



(86) Date de dépôt PCT/PCT Filing Date: 2007/10/31
(87) Date publication PCT/PCT Publication Date: 2008/05/08
(85) Entrée phase nationale/National Entry: 2009/03/06
(86) N° demande PCT/PCT Application No.: US 2007/022988
(87) N° publication PCT/PCT Publication No.: 2008/054777
(30) Priorité/Priority: 2006/10/31 (US11/590,456)

(51) Cl.Int./Int.Cl. *C08G 63/672* (2006.01),
C08J 5/18 (2006.01), *C08K 5/00* (2006.01),
C08L 67/02 (2006.01), *D01F 6/86* (2006.01)
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(54) Titre : COMPOSITION ELASTOMERE D'ESTER DE POLYETHER
(54) Title: POLYETHER ESTER ELASTOMER COMPOSITION

(57) **Abrégé/Abstract:**

Disclosed are polyether ester elastomer compositions having polytrimethylene ether ester soft segments and polyethylene ester hard segments and containing a nucleating agent. Shaped articles can be made from these compositions, particularly molded articles, films and fibers.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 May 2008 (08.05.2008)

PCT

(10) International Publication Number
WO 2008/054777 A3

(51) International Patent Classification:

C08G 63/672 (2006.01) *C08J 5/18* (2006.01)
C08K 5/00 (2006.01) *D01F 6/86* (2006.01)
C08L 67/02 (2006.01)

(21) International Application Number:

PCT/US2007/022988

(22) International Filing Date: 31 October 2007 (31.10.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11/590,456 31 October 2006 (31.10.2006) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

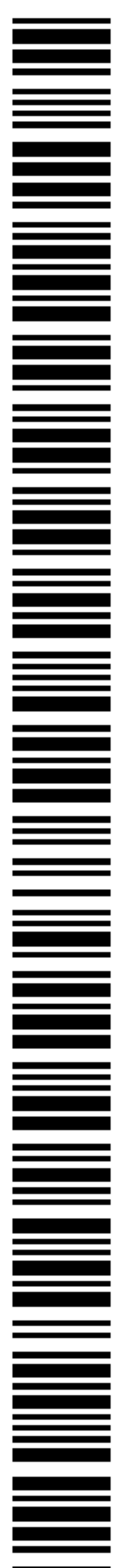
- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:

19 June 2008

(54) Title: POLYETHER ESTER ELASTOMER COMPOSITION

(57) Abstract: Disclosed are polyether ester elastomer compositions having polytrimethylene ether ester soft segments and polyethylene ester hard segments and containing a nucleating agent. Shaped articles can be made from these compositions, particularly molded articles, films and fibers.



WO 2008/054777 A3

TITLE

POLYETHER ESTER ELASTOMER COMPOSITION

This application claims the benefit of U.S. National Application No. 11/590,456,
5 filed October 31, 2006, which is incorporated in its entirety as a part hereof for all purposes.

FIELD OF THE INVENTION

This invention relates to thermoplastic polyether ester elastomers comprising
polytrimethylene ether ester soft segment and polyethylene terephthalate ester hard
10 segment containing nucleating agents, and manufacture and use thereof.

BACKGROUND OF THE INVENTION

Thermoplastic elastomers (TPEs) are a class of polymers which combine the
properties of two other classes of polymers, namely thermoplastics, which may be re-
formed upon heating, and elastomers which are rubber-like polymers. One form of
15 TPE is a block copolymer, usually containing some blocks whose polymer properties
usually resemble those of thermoplastics, and some blocks whose properties usually
resemble those of elastomers. Those blocks whose properties resemble thermoplas-
tics are often referred to as "hard" segments, while those blocks whose properties re-
semble elastomers are often referred to as "soft" segments. It is believed that the hard
20 segments provide properties similar to chemical crosslinks in traditional thermosetting
elastomers, while the soft segments provide rubber-like properties.

Polyether ester thermoplastic elastomers comprising polytrimethylene ether es-
ter soft segments and tetramethylene ester hard segments are known, for example,
from US6562457. Polyether ester thermoplastic elastomers comprising polytrimethyl-
25 ene ether ester soft segments and trimethylene ester hard segments are known, for
example, from US6599625. The polyether ester thermoplastic elastomers disclosed in
these publications and useful, for example, in making fibers, films and other shaped
articles.

Polyether ester thermoplastic elastomers comprising polytrimethylene ether es-
30 ter soft segments, in particular polytrimethylene terephthalate, and polyethylene ester

hard segments, in particular polyethylene terephthalate, have also been described
US20050282966A1. These flexible materials have a potential advantage for some
uses because the melting point and thermal stability of the polyethylene terephthalate
hard segments is higher than those of the hard segments based on tetramethylene or
5 trimethylene esters. Their utility, however, has been limited, particularly in engineering
resin applications, because of their relatively low rates of crystallization. In fact, the
unmodified polyether ester comprising polytrimethylene ether terephthalate soft seg-
ment and polyethylene terephthalate hard segment is unsuitable for most injection
molding applications. Low crystallization rates cause the polymer to be difficult to pel-
10 letize or flake, difficult to spin into fibers, and difficult to process into shaped articles by
such methods as thermoforming, injection molding and blow molding, because ejection
from the mold of an insufficiently crystallized molding would mean that the article could
continue to crystallize when in service with appropriate volume changes.

Additives such as crystallization nucleants and plasticizers that improve crystal-
15 lization rates of polyesters are in a general sense known. For example, US6245844
discloses polyester compositions comprising poly(trimethylene dicarboxylate) and a
nucleating agent that is a mono sodium salt of a dicarboxylic acid selected from the
group consisting of monosodium terephthalate, monosodium naphthalene dicarboxylic
acid, and monosodium isophthalate. It is, however, also generally known that a spe-
20 cific additive that works very efficiently for a particular polyester may not work well for
others.

US3761450 describes molding compositions based on linear saturated polyes-
ters comprising small amounts of lithium and/or sodium salts of polycarboxylic acids to
bring about a high crystallinity in the heated mold after a short time. Polyesters and
25 salts of polycarboxylic acids are disclosed generally. Poly(ethylene terephthalate) and
disodium 1,10-dodecanedicarboxylate are exemplified.

US5264477 discloses an improved melt processible liquid crystalline polyester
composition capable of forming an anisotropic melt phase and having an improved
heat distortion temperature under a load by using 0.05 to 1.0 wt% of a divalent metal
30 salt of an aromatic dicarboxylic acid, wherein the metal is zinc, calcium, cadmium, bar-
ium or mixtures thereof.

US4380621 discloses fast crystallizing polyesters in which at least some of the
acid end groups of the polyester have the formula $-\text{COO}^- \text{M}^+$, wherein M^+ is an alkaline

metal ion. Poly(ethylene terephthalate) and poly(butylene terephthalate) are disclosed as polyesters. Sodium containing species exemplified include sodium hydroxide, sodium benzoate and sodium o-chlorobenzoate.

5 There remains a need for nucleating agents that can improve the rate of crystallization of polyether ester thermoplastic elastomers comprising polytrimethylene ether ester soft segments and polyethylene ester hard segments and thereby take advantage of their high melting points in production of fibers, films and other shaped articles.

SUMMARY OF THE INVENTION

10 This invention is directed to a polyether ester elastomer composition comprising (i) a polyether ester elastomer based on a polytrimethylene ether ester soft segment and a polyethylene ester hard segment; and (ii) a nucleating agent selected from the group consisting of an alkali metal salt, an alkaline earth metal salt and mixtures thereof.

15 The amount of nucleating agent utilized is such that the polyether ester containing nucleating agent exhibits a lower crystallization half time and earlier onset of the crystallization time during the cooling phase of molding, as compared to the same polyether ester without nucleating agent (an "effective amount").

20 In one preferred embodiment of the invention, the polyether ester composition is prepared by the steps of providing and reacting:

(a) a polytrimethylene ether glycol ("PO3G");

(b) ethylene glycol; and

(c) a dicarboxylic acid equivalent,

in the presence of the nucleating agent.

