exothermic and agitation also prevents "hot spots" from forming. If the process temperature increases appreciably, refluxing of a volatile monomer (or solvent) may be used to cool the process. The polymerization may take as long as a day, however, more
25 common times are 1 to 2 hours. It is preferred to run the polymerization under dry (water free) conditions to avoid needless decomposition of the ingredients and/or products, and therefor the ingredients should also preferably be dry. It is convenient to use an inert
30 atmosphere such as dry nitrogen. The polymer may be isolated by removing volatiles by evaporation, or if the polymer is insoluble, by filtration. In general, the catalyst may be removed from the copolymer by washing the copolymer with water. In many cases, the catalyst
35 may be reused in the polymerization.

The molar ratio of the THF to cyclic carboxylic anhydride can be about 0.2 to about 60, preferably about 2 to about 15, and most preferably about 5.

The polymerization process may be carried out in a number of ways known to the artisan. It can be done by batch, semibatch and continuous processes. Continuous processes include continuous stirred tank reactor(s) and/or plug flow reactors.

The polymer produced by the instant process contains the repeat units $-OCHR^1CR^2R^3CR^2R^3CHR^4-$ and $-O(O)CQC(O)-$, wherein the repeat units are randomly incorporated, except that $-O(O)CQC(O)-$ cannot be adjacent to itself. The definitions of R^1 , R^2 , R^3 , R^4 and Q are as given above. The copolymers may be hydrogenated to a polytetrahydrofuran if succinic anhydride is used, or a mixed polyether if another anhydride is used. The copolymers, particularly those containing relatively small amounts of repeat units derived from cyclic carboxylic anhydrides, may also be completely hydrolyzed to polytetrahydrofuran. Such polyethers are useful (usually in their diol form) as monomers for condensation polymers such as polyesters or polyurethanes.

Synthesis of the catalysts used herein are demonstrated by Experiments 1-3 below.

EXPERIMENT 1

Preparation of Bis(*n*-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)hafnium

In a dry box, hafnocene dichloride (9.93 g) was dissolved in THF (300 mL). To this solution, with stirring, was added a solution of silver triflate (14.12 g) in THF (100 mL). After 10 minutes the precipitated silver chloride was filtered off and the resulting filtrate concentrated to approximately half its volume at reduced pressure. Hexane (250 mL) was



added and the resulting mixture placed in the freezer. The resulting precipitate was filtered and then dried under vacuum. Yield: 10.02 g. ^1H NMR (CDCl_3): 6.68 (s, 10 H), 3.76 (m, 4H), 1.84 (m, 4H).

5

EXPERIMENT 2

Preparation of Bis(pentamethyl-*n*-cyclopentadienyl)-bis(trifluoromethanesulfonato)zirconium

In a dry box, bis(pentamethylcyclopentadienyl)-zirconium dichloride (10.00 g) was dissolved in THF (300 mL). To this solution, with stirring, was added a solution of silver triflate (12.46 g) in THF (100 mL). After 15 minutes the precipitated silver chloride was filtered off and the resulting filtrate concentrated to approximately half its volume at reduced pressure. Hexane (250 mL) was added and the resulting mixture placed in the freezer. The resulting yellow precipitate was filtered and then dried under vacuum. Yield: 6.02 g. ^1H NMR (CDCl_3): 2.12 (s).

10

15

EXPERIMENT 3

20

Preparation of Bis(*n*-cyclopentadienyl)-bis(trifluoromethanesulfonato)vanadium

In a dry box, vanadocene dichloride (5.00 g) was dissolved in THF (300 mL). To this solution, with stirring, was added a solution of silver triflate (11.19 g) in THF (100 mL). After 15 minutes the precipitated silver chloride was filtered off and the resulting filtrate concentrated to approximately half its volume at reduced pressure. Hexane (250 mL) was added and the resulting mixture placed in the freezer. The resulting green precipitate was filtered and then dried under vacuum. Yield: 6.99 g.

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In the Examples, the following abbreviations are used:

35

GPC - gel permeation chromatography

Mn - number average molecular weight

Mw - weight average molecular weight

PD - polydispersity, Mw/Mn

PS - polystyrene

RB - round-bottomed

5 THF - the compound tetrahydrofuran

EXAMPLE 1

Yttrium Triflate Catalyzed Copolymerization of Maleic Anhydride and THF

In a dry box, yttrium triflate (1.00 g) and maleic
10 anhydride (2.00 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
and a nitrogen bleed attached. THF (20 mL) was added
via syringe. After 2 hrs. the polymerization was
15 terminated via the addition of water (25 mL) and THF
(50 mL), the organic phase was separated, concentrated
at reduced pressure and dried under vacuum. Polymer
yield: 3.38 g. GPC analysis: Mn = 96800, Mw = 188000,
PD = 1.95 (PS STD.). ¹H NMR analysis indicates the THF
20 to anhydride ratio to be ~15.