25 In another preferred embodiment of the present invention, the polyether ester is prepared by the steps of:

(a) heating

(i) a polymeric ether glycol component comprising at least about 50 wt% PO3G,

(ii) terephthalic acid and/or dimethyl terephthalate,

(iii) a molar excess of a diol component comprising at least about 75 mole % ethylene glycol, and

(iv) a nucleating agent selected from the group consisting of an alkali metal salt, an alkaline earth metal salt and mixtures thereof,

5

in the presence of a catalyst at a temperature in the range of from about 150°C to about 250°C while removing water or methanol by-product to form a precondensation product; and

(b) polymerizing the precondensation product under vacuum at temperature in the range of from about 220°C to about 290°C while removing excess diol to form a polyether ester having polytrimethylene ether terephthalate soft segment and polyethylene terephthalate hard segment.

10

In yet another preferred embodiment, the polyether ester is prepared by the steps of:

(a) heating

15

(i) a polymeric ether glycol component comprising at least about 50 wt% PO3G,

(ii) terephthalic acid and/or dimethyl terephthalate, and

(iii) a molar excess of a diol component comprising at least about 75 mole % ethylene glycol,

20

in the presence of a catalyst at temperature in the range of from about 150°C to about 250°C while removing water and/or methanol by-product to form a precondensation product;

(b) adding a nucleating agent to the precondensation product, the nucleating agent being selected from the group consisting of an alkali metal salt, an alkaline earth metal salt and mixtures thereof; and

25

(c) polymerizing the precondensation product under vacuum at a temperature in the range of from about 220°C to about 290°C while removing excess diol to form a

polyether ester having polytrimethylene ether terephthalate soft segment and polyethylene terephthalate hard segment.

The invention also relates to shaped articles prepared from the polyether ester, such as fibers and films.

5 Polyether esters containing the nucleating agents in accordance with the present invention exhibit short crystallization half times ($t_{1/2}$) and early onsets of crystallization as measured by differential scanning calorimeter (DSC) in the heating and cooling cycle. Crystallization half time is the time needed for the degree of crystallinity to reach
10 half of its ultimate value. The higher the onset crystallization temperature (T_{rc}), the faster the crystallization rate. The presence of the nucleating agent used in accordance with the present invention lowers the crystallization half time of the polymer and speeds up the onset of the crystallization time (as well as the early appearance of the crystallization peak temperature) during the cooling phase of the polymer, all as measured by DSC analysis, to the extent necessary to effectively utilize the polymer in a variety of end-use applications.
15

These are desirable effects because such polymers can quickly become rigid, leading to faster demold times and shorter cycle times in processing them into shaped articles by such methods as thermoforming, injection molding, and blow molding. The ability to melt spin the polyether ester into fiber is also greatly enhanced by the effects
20 of the nucleating agents.

A further result achieved by the practice of this invention is the improvement of physical properties of polyester polymers by increasing the crystallization rate and increasing the crystallinity.

When the compositions of this invention are compared to the same polyether
25 ester polymers containing no nucleating agent, the polymers containing nucleating agent exhibit lower crystallization half times and earlier onsets of the crystallization time (early arrival of the crystallization peak temperature) during the cooling phase. It has also been found that the polyether ester comprising polytrimethylene ether ester soft segment and polyethylene ester hard segment exhibits improvement in brittleness,
30 heat resistance and impact resistance.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

5 Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

Except where expressly noted, trademarks are shown in upper case.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

10 When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical
15 values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

20 When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

25 As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present)
30 and B is true (or present), and both A and B are true (or present).

Use of "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

5 The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

10 As indicated above, the present invention is directed to a polyether ester composition comprising a certain polyether ester elastomer containing a specified nucleating agent.

The polyether ester elastomer preferably comprises:

15 from about 10 to about 90 wt%, more preferably from about 20 to about 80 wt%, and still more preferably from about 30 to about 70 wt%, polytrimethylene ether ester soft segment, and

from about 10 to about 90 wt%, more preferably from about 20 to about 80 wt%, and still more preferably from about 30 to about 70 wt%, polyethylene ester hard segment,

based on the weight of the polyether ester elastomer.

20 The polyether ester elastomer preferably has an inherent viscosity of at least about 0.6 dl/g, more preferably at least about 1.0 dl/g, and preferably up to about 2.4 dl/g, more preferably up to about 1.9 dl/g.

25 "Polytrimethylene ether ester soft segment" and "soft segment" are used in connection with the present invention to refer to the reaction product of a polymeric ether glycol and a "dicarboxylic acid equivalent", via ester linkage, wherein at least about 50 wt%, more preferably at least about 85 wt%, and still more preferably from about 95 to 100 wt%, of the polymeric ether glycol used to form the soft segment is PO3G.

30 "Polyethylene ester hard segment" and "hard segment" are used in connection with the present invention to refer to the reaction product of one or more diols and one

or more dicarboxylic acid equivalents, via ester linkage, wherein greater than about 50 mole%, more preferably at least about 75 mole%, even more preferably at least about 85 mole%, and still more preferably from about 95 to 100 mole%, of the diol used to form the hard segment is ethylene glycol.

5 By "dicarboxylic acid equivalent" is meant dicarboxylic acids and their equivalents, which are compounds that perform substantially like dicarboxylic acids in reaction with polymeric glycols and diols, as would be generally recognized by a person of ordinary skill in the relevant art. In addition to dicarboxylic acids, dicarboxylic acid
10 equivalents for the purpose of the present invention include, for example, mono- and diesters of dicarboxylic acids, and diester-forming derivatives such as acid halides (e.g., acid chlorides) and anhydrides.

Polymeric Ether Glycol for Soft Segment

PO3G for the purposes of the present invention is an oligomeric and/or polymeric ether glycol in which at least 50% of the repeating units are trimethylene ether units.
15 More preferably from about 75% to 100%, still more preferably from about 90% to 100%, and even more preferably from about 99% to 100%, of the repeating units are trimethylene ether units.

PO3G is preferably prepared by polycondensation of monomers comprising 1,3-propanediol, thus resulting in polymers or copolymers containing $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})-$
20 linkage (e.g, trimethylene ether repeating units).

In addition to the trimethylene ether units, lesser amounts of other units, such as other polyalkylene ether repeating units, may be present. In the context of this disclosure, the term "polytrimethylene ether glycol" encompasses PO3G made from essentially pure 1,3-propanediol, as well as those oligomers and polymers (including
25 those described below) containing up to 50% by weight of comonomers.

The 1,3-propanediol employed for preparing the PO3G may be obtained by any of the various well known chemical routes or by biochemical transformation routes. Preferred routes are described in, for example, US5015789, US5276201, US5284979, US5334778, US5364984, US5364987, US5633362, US5686276, US5821092,
30 US5962745, US6140543, US6232511, US6235948, US6277289, US6297408, US6331264, US6342646, US7038092, US20040225161A1, US20040260125A1, US20040225162A1 and US20050069997A1.

Preferably, the 1,3-propanediol is obtained biochemically from a renewable source ("biologically-derived" 1,3-propanediol).

5 A particularly preferred source of 1,3-propanediol is via a fermentation process using a renewable biological source. As an illustrative example of a starting material from a renewable source, biochemical routes to 1,3-propanediol (PDO) have been described that utilize feedstocks produced from biological and renewable resources such as corn feed stock. For example, bacterial strains able to convert glycerol into 1,3-propanediol are found in the species *Klebsiella*, *Citrobacter*, *Clostridium*, and *Lactobacillus*. The technique is disclosed in several publications, including previously incorporated
10 US5633362, US5686276 and US5821092. US5821092 discloses, *inter alia*, a process for the biological production of 1,3-propanediol from glycerol using recombinant organisms. The process incorporates *E. coli* bacteria, transformed with a heterologous pdu diol dehydratase gene, having specificity for 1,2-propanediol. The transformed *E. coli* is grown in the presence of glycerol as a carbon source and 1,3-propanediol is isolated from the growth media. Since both bacteria and yeasts can
15 convert glucose (e.g., corn sugar) or other carbohydrates to glycerol, the processes disclosed in these publications provide a rapid, inexpensive and environmentally responsible source of 1,3-propanediol monomer.

The biologically-derived 1,3-propanediol, such as produced by the processes
20 described and referenced above, contains carbon from the atmospheric carbon dioxide incorporated by plants, which compose the feedstock for the production of the 1,3-propanediol. In this way, the biologically-derived 1,3-propanediol preferred for use in the context of the present invention contains only renewable carbon, and not fossil fuel-based or petroleum-based carbon. The PO3G and elastomers based thereon utilizing the biologically-derived 1,3-propanediol, therefore, have less impact on the environment as the 1,3-propanediol used in the compositions does not deplete diminishing fossil fuels and, upon degradation, releases carbon back to the atmosphere for use by plants once again. Thus, the compositions of the present invention can be characterized as more natural and having less environmental impact than similar compositions
25 comprising petroleum based glycols.
30

The biologically-derived 1,3-propanediol, and PO3G and elastomers based thereon, may be distinguished from similar compounds produced from a petrochemical source or from fossil fuel carbon by dual carbon-isotopic finger printing. This method usefully distinguishes chemically-identical materials, and apportions carbon in the co-

polymer by source (and possibly year) of growth of the biospheric (plant) component. The isotopes, ^{14}C and ^{13}C , bring complementary information to this problem. The radiocarbon dating isotope (^{14}C), with its nuclear half life of 5730 years, clearly allows one to apportion specimen carbon between fossil ("dead") and biospheric ("alive") feedstocks (Currie, L. A. "Source Apportionment of Atmospheric Particles," Characterization of Environmental Particles, J. Buffle and H.P. van Leeuwen, Eds., 1 of Vol. I of the IUPAC Environmental Analytical Chemistry Series (Lewis Publishers, Inc) (1992) 3-74). The basic assumption in radiocarbon dating is that the constancy of ^{14}C concentration in the atmosphere leads to the constancy of ^{14}C in living organisms. When dealing with an isolated sample, the age of a sample can be deduced approximately by the relationship:

$$t = (-5730/0.693)\ln(A/A_0)$$

wherein t = age, 5730 years is the half-life of radiocarbon, and A and A_0 are the specific ^{14}C activity of the sample and of the modern standard, respectively (Hsieh, Y., Soil Sci. Soc. Am J., 56, 460, (1992)). However, because of atmospheric nuclear testing since 1950 and the burning of fossil fuel since 1850, ^{14}C has acquired a second, geochemical time characteristic. Its concentration in atmospheric CO_2 , and hence in the living biosphere, approximately doubled at the peak of nuclear testing, in the mid-1960s. It has since been gradually returning to the steady-state cosmogenic (atmospheric) baseline isotope rate ($^{14}\text{C}/^{12}\text{C}$) of *ca.* 1.2×10^{-12} , with an approximate relaxation "half-life" of 7-10 years. (This latter half-life must not be taken literally; rather, one must use the detailed atmospheric nuclear input/decay function to trace the variation of atmospheric and biospheric ^{14}C since the onset of the nuclear age.) It is this latter biospheric ^{14}C time characteristic that holds out the promise of annual dating of recent biospheric carbon. ^{14}C can be measured by accelerator mass spectrometry (AMS), with results given in units of "fraction of modern carbon" (f_M). f_M is defined by National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) 4990B and 4990C, known as oxalic acids standards HOxI and HOxII, respectively. The fundamental definition relates to 0.95 times the $^{14}\text{C}/^{12}\text{C}$ isotope ratio HOxI (referred to AD 1950). This is roughly equivalent to decay-corrected pre-Industrial Revolution wood. For the current living biosphere (plant material), $f_M \approx 1.1$.

The stable carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$) provides a complementary route to source discrimination and apportionment. The $^{13}\text{C}/^{12}\text{C}$ ratio in a given biosourced material is a consequence of the $^{13}\text{C}/^{12}\text{C}$ ratio in atmospheric carbon dioxide at the time

the carbon dioxide is fixed and also reflects the precise metabolic pathway. Regional variations also occur. Petroleum, C₃ plants (the broadleaf), C₄ plants (the grasses), and marine carbonates all show significant differences in ¹³C/¹²C and the corresponding δ¹³C values. Furthermore, lipid matter of C₃ and C₄ plants analyze differently than materials derived from the carbohydrate components of the same plants as a consequence of the metabolic pathway. Within the precision of measurement, ¹³C shows large variations due to isotopic fractionation effects, the most significant of which for the instant invention is the photosynthetic mechanism. The major cause of differences in the carbon isotope ratio in plants is closely associated with differences in the pathway of photosynthetic carbon metabolism in the plants, particularly the reaction occurring during the primary carboxylation, i.e., the initial fixation of atmospheric CO₂. Two large classes of vegetation are those that incorporate the "C₃" (or Calvin-Benson) photosynthetic cycle and those that incorporate the "C₄" (or Hatch-Slack) photosynthetic cycle. C₃ plants, such as hardwoods and conifers, are dominant in the temperate climate zones. In C₃ plants, the primary CO₂ fixation or carboxylation reaction involves the enzyme ribulose-1,5-diphosphate carboxylase and the first stable product is a 3-carbon compound. C₄ plants, on the other hand, include such plants as tropical grasses, corn and sugar cane. In C₄ plants, an additional carboxylation reaction involving another enzyme, phosphoenol-pyruvate carboxylase, is the primary carboxylation reaction. The first stable carbon compound is a 4-carbon acid, which is subsequently decarboxylated. The CO₂ thus released is refixed by the C₃ cycle.

Both C₄ and C₃ plants exhibit a range of ¹³C/¹²C isotopic ratios, but typical values are ca. -10 to -14 per mil (C₄) and -21 to -26 per mil (C₃) (Weber et al., J. Agric. Food Chem., 45, 2942 (1997)). Coal and petroleum fall generally in this latter range. The ¹³C measurement scale was originally defined by a zero set by pee dee belemnite (PDB) limestone, where values are given in parts per thousand deviations from this material. The "δ¹³C" values are in parts per thousand (per mil), abbreviated ‰, and are calculated as follows:

$$\delta^{13}\text{C} \equiv \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000\text{‰}$$

Since the PDB reference material (RM) has been exhausted, a series of alternative RMs have been developed in cooperation with the IAEA, USGS, NIST, and other selected international isotope laboratories. Notations for the per mil deviations from PDB

is $\delta^{13}\text{C}$. Measurements are made on CO_2 by high precision stable ratio mass spectrometry (IRMS) on molecular ions of masses 44, 45 and 46.

Biologically-derived 1,3-propanediol, and compositions comprising biologically-derived 1,3-propanediol, therefore, may be completely distinguished from their petrochemical derived counterparts on the basis of ^{14}C (f_M) and dual carbon-isotopic fingerprinting, indicating new compositions of matter. The ability to distinguish these products is beneficial in tracking these materials in commerce. For example, products comprising both "new" and "old" carbon isotope profiles may be distinguished from products made only of "old" materials. Hence, the instant materials may be followed in commerce on the basis of their unique profile and for the purposes of defining competition, for determining shelf life, and especially for assessing environmental impact.

Preferably the 1,3-propanediol used as the reactant or as a component of the reactant will have a purity of greater than about 99%, and more preferably greater than about 99.9%, by weight as determined by gas chromatographic analysis. Particularly preferred are the purified 1,3-propanediols as disclosed in previously incorporated US7038092, US20040260125A1, US20040225161A1 and US20050069997A1, as well as PO3G made therefrom as disclosed in US20050020805A1.

The purified 1,3-propanediol preferably has the following characteristics:

(1) an ultraviolet absorption at 220 nm of less than about 0.200, and at 250 nm of less than about 0.075, and at 275 nm of less than about 0.075; and/or

(2) a composition having $L^*a^*b^*$ "b*" color value of less than about 0.15 (ASTM D6290), and an absorbance at 270 nm of less than about 0.075; and/or

(3) a peroxide composition of less than about 10 ppm; and/or

(4) a concentration of total organic impurities (organic compounds other than 1,3-propanediol) of less than about 400 ppm, more preferably less than about 300 ppm, and still more preferably less than about 150 ppm, as measured by gas chromatography.