EXAMPLE 2

Yttrium Triflate Catalyzed Copolymerization of Succinic Anhydride and THF

In a dry box, yttrium triflate (1.00 g) and
25 succinic anhydride (2.00 g) were weighed in an oven
dried 100 mL RB flask equipped with a stirring bar.
After sealing with a rubber septum the flask was removed
from the dry box and a nitrogen bleed attached. THF
(20 mL) was added via syringe. After 2 hrs. the
30 polymerization was terminated via the addition of water
(25 mL) and THF (50 mL). The resulting organic phase
was separated, concentrated at reduced pressure and
dried under vacuum. Polymer yield: 5.00 g. GPC
analysis: Mn = 80900, Mw = 171000, PD = 2.12 (PS STD.).

¹H NMR analysis indicates the THF to anhydride ratio to be ~4.5.

EXAMPLE 3

Yttrium Triflate Catalyzed Copolymerization of Maleic Anhydride and THF at 40°C

5 In a dry box, yttrium triflate (1.00 g) and maleic anhydride (3.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum, the flask was removed from the dry
10 box and a nitrogen bleed attached, the flask was then placed in an oil bath maintained at 40°C. THF (20 mL) was then added via syringe. After 2 hrs. the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and diethyl ether (25 mL) the
15 resulting organic phase was separated, concentrated at reduced pressure and dried under vacuum. Polymer yield: 6.16 g. GPC analysis: Mn = 34800, Mw = 74100, PD = 2.13 (PS STD.).

EXAMPLE 4

Yttrium Triflate Catalyzed Copolymerization of Phthalic Anhydride and THF at 40°C

20 In a dry box, yttrium triflate (1.00 g) and phthalic anhydride (3.00 g) were 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. A nitrogen purge was attached and the flask placed in an oil bath maintained at 40°C. THF (20 mL) was immediately added and the resulting solution stirred at this temperature for 2 hrs. The
30 polymerization was terminated by the addition of water (25 mL) and THF (50 mL), the resulting organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 7.04 g. GPC analysis: Mn = 69400, Mw = 128000, PD = 1.85 (PS STD.).

^1H NMR analysis indicates the THF to anhydride ratio to be ~3.6.

EXAMPLE 5

5 Ytterbium Triflate Catalyzed Copolymerization
 of Cis-1,2-Cyclohexane-Dicarboxylic Anhydride
 and THF at 40°C

 In a dry box, ytterbium triflate (1.00 g) and
cis-1,2-cyclohexanedicarboxylic anhydride (1.5 g) were
weighed in an oven dried 100 mL RB flask equipped with a
10 stirring bar. The flask was sealed with a rubber septum
and removed from the dry box. A nitrogen purge was
attached and the flask placed in an oil bath maintained
at 40°C. THF (20 mL) was immediately added and the
resulting solution stirred at this temperature for
15 60 min. The polymerization was terminated by the
addition of water (25 mL) and THF (50 mL), the resulting
organic phase was separated, concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
9.26 g. GPC analysis: $M_n = 38100$, $M_w = 83500$,
20 PD = 2.15 (PS STD.).

EXAMPLE 6

Yttrium Triflate Catalyzed Copolymerization
 of Norbornene-2,3-dicarboxylic Anhydride
 and THF at 40°C

25 In a dry box, yttrium triflate (1.00 g) and
norbornene-2,3-dicarboxylic anhydride (4.0 g, 96%) 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
30 nitrogen purge THF (20 mL) was added and the resulting
solution stirred at room temperature for 60 min. The
polymerization was terminated by the addition of water
(25 mL) and THF (50 mL), the resulting organic phase was
separated, concentrated at reduced pressure and then

dried under vacuum. Polymer yield: 5.13 g. GPC analysis: $M_n = 52400$, $M_w = 111000$, $PD = 2.13$ (PS STD.).

EXAMPLE 7

5 Erbium Triflate Catalyzed Copolymerization of Cis-1,2-Cyclohexane-Dicarboxylic Anhydride and THF

 In a dry box, erbium triflate (1.00 g) and cis-1,2-cyclohexane-dicarboxylic anhydride (1.5 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum
10 and removed from the dry box. A nitrogen purge was attached, THF (20 mL) was immediately added and the resulting solution stirred at room temperature for 120 min. The polymerization was terminated by the addition of water (25 mL) and THF (50 mL), the resulting
15 organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 3.03 g.