The starting material for making PO3G will depend on the desired PO3G, availability of starting materials, catalysts, equipment, etc., and comprises "1,3-propanediol reactant." By "1,3-propanediol reactant" is meant 1,3-propanediol, and oligomers and prepolymers of 1,3-propanediol preferably having a degree of polymerization of 2 to 9,

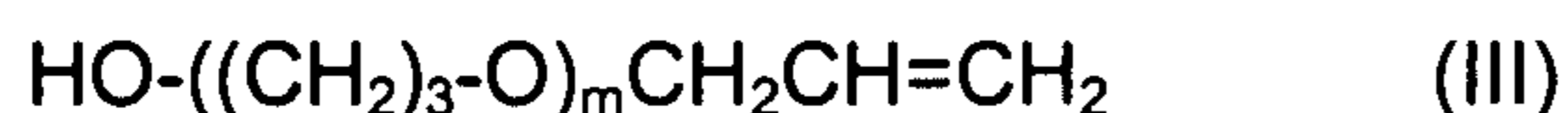
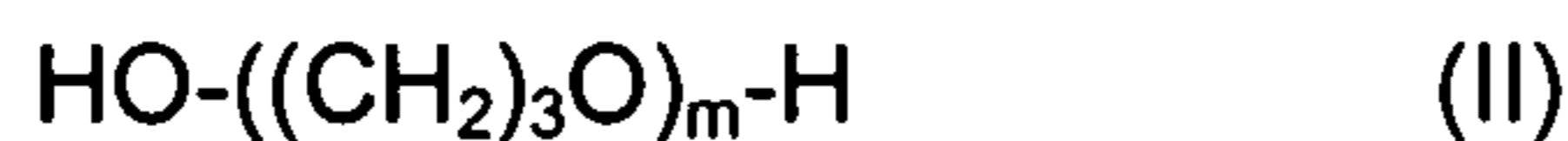
and mixtures thereof. In some instances, it may be desirable to use up to 10% or more of low molecular weight oligomers where they are available. Thus, preferably the starting material comprises 1,3-propanediol and the dimer and trimer thereof. A particularly preferred starting material is comprised of about 90% by weight or more 1,3-
5 propanediol, and more preferably about 99% by weight or more 1,3-propanediol, based on the weight of the 1,3-propanediol reactant.

PO3G can be made via a number of processes known in the art, such as disclosed in US6977291 and US6720459. A preferred process is as set forth in previously incorporated US20050020805A1.

10 As indicated above, PO3G may contain lesser amounts of other polyalkylene ether repeating units in addition to the trimethylene ether units. The monomers for use in preparing polytrimethylene ether glycol can, therefore, contain up to 50% by weight (preferably about 20 wt% or less, more preferably about 10 wt% or less, and still more preferably about 2 wt% or less), of comonomer polyols in addition to the
15 1,3-propanediol reactant. Suitable comonomer polyols include aliphatic diols, for example, ethylene glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 3,3,4,4,5,5-hexafluoro-1,5-pentanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, and
20 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-dodecanediol; cycloaliphatic diols, for example, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol and isosorbide; and polyhydroxy compounds, for example, glycerol, trimethylolpropane and pentaerythritol. A preferred group of comonomer diols is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, C₆ – C₁₀ diols (such as
25 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol) and isosorbide, and mixtures thereof. Particularly preferred diols other than 1,3-propanediol include ethylene glycol, 2-methyl-1,3-propanediol and C₆ – C₁₀ diols.

30 One preferred PO3G containing comonomers is poly(trimethylene-ethylene ether) glycol such as described in US20040030095A1. Preferred poly(trimethylene-ethylene ether) glycols are prepared by acid catalyzed polycondensation of from greater than 50 to about 99 mole% (preferably from about 60 to about 98 mole%, and more preferably from about 70 to about 98 mole%) 1,3-propanediol, and up to 50 to about 1 mole% (preferably from about 40 to about 2 mole%, and more preferably from about 30 to about 2 mole%) ethylene glycol.

Preferably, the PO3G after purification has essentially no acid catalyst end groups, but may contain very low levels of unsaturated end groups, predominately allyl end groups, in the range of from about 0.003 to about 0.03 meq/g. Such a PO3G can be considered to comprise (consist essentially of) the compounds having the following
 5 formulae (II) and (III):



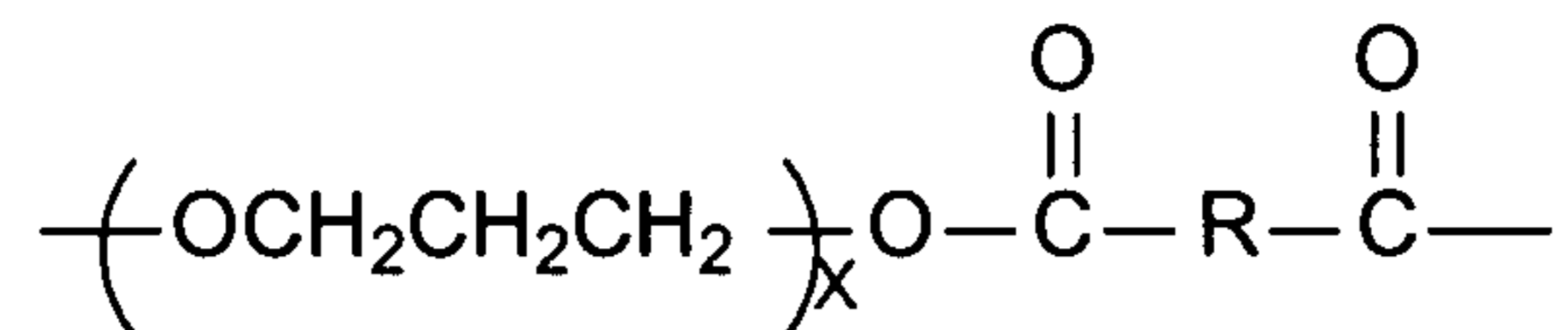
wherein m is in a range such that the Mn (number average molecular weight) is within the range of from about 200 to about 5000, with compounds of formula (III) being pre-
 10 sent in an amount such that the allyl end groups (preferably all unsaturation ends or end groups) are present in the range of from about 0.003 to about 0.03 meq/g. The small number of allyl end groups in the PO3G are useful to control elastomer molecular weight, while not unduly restricting it, so that compositions ideally suited, for example, for fiber end-uses can be prepared.

15 The preferred PO3G for use in the invention has an Mn of at least about 250, more preferably at least about 1000, and still more preferably at least about 2000. The Mn is preferably less than about 5000, more preferably less than about 4000, and still more preferably less than about 3500. Blends of PO3Gs can also be used. For ex-
 20 ample, the PO3G can comprise a blend of a higher and a lower molecular weight PO3G, preferably wherein the higher molecular weight PO3G has a number average molecular weight of from about 1000 to about 5000, and the lower molecular weight PO3G has a number average molecular weight of from about 200 to about 950. The Mn of the blended PO3G will preferably still be in the ranges mentioned above.

25 PO3G preferred for use herein is typically a polydisperse polymer having a polydispersity (i.e. Mw/Mn) of preferably from about 1.0 to about 2.2, more preferably from about 1.2 to about 2.2, and still more preferably from about 1.5 to about 2.1. The polydispersity can be adjusted by using blends of PO3G.

PO3G for use in the present invention preferably has a color value of less than about 100 APHA, and more preferably less than about 50 APHA.

When a PO3G based substantially on 1,3-propanediol is used to form the soft segment, the soft segment can be represented as comprising units represented by the following structure:

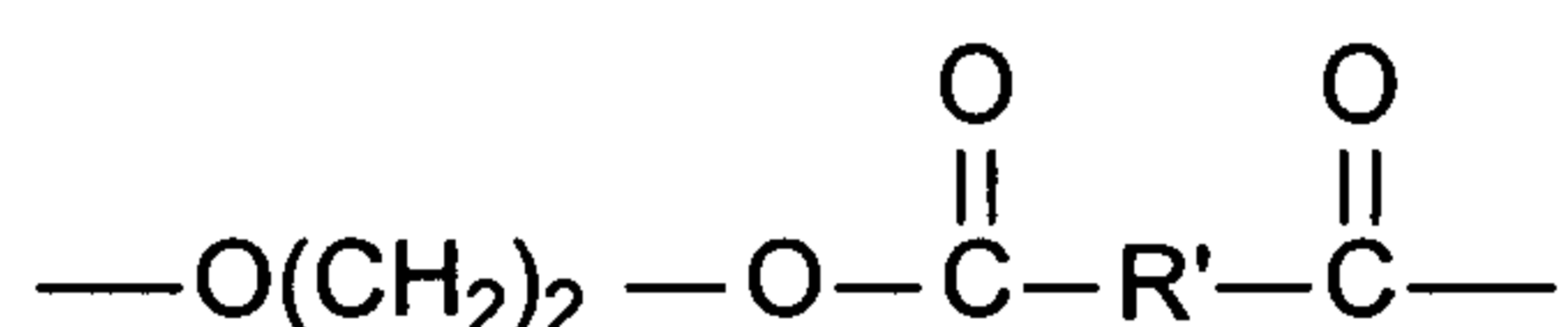


- 5 wherein R represents a divalent radical remaining after removal of carboxyl functionalities from a dicarboxylic acid equivalent, and x is a whole number representing the number of trimethylene ether units in the PO3G.

The polymeric ether glycol used to prepare the polytrimethylene ether ester soft segment of the polyether ester may also include up to 50 wt% of a polymeric ether glycol other than PO3G. Preferred such other polymeric ether glycols include, for example, polyethylene ether glycol, polypropylene ether glycol, polytetramethylene ether glycol, polyhexamethylene ether glycol, copolymers of tetrahydrofuran and 3-alkyl tetrahydrofuran, and mixtures thereof.

Diol for Hard Segment

- 15 When ethylene glycol is used to form the hard segment, the hard segment can be represented as comprising units having the following structure:



- 20 wherein R' represents a divalent radical remaining after removal of carboxyl functionalities from a dicarboxylic acid equivalent. In most cases, the dicarboxylic acid equivalents used to prepare the soft segment and the hard segment of the polyether ester of this invention will be the same.

- 25 The hard segment can also be prepared with less than 50 mole %, preferably up to about 25 mole %, more preferably up to about 15 mole %, and still more preferably up to about 5 mole %, of diols other than ethylene glycol, preferably having a molecular weight lower than about 400. The other diols are preferably aliphatic diols and can be acyclic or cyclic. Preferred are diols with 3-15 carbon atoms such as trimethylene, tetramethylene, isobutylene, butylene, pentamethylene, 2,2-dimethyltrimethylene, 2-methyltrimethylene, hexamethylene and decamethylene glycols; dihydroxy cyclohex-

ane; cyclohexane dimethanol; and hydroquinone bis(2-hydroxyethyl) ether. More preferred are aliphatic diols containing 3-8 carbon atoms, especially 1,3-propanediol (trimethylene glycol) and/or 1,4-butanediol (tetramethylene glycol). Two or more other diols can be used.

5 Dicarboxylic Acid Equivalent

The dicarboxylic acid equivalent can be aromatic, aliphatic or cycloaliphatic. In this regard, "aromatic dicarboxylic acid equivalents" are dicarboxylic acid equivalents in which each carboxyl group is attached to a carbon atom in a benzene ring system such as those mentioned below. "Aliphatic dicarboxylic acid equivalents" are dicarboxylic acid equivalents in which each carboxyl group is attached to a fully saturated carbon atom or to a carbon atom which is part of an olefinic double bond. If the carbon atom is in a ring, the equivalent is "cycloaliphatic." The dicarboxylic acid equivalent can contain any substituent groups or combinations thereof, so long as the substituent groups do not interfere with the polymerization reaction or adversely affect the properties of the polyether ester product.

Preferred are the dicarboxylic acid equivalents selected from the group consisting of dicarboxylic acids and diesters of dicarboxylic acids. More preferred are dimethyl esters of dicarboxylic acids.

Preferred are the aromatic dicarboxylic acids or diesters by themselves, or with small amounts of aliphatic or cycloaliphatic dicarboxylic acids or diesters. Especially preferred are the dimethyl esters of aromatic dicarboxylic acids.

Representative aromatic dicarboxylic acids useful in the present invention include terephthalic acid, isophthalic acid, bibenzoic acid, naphthalic acid, substituted dicarboxylic compounds with benzene nuclei such as bis(p-carboxyphenyl)methane, 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 4,4'-sulfonyl dibenzoic acid, and C1-C10 alkyl and other ring substitution derivatives such as halo, alkoxy or aryl derivatives. Hydroxy acids such as p-(hydroxyethoxy)benzoic acid can also be used providing an aromatic dicarboxylic acid is also present. Representative aliphatic and cycloaliphatic dicarboxylic acids useful in this invention are sebacic acid, 1,3- or 1,4-cyclohexane dicarboxylic acid, adipic acid, dodecanedioic acid, glutaric acid, succinic acid, oxalic acid, azelaic acid, diethylmalonic acid, fumaric acid, citraconic acid, allylmalonate acid, 4-cyclohexene-1,2-dicarboxylate acid, pimelic acid, suberic acid, 2,5-diethyladipic acid, 2-ethylsuberic

acid, 2,2,3,3-tetramethyl succinic acid, cyclopentanenedicarboxylic acid, decahydro-1,5- (or 2,6-)naphthalene dicarboxylic acid, 4,4'-bicyclohexyl dicarboxylic acid, 4,4'methylenebis(cyclohexylcarboxylic acid), 3,4-furan dicarboxylate, and 1,1-cyclobutane dicarboxylate. The dicarboxylic acid equivalents in the form of diesters, acid halides and anhydrides of the aforementioned aliphatic dicarboxylic acids are also useful to provide the polyether ester of the present invention. Representative aromatic diesters include dimethyl terephthalate, bibenzoate, isophthalate, phthalate and naphthalate.

Of the above, preferred are terephthalic, bibenzoic, isophthalic and naphthalic acid; dimethyl terephthalate, bibenzoate, isophthalate, naphthalate and phthalate; and mixtures thereof. Particularly preferred dicarboxylic acid equivalents are the equivalents of phenylene dicarboxylic acids especially those selected from the group consisting of terephthalic and isophthalic acid and their diesters, especially the dimethyl esters, dimethyl terephthalate and dimethyl isophthalate. In addition, two or more dicarboxylic acids equivalents can be used. For instance, terephthalic acid and/or dimethyl terephthalate can be used with small amounts of the other dicarboxylic acid equivalents.

In a preferred embodiment, at least about 70 mole% (more preferably at least about 80 mole%, still more preferably at least about 90 mole%, and still more preferably from about 95 to 100 mole%) of the dicarboxylic acid equivalent is terephthalic acid and/or dimethyl terephthalate.

Nucleating Agent

The compositions of the invention include a nucleating agent. Preferred nucleating agents for use in the invention are alkali metal (Group IA) or alkaline earth metal (Group IIA) salts of, for example, sulfinates, phosphinates, phosphates, sulfates, sulfonates, phosphates, hydroxides, aliphatic carboxylates and aromatic carboxylates. That is, the salts comprise an alkali metal (lithium, sodium, potassium, rubidium or cesium) or alkaline earth metal (magnesium, calcium, strontium, or barium) cation and an anion preferably selected from the group consisting of carboxylate, sulfinate, phosphinate, sulfate, sulfonate, phosphate, hydroxide, aliphatic carboxylate and aromatic carboxylate. Preferred metal cations are lithium, sodium, potassium and calcium. Preferred anions are phosphate, sulfate, aliphatic carboxylates such as acetate and propionate, and aromatic carboxylates such as benzoate acid, terephthalate, isophthalate

and phthalate. Particularly preferred nucleating agents are trisodium phosphate and sodium acetate.

Preferably the nucleating agent is present at a level of from about 0.005 to about 2 wt%, and more preferably from about 0.01 to about 1 wt%, based on the weight of the polyethylene ester hard segment.

Process of Making

The polyether ester is preferably prepared by providing and reacting (a) a PO3G, (b) ethylene glycol and (c) a dicarboxylic acid equivalent. The other glycols, diols, etc., as described above are can also be provided and reacted.

10 The polyether ester of this invention is conveniently made starting with a conventional ester exchange reaction, esterification or transesterification depending on the starting dicarboxylic acid equivalent. For example, dimethyl terephthalate is heated with polytrimethylene ether glycol and an excess of ethylene glycol in the presence of a catalyst at 150-250°C, while distilling off the methanol formed by the ester exchange.