EXAMPLE 8

20 Neodymium Triflate Catalyzed Copolymerization of Cis-1,2-Cyclohexanedicarboxylic Anhydride and THF

 In a dry box, neodymium triflate (1.00 g) and cis-1,2-cyclohexanedicarboxylic anhydride (1.5 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum
25 and removed from the dry box. A nitrogen purge was attached, THF (20 mL) was immediately added and the resulting solution stirred at room temperature for 120 min. The polymerization was terminated by the addition of water (25 mL) and THF (50 mL), the resulting
30 organic phase was separated, concentrated at reduced pressure and then dried under vacuum. Polymer yield: 1.39 g.

EXAMPLE 9Dysprosium Triflate Catalyzed Copolymerization of
Cis-1,2-Cyclohexanedicarboxylic Anhydride and THF

In a dry box, dysprosium triflate (1.00 g) and
5 cis-1,2-cyclohexanedicarboxylic anhydride (1.5 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. A nitrogen purge was
attached, THF (20 mL) was immediately added and the
10 resulting solution stirred at room temperature for
120 min. The polymerization was terminated by the
addition of water (25 mL) and THF (50 mL), the resulting
organic phase was separated, concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
15 1.96 g.

EXAMPLE 10Scandium Triflate Catalyzed Copolymerization of
Cis-1,2-Cyclohexanedicarboxylic Anhydride and THF

In a dry box, scandium triflate (1.00 g) and
20 cis-1,2-cyclohexanedicarboxylic anhydride (1.5 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. A nitrogen purge was
attached, THF (20 mL) was immediately added and the
25 resulting solution stirred at room temperature for
120 min. The polymerization was terminated by the
addition of water (25 mL) and THF (50 mL), the resulting
organic phase was separated, concentrated at reduced
pressure and then dried under vacuum. Polymer yield:
30 1.30 g.

EXAMPLE 11Ytterbium Triflate Catalyzed Copolymerization of
Succinic Anhydride, THF and 3-Methyl-THF

In a dry box, ytterbium triflate (2.00 g) and
35 succinic anhydride (2.00 g) were weighed in an oven

dried 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum the flask was removed from the dry box and a nitrogen bleed attached. THF (15.00 mL) and 3-methyl-THF (5.00 mL) were added via
5 syringe. After 2 hrs the polymerization was terminated via the addition of water (25 mL) and THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and dried under vacuum. Polymer yield: 4.32 g. GPC analysis
10 (PS STD.): Mn = 26100, Mw = 43100, PD = 1.65.

EXAMPLE 12

Ytterbium Triflate Catalyzed Copolymerization of Succinic Anhydride, THF and 3-Methyl-THF

In a dry box, ytterbium triflate (2.00 g) and
15 succinic anhydride, (3.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum the flask was removed from the dry box and a nitrogen bleed attached. THF (15.00 mL) and 3-methyl-THF (5.00 mL) were added via
20 syringe. After 2 hrs the polymerization was terminated via the addition of water (25 mL) and THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced pressure and dried under vacuum. Polymer yield: 7.27 g. GPC Analysis
25 (PS STD.): Mn = 30600, Mw = 52400, PD = 1.71.

EXAMPLE 13

Zirconium Triflate Catalyzed Copolymerization of 1,2,4,5-Benzenetetracarboxylic Dianhydride and THF

In a dry box, zirconium triflate (2.00 g) and
30 1,2,4,5-benzenetetracarboxylic dianhydride (4.00 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. After sealing with a rubber septum the flask was removed from the dry box and a nitrogen bleed attached. THF (20.00 mL) was added via syringe. After
35 2 hrs the polymerization was terminated via the addition

of water (25 mL). The resulting slurry was concentrated at reduced pressure, resulting in a thick viscous material. This material was washed repeatedly with water and then dried under vacuum. Polymer yield:

5 7.12 g.

EXAMPLE 14

Bis(n-cyclopentadienyl)tetrahydrofuran- bis(trifluoromethanesulfonato)zirconium Catalyzed Copolymerization of Maleic Anhydride and THF

10 In a dry box, bis(n-cyclopentadienyl)tetrahydrofuran-bis(trifluoromethanesulfonato)zirconium (0.50 g) and maleic anhydride (1.00 g) were added 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
15 box. After the attachment of a nitrogen bleed THF (10 mL) was added to the flask. After 75 min. the polymerization was terminated via the addition of water (25 mL), THF (50 mL) and ether (25 mL). The resulting organic phase was separated, concentrated at reduced
20 pressure and then dried under vacuum. Polymer yield: 0.73 g. GPC analysis (PS STD.): Mn = 56500, Mw = 71600, PD = 1.27.