15 This reaction is typically performed at a pressure of about 1 atmosphere. The reaction product, referred to herein as "precondensation product", is a mixture of the ester exchange reaction products of the dimethyl terephthalate and the polytrimethylene ether glycol and ethylene glycol, primarily bis(hydroxyethyl) terephthalate with varying amounts of (hydroxy-polytrimethylene ether) terephthalates, along with a small amount

20 of the corresponding oligomers. This precondensation product mixture then undergoes polymerization or polycondensation to a copolymer of an elastomeric polyether ester with a polytrimethylene ether glycol soft segment and a polyethylene terephthalate hard segment (condensation product of ethylene glycol and dimethyl terephthalate). The polymerization (polycondensation) involves additional ester exchange and distillation to remove the diol to increase molecular weight. The polycondensation is typically performed under vacuum. Pressure is typically in the range of from about 0.01 to about 18 mm Hg (1.3 to 2400 Pa), preferably in the range of from about 0.05 to about 4 mm Hg (6.7 to 553 Pa), and more preferably from about 0.05 to about 2 mm Hg. The polycondensation is typically carried out at a temperature in the range of from about

25 220°C to about 290°C.

30 The precondensation (ester exchange) and polymerization steps may involve alternative processes than those described above. For example, polytrimethylene ether glycol can be reacted with polydimethylene ester (e.g., polyethylene terephthalate) in

the presence of catalyst (such as those described for the ester exchange, preferably the titanium catalysts such as tetrabutyl titanate) until randomization occurs. Both processes result in block copolymers.

To avoid excessive residence time at high temperatures and possible accompanying thermal degradation, a catalyst can be (and preferably is) employed in the ester exchange. Catalysts useful in the ester exchange process include organic and inorganic compounds of titanium, lanthanum, tin, antimony, zirconium, manganese, zinc, phosphorus and mixtures thereof. Manganese acetate is a preferred transesterification catalyst and antimony trioxide is a preferred polycondensation catalyst. Titanium catalysts, such as tetraisopropyl titanate and tetrabutyl titanate, are also preferred and are added in an amount of at least about 25 ppm (preferably at least about 50 ppm and more preferably at least about 100 ppm) and up to about 1000 ppm (preferably up to about 500 ppm and more preferably up to about 400 ppm) titanium by weight, based on the weight of the finished polymer. Additional catalyst may be added after ester exchange or direct esterification reaction and prior to polymerization.

Ester exchange polymerizations are generally conducted in the melt without added solvent, but inert solvents can be added to facilitate removal of volatile components, such as water and diols at low temperatures. This technique is useful during reaction of the polytrimethylene ether glycol or the diol with the dicarboxylic acid equivalent, especially when it involves direct esterification, i. e., the dicarboxylic acid equivalent is a diacid. Other special polymerization techniques can be useful for preparation of specific polymers. Polymerization (polycondensation) can also be accomplished in the solid phase by heating divided solid product from the reaction of polytrimethylene ether glycol, a dicarboxylic acid equivalent, and ethylene glycol in a vacuum or in a stream of inert gas to remove liberated diol. This type of polycondensation is referred to herein as "solid phase polymerization" (or abbreviated "SPP").

Batch or continuous methods can be used for the processes described above or for any stage of polyether ester preparation. Continuous polymerization, by ester exchange, is preferred.

In preparing the polyether ester elastomers of this invention, it is sometimes desirable to incorporate known branching agents to increase melt strength. In such instances, a branching agent is typically used in a concentration of from about 0.00015 to about 0.005 equivalents per 100 grams of polymer. The branching agent can be a

polyol having 3-6 hydroxyl groups, a polycarboxylic acid having 3 or 4 carboxyl groups, or a hydroxy acid having a total of 3-6 hydroxyl and carboxyl groups. Representative polyol branching agents include glycerol, sorbitol, pentaerytritol, 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane, trimethylol propane, and 1,2,6-hexane triol. Suitable polycarboxylic acid branching agents include hemimellitic, trimellitic, trimesic pyromellitic, 1,1,2,2-ethanetetracarboxylic, 1,1,2-ethanetricarboxylic, 1,3,5-pentanetricarboxylic, 1,2,3,4-cyclopentanetetracarboxylic and like acids. Although the acids can be used as is, it is preferred to use them in the form of their lower alkyl esters.

10 Properties of the polyether ester will be influenced by varying the composition (dicarboxylic acid equivalent, ethylene glycol, polytrimethylene ether glycol, other diol, other glycol, etc.), the weight % of hard segment, and the mole ratio of hard segment to soft segment. Depending on amount of polytrimethylene ether glycol incorporated, a soft rubbery elastomer to a hard resin can be made. The preferred amount of poly-
15 trimethylene ether glycol for soft grade polymer is from about 60 to about 90%, for medium grade polymer is from about 30 to about 59% and for hard grade polymer is from about 1 to about 29%, by weight based on the weight of the polymer. The preferred molecular weight (Mn) of polytrimethylene ether glycol for soft polymer is from about 1500 to about 5000, for a medium grade polymer is from about 800 to about 2000, and
20 a hard grade polymer is from about 250 to about 1200.

The nucleating agent can be introduced to the polyether ester in several ways. It can be added at any time during the synthesis of the polymer. That is, it can be added during the (trans)esterification and/or the polycondensation steps. It is also possible to mix the nucleating agent with the finished polyether ester while it is being processed in an extruder or other melt mixer. Preferably, the nucleating agent is added
25 during the (trans)esterification stage. It may be added as a pure compound or as a masterbatch in the same or different polyether ester to which it is being added.

The compositions of the present invention may include a plasticizer to improve their processability. Preferred plasticizers include, for example, diesters of polyethylene glycol such as diethylene glycol di(2-ethylhexonate), triethylene glycol di(2-ethylhexonate), tetraethylene glycol diheptanoate, triethylene glycol di(2-ethylbutyrate), di-2ethylhexyl phthalate, and di-2-ethylhexyl adipate. The preferred amount of plasticizer in the composition is from about 0.1 to about 15%, and more preferably from about 1 to about 10%, by weight based on the total weight of the polymer.

Besides nucleating agents and plasticizers, the compositions of the present invention may also include other well-known additives such as antioxidants, branching agents, heat and UV stabilizers, fillers, dyes, pigments and epoxides.

End Uses of the Polyether Esters

5 The nucleated polyether esters of this invention are useful, for example, in making fibers, films and other shaped articles.

10 The fibers include monocomponent and multicomponent fiber such as bicomponent fiber (containing the polyether ester as at least one component), and can be continuous filaments or staple fiber. The fibers are used to prepare woven, knit and nonwoven fabrics. The nonwoven fabrics can be prepared using conventional techniques such as use for meltblown, spunbonded and card and bond fabrics, including heat bonding (hot air and point bonding), air entanglement, etc.

15 Yarns (also known as "bundles") preferably comprise at least about 2, and more preferably at least about 25 filaments. The yarns typically have a total denier of from about 1 to about 500, preferably at least about 20, more preferably at least about 50, and even more preferably from about 50 to about 100. Filaments are preferably at least about 0.5 denier per filament (dpf), more preferably at least about 1 dpf, and up to about 20 or more dpf, more preferably up to about 10 dpf. Typical filaments are about 3 to 10 dpf, and fine filaments are about 0.5 to about 2.5 dpf.

20 Spinning speeds can be at least about 200 meters/minute (m/min), more preferably at least about 1000 m/min, and ever more preferably at least about 500 m/min, and can be up to about 4000 m/min or higher.

25 The fibers can be drawn from about 1.5x to about 6x, preferably at least about 1.5x, and preferably up to about 4x. Single step draw is the preferred drawing technique. In most cases it is preferred not to draw the fibers.

 The fibers can be heat set, and preferably the temperature is at least about 140°C and preferably up to about 160°C.

30 Finishes can be applied for spinning or subsequent processing, and include silicon oil, mineral oil, and other spin finishes used for polyesters and polyether ester elastomers, etc.

The fibers are stretchy, have good chlorine resistance, can be dyed under normal polyester dyeing conditions, and have excellent physical properties, including superior strength and stretch recovery properties, particularly improved unload power and stress decay.

5 Conventional additives can be incorporated into the polyether ester or fiber by known techniques. The additives include delusterants (e.g., TiO₂, zinc sulfide and/or zinc oxide), colorants (e.g., dyes), stabilizers (e.g., antioxidants, ultraviolet light stabilizers, heat stabilizers, etc.), fillers, flame retardants, pigments, antimicrobial agents, antistatic agents, optical brighteners, extenders, processing aids, viscosity boosters, and
10 other functional additives.

Particularly useful shaped articles are flexible films and sheets, particularly those having a thickness of from about 1 μm to about 500 μm . The shaped article may, for example, comprise multilayers wherein at least one layer has a thickness of about 5 μm or less.

15 The present invention provides flexible films comprising polytrimethylene ether ester elastomers having desirable mechanical properties such as tenacity, elasticity, toughness and flexibility, optionally without the use of plasticizers. In addition, the films also possess very good breathability (high water vapor permeation rates). Such films can be useful in making bags and packaging, e.g., for food, storage and transportation.
20 The films can be prepared from the polymers using methods known to those skilled in the art. The flexible films can be cast films or oriented films. Oriented films can be uniaxially oriented or biaxially oriented. Orientation can be effected by any process known in the art, such as, for example a tubular or flat film process. Orientation of films is disclosed, for example, in WO01/48062.

25

EXAMPLES

The following examples are presented for the purpose of illustrating the invention and are not intended to be limiting. All parts, percentages, etc., are by weight unless otherwise indicated.

30 The 1,3-propanediol utilized in the examples was prepared by biological methods described in US2005/0069997A1, and had a purity of >99.8%

PO3G was prepared from 1,3-propanediol as described in US20050020805A1.

Number-average molecular weights (M_n) were determined by end-group analysis using NMR spectroscopic methods.

Melting point (T_m), (re)crystallization temperature (T_{rc}), glass transition temperature (T_g), and ΔH (the heat caused by the polymer crystallization) were determined in accordance with ASTM D-3418 (1988) using a DuPont DSC Instrument Model 2100 (E.I. du Pont de Nemours and Co., Wilmington, DE). About 3 mg of sample was sealed in a DSC aluminum pan and the sample was heated to 270°C under a nitrogen atmosphere and then cooled. The heating and cooling rates were 10°C per minute.

Crystallization behavior of polyether ester elastomers was investigated by differential scanning calorimetry (DSC). The inherent viscosity (IV) of the polymer sample was analyzed on a PolyVISC® automated viscometer (Cannon Instrument Co.) at a temperature of 30°C in m-cresol with a 0.5% concentration.

Comparative Example 1

This comparative example describes the synthesis of a polyether ester having 45 wt% polyethylene terephthalate and 5 wt% polybutylene terephthalate hard segments, and 50 wt% polytrimethylene ether terephthalate soft segment. No nucleating agent was utilized.

A 25 gallon autoclave was charged with 33.2 lbs of dimethyl terephthalate, 30 lbs of PO3G (M_n of 2250), 14 lbs of ethylene glycol, 2 lbs of 1,4-butanediol, 80 g of ETHANOX® 330 antioxidant (Albemarle), and 12 g of TYZOR® TPT catalyst (E.I. DuPont de Nemours and Company). The reactant charge was designed to achieve a weight ratio of polyethylene terephthalate:polybutylene terephthalate:polytrimethylene ether glycol terephthalate of 45:5:50.

Under a nitrogen atmosphere the temperature was raised to 215°C, and methanol generated was removed by distillation as a liquid condensate. The temperature was held at 210°C for about 1.5 hours until no more methanol evolved, indicating the end of the transesterification reaction.

The temperature was then raised to 250°C and held at that temperature at a pressure of 0.3 mm Hg for 3 hours. The polymer obtained could not successfully be extruded into ribbons.

Example 1

This example illustrates the preparation of a polyether ester with the same stoichiometry as that prepared in Comparative Example 1, but in this case including trisodium phosphate nucleating agent.

- 5 A 25 gallon autoclave was charged with 33.2 lbs of dimethyl terephthalate, 30 lbs of PO3G (Mn of 2440), 14 lbs of ethylene glycol, 2 lbs of 1,4-butanediol, 80 g of ETHANOX® 330 antioxidant, 12 g of TYZOR® TPT as catalyst, and 136 g of trisodium phosphate as nucleating agent. The temperature was raised to 215°C, and methanol generated was removed with a nitrogen flush by distillation as a liquid condensate.
- 10 The temperature was held at 210°C for about 1.5 hours until no more methanol evolved indicating the end of the transesterification reaction.

The temperature was then raised to 250°C and held at that temperature at a pressure of 0.3 mm Hg for 2.5 hours. The polymer was extruded into ribbons and converted into flakes.

15 Comparative Example 2

This comparative example describes the synthesis of a polyether ester having 55 wt% polyethylene terephthalate hard segment and 45 wt% polytrimethylene ether terephthalate soft segment. No nucleating agent was utilized.

- 20 A 250 ml three-necked flask was charged with 42.1 g of dimethyl terephthalate, 29.3 g of PO3G (Mn of 1770), 20 g of ethylene glycol, 0.15 g of IRGANOX® 1098 antioxidant (Ciba Specialty Chemicals Inc.), and 25 mg of TYZOR® TPT catalyst. The temperature was raised to 215°C under nitrogen flush, and methanol generated was removed by distillation as a liquid condensate. The temperature was held at 210°C for about 1.5 hours until no more methanol evolved indicating the end of transesterification
- 25 reaction.

The temperature was then raised to 250°C and held at that temperature at a pressure of 0.2 mm Hg for 2 hours. The reaction was ended by removing the heat and vacuum.

Example 2

This example illustrates the preparation of a polyether ester with the same stoichiometry as that prepared in Comparative Example 2 but including trisodium phosphate nucleating agent.

5 A 250 ml three-necked flask was charged with 42.1 g of dimethyl terephthalate, 29.3 g of PO3G (Mn of 1770), 20 g of ethylene glycol, 0.15 g of IRGANOX® 1098 anti-oxidant, 25 mg of TYZOR® TPT catalyst, and 0.36 g of trisodium phosphate (2100 ppm of sodium based on the final polymer) as nucleating agent. The temperature was raised to 215°C under nitrogen, and the methanol generated was removed as a liquid condensate by distillation. The temperature was held at 210°C for about 1.5 hours un-
10 til no more methanol evolved, indicating the end of transesterification reaction.

The temperature was raised to 250°C and held at that temperature at a pressure of 0.2 mm Hg for 2 hours. Then the reaction was stopped by removal of the heat and vacuum, and the polymer was collected.

Example 3

15 A polyether ester was prepared as described in Example 2 except that the amount of trisodium phosphate used was 0.26 g (corresponding to 1700 ppm of sodium based on the final polymer).

Example 4

20 A polyether ester was prepared as described in Example 2 except the trisodium phosphate of Example 2 was replaced with 0.41 g of sodium acetate (corresponding to 1700 ppm of sodium based on the final polymer).

Example 5

This example describes synthesis of a polyether ester having 50 wt% polyethylene terephthalate hard segments and 50 wt% polytrimethylene ether terephthalate
25 soft segments in the presence of trisodium phosphate nucleating agent

A 25 gallon autoclave was charged with 36.5 lbs of dimethyl terephthalate, 30 lbs of PO3G (Mn of 1770), 16 lbs of ethylene glycol, 87 g of ETHANOX® 330 antioxidant, 12 g of TYZOR® TPT catalyst, 22 g trimethyl-trimellitate (1,2,4-benzene-tricarboxylic acid, methyl ester) and 150 g of sodium phosphate nucleating agent. The
30 temperature was raised to 215°C under nitrogen, and the methanol generated was re-

moved as a liquid condensate by distillation. The temperature was held at 210°C for about 1.5 hours until no more methanol evolved, indicating the end of transesterification reaction.

5 The temperature was then raised to 250°C and held at that temperature at a pressure of 0.3 mmHg for 2.5 hours. The polymer was extruded into ribbons and converted into flakes.

The properties of the polymers prepared in the above examples are listed in Table 1.

Table 1

10 Effect of Nucleating Agents on Crystallization Temperature and Half-Time

Ex.	Composition	Nucleating Agent	T _m (°C)	T _{rc} (°C)	ΔH (J/g)	T _{1/2} at 215°C (min)
C1	PET(45%)PBT(5%)/PO3G(50%)	None	227.5	142.4	9.96	--
1	PET(45%)PBT(5%)/PO3G(50%)	Na ₃ PO ₄ (2100 ppm of Na)	230.0	183.9	19.4	6.40
C2	PET(55%)/PO3G (45%)	None	244.6	174.1	24.4	8.18
2	PET(55%)/PO3G (45%)	Na ₃ PO ₄ (2100 ppm of Na)	241.9	214.3	24.8	0.23
3	PET(55%)/PO3G (45%)	Na ₃ PO ₄ (1700 ppm of Na)	235.9	214.1	29.5	0.30
4	PET(55%)/PO3G (45%)	NaAc (1700 ppm of Na)	237.9	201.5	23.2	--
5	PET(50%)/PO3G (50%)	Na ₃ PO ₄ (2100 ppm of Na)	233.0	187	16.5	3.20

The increase in T_{rc} and decrease in t_{1/2} suggest that the presence of nucleating agent in the elastomer effectively increases the crystallization rate.