EXAMPLE 15

Tin Triflate Catalyzed Copolymerization of 25 Cis-1,2-CyclohexaneDicarboxylic Anhydride and THF

In a dry box, tin triflate (1.00 g) and cis-1,2-cyclohexanedicarboxylic anhydride (1.5 g) were weighed in an oven dried 100 mL RB flask equipped with a stirring bar. The flask was sealed with a rubber septum
30 and removed from the dry box. A nitrogen purge was attached, THF (20 mL) was immediately added and the resulting solution stirred at room temperature for 120 min. The polymerization was terminated by the addition of water (25 mL) and THF (50 mL), the resulting
35 organic phase was separated, concentrated at reduced

pressure and then dried under vacuum. Polymer yield:
1.41 g.



What is claimed is:

1. A process for the production of a poly(ester-ether), comprising, contacting one or more cyclic carboxylic anhydrides, one or more tetrahydrofurans, and
5 a catalyst of the formula $MZ_s \cdot Q_t$, and an accelerator selected from the group consisting of carboxylic acids whose pKa in water is less than 6, carboxylic anhydrides and acyl halides, wherein:

- M is a metal selected from the group
10 consisting of cobalt, vanadium, niobium, tungsten, strontium, barium, scandium, yttrium, the rare earth metals, titanium, zirconium, hafnium, chromium, molybdenum, tantalum, rhenium, iron, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold,
15 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 $^{-}OSO_2R^5$, wherein R^5 is perfluoroalkyl containing 1 to 12
20 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;

- 25 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,
30 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;

- 35 s is 6 when M is tungsten;

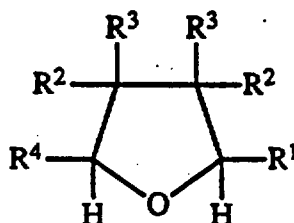
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Q is a neutral ligand;
t is 0 or an integer of 1 to 6; and
provided that each oxo group present counts as two
of s.

- 5 2. The process as recited in Claim 1 wherein said tetrahydrofuran has the formula



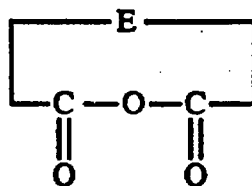
- 10 wherein each R¹, R², R³ and R⁴ is independently hydrogen or hydrocarbyl containing 1 to 20 carbon atoms.

3. The process as recited in Claim 2 wherein R¹, one of R², R³, and R⁴ are hydrogen, and remaining R² is alkyl containing 1 to 4 carbon atoms.

- 15 4. The process as recited in Claim 3 wherein said remaining R² is methyl.

5. The process as recited in Claim 2 wherein all of R¹, R², R³ and R⁴ are hydrogen.

- 20 6. The process as recited in Claim 1 wherein said carboxylic anhydride has the formula

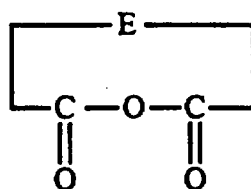


- 25 wherein E is a divalent organic radical which is bound to each free valence of the carboxylic anhydride group through a carbon atom.

7. The process as recited in Claim 2 wherein said carboxylic anhydride has the formula



20



wherein E is a divalent organic radical which is bound to each free valence of the carboxylic anhydride group through a carbon atom.

8. The process as recited in Claim 6 wherein E is n-alkylene containing 1 to 4 carbon atoms or alkyl substituted n-alkylene wherein said n-alkylene group contains 1 to 4 carbon atoms and E contains a total of 2 to 20 carbon atoms.

9. The process as recited in Claim 1 wherein said anhydride is selected from the group consisting of succinic, maleic, phthalic, 5-methyl-5-nobornene-dicarboxylic acid and 1,2-cyclohexanedicarboxylic acid anhydrides. preferred cyclic carboxylic anhydrides include maleic, succinic, phthalic and 1,2-cyclohexanedicarboxylic acid anhydrides.

10. The process as recited in Claim 9 wherein said anhydride is selected from the group consisting of maleic, succinic, phthalic and 1,2-cyclohexanedicarboxylic acid anhydrides.

11. 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.

12. The process as recited in Claim 1 wherein all of Z is an anion of the formula $^{-}\text{OSO}_2\text{R}^5$, and wherein R^5 is trifluoromethyl.



13. The process as recited in Claim 12 wherein all of Z is an anion of the formula $^{-}\text{OSO}_2\text{R}^5$, and wherein R^5 is trifluoromethyl.

14. The process as recited in Claim 1 wherein said process is carried out at a temperature of about -80°C to about 110°C .

15. The process as recited in Claim 15 wherein said temperature is about 0°C to about 110°C .

16. The process as recited in Claim 15 wherein said temperature is about 25°C to about 65°C .

17. The process as recited in Claim 1 carried out in the absence of solvent.

18. The process as recited in Claim 1 wherein the molar ratio of said tetrahydrofuran to said anhydride is about 0.2 to about 60.

19. The process as recited in Claim 18 wherein said ratio is about 2 to about 15.

20. The process as recited in Claim 19 wherein said ratio is about 5.

21. 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.