15 The mechanical properties of the polymer prepared in Example 5 were compared with those of HYTREL® 5556 polymer resin, a commercial thermoplastic elas-

tomers available from E.I. duPont de Nemours and Company. The data in Table 2 shows the excellent mechanical properties of the composition of the present invention.

Table 2

Property	HYTREL® 5556	Example 5
Soft segment Tg (°C)	-50	-63
Hard segment Tm (°C)	203	233
Hardness shore D	55	41
Tensile strength (psi)	3282	3156
% Elongation	448	616
Strength at 100% (psi)	2024	1340

From the data in Table 2, the polymer of Example 5 has unique combination of properties: a lower glass transition temperature, higher melt temperature, and excellent mechanical properties.

Example 6

This example demonstrates preparation of film from the nucleated polyether ester of Example 5.

The films were made using a 28 mm extruder (Werner & Pfleiderer), equipped with Foremost #15 feeder, #3 casting drum, and #4 winder. The hopper and throat of the extruder had a nitrogen blanket.

The polyether ester described in Example 5 was dried and fed through the hopper into the twin screw extruder. The sample was heated to melt and fed into a film die. The aperture of the die was set to roughly 5 mil thickness (1mil = 1/1000 inches = 25.4 microns) and the film was extruded continuously at the approximate rate of 3 feet per minute. The film was then cooled to 29°C on a casting drum, which was equipped with a cooling water jacket. The cooled film was then wound onto a roll with a winder.

The properties of the film are in Table 3.

Table 3 - Properties of Polyether Ester Film

Property	Test Method	Example 6
Water Vapor Permeation Rate (mil-gm/(m ² -day))	ASTM F1249	2733
Oxygen Permeation Rate (mil-cc/(m ² -day))		8700
Stress at break (ksi)	ASTM D882-02	2.767
Strain at break (%)		426

Example 7

This example describes synthesis of a polyether ester having 28 wt% polyethylene terephthalate hard segment and 72 wt% polytrimethylene ether terephthalate soft segment in the presence of trisodium phosphate nucleating agent.

A 25 gallon autoclave was charged with 19.8 lbs of dimethyl terephthalate, 40 lbs of PO3G (Mn of 2270), 10.7 lbs of ethylene glycol, 79.6 g of ETHANOX® 330 antioxidant, 24 g of TYZOR® TPT catalyst, and 73.5 g of sodium phosphate nucleating agent. The temperature was raised to 215°C under nitrogen, and the methanol generated was removed as a liquid condensate by distillation. The temperature was held at 210°C for about 1.5 hours until no more methanol evolved, indicating the end of transesterification reaction.

The temperature was then raised to 250°C and held at that temperature at a pressure of 0.3 mm Hg for 2.5 hours. The polymer was extruded into ribbons and converted into flakes. The polymer had a T_m of 216.5°C, a T_{rc} of 184°C, and an IV of 1.105 dL/g.

Example 8 – Fibers

Spinning Procedure – The polymer of Example 7 was extruded through a sand filter spin pack and a three hole spinneret (0.3 mm diameter and 0.56 mm capillary depth holes, maintained at 257-259°C. The filamentary streams leaving the spinneret were quenched with air at 21°C, and converged to a bundle. The spinning conditions for the yarns are described in Table 4.

The properties of the fibers obtained at two different winding speeds are reported in Table 4 (according to ASTM D2731 method).

Table 4

Spinning speed, mpm	1200	3000
Denier	80	54.5
Draw ratio	1.0	1.0
% stretch for 5 cycle	200	200
Load at 100% (g/den)	0.247	0.238
Load at 200% (g/den)	0.545	1.054
Load at 200% after 5 cycles	0.385	0.688
Unload at 200% stretch (g/den)	0.311	0.553
Unload at 100% stretch (g/den)	0.029	0.039
Tenacity (g/d)	0.829	1.262
Elongation (%)	282	235
Stress decay (%)	19.3	19.9
Set (%)	22.5	16.1

What is claimed is:

1. A polyether ester elastomer composition comprising (i) a polyether ester elastomer based on a polytrimethylene ether ester soft segment and a polyethylene ester hard segment; and (ii) a nucleating agent selected from the group consisting of an alkali metal salt, an alkaline earth metal salt and mixtures thereof.
5
2. The polyether ester elastomer composition of claim 1, comprising from about 10 to about 90 wt% polytrimethylene ether ester soft segment, and from about 10 to about 90 wt% polyethylene ester hard segment, based on the weight of the polyether ester elastomer.
- 10 3. The polyether ester elastomer composition of claim 1, wherein the nucleating agent is present at a level of from about 0.005 to about 2 wt%, based on the weight of the polyethylene ester hard segment.
4. The polyether ester elastomer composition of claim 1, wherein the nucleating agent comprises a metal cation selected from the group consisting of lithium, sodium, potassium and calcium, and an anion selected from the group consisting of phosphate, sulfate and carboxylate.
15
5. The polyether ester elastomer composition of claim 4, wherein the nucleating agent comprises trisodium phosphate and/or sodium acetate.
6. The polyether ester elastomer composition of claim 1, wherein the poly-
20 trimethylene ether ester soft segment is the reaction product of a polymeric ether glycol and a dicarboxylic acid equivalent, via ester linkage, wherein at least about 50 wt% of the polymeric ether glycol used to form the soft segment is a polytrimethylene ether glycol.
7. The polyether ester elastomer composition of claim 1, wherein from about 95 to
25 100 wt% of the polymeric ether glycol used to form the soft segment is a polytrimethylene ether glycol.
8. The polyether ester elastomer composition of claim 6, wherein the polytrimethylene ether glycol is an oligomeric and/or polymeric ether glycol in which at least 50% of the repeating units are trimethylene ether units.

9. The polyether ester elastomer composition of claim 8, wherein the poly-trimethylene ether glycol is an oligomeric and/or polymeric ether glycol in which about 99 to 100% of the repeating units are trimethylene ether units.
10. The polyether ester elastomer of claim 6, wherein the polytrimethylene ether glycol is prepared by the acid catalyzed polycondensation of monomers comprising at least 50 mole% 1,3-propane diol.
11. The polyether ester elastomer of claim 10, wherein the 1,3-propane diol is derived from a fermentation process using a renewable biological source.
12. The polyether ester elastomer composition of claim 6, wherein the poly-trimethylene ether glycol has number average molecular weight of from about 250 to about 5000.
13. The polyether ester elastomer composition of claim 1, wherein the polyethylene ester hard segment is the reaction product of a diol and a dicarboxylic acid equivalent, via ester linkage, wherein greater than about 50 mole% of the diol used to form the hard segment is ethylene glycol.
14. The polyether ester elastomer composition of claim 1, wherein the dicarboxylic acid equivalent is selected from the group consisting of terephthalic acid, dimethyl terephthalate and mixtures thereof.
15. The polyether ester elastomer composition of claim 1, having an inherent viscosity of at least about 0.6 dl/g up to about 2.4 dl/g.
16. The polyether ester elastomer composition of claim 1, prepared by the steps of providing and reacting:
- (a) a polymeric ether glycol component comprising at least about 50 wt% of a polytrimethylene ether glycol;
 - (b) a diol component comprising at least about 50 mole% ethylene glycol; and
 - (c) a dicarboxylic acid equivalent,
- in the presence of the nucleating agent.
17. The polyether ester elastomer composition of claim 16, prepared by the steps of:

(a) heating

(i) a polymeric ether glycol component comprising at least about 50 wt% of a polytrimethylene ether glycol,

(ii) terephthalic acid and/or dimethyl terephthalate,

5 (iii) a molar excess of a diol component comprising at least about 75 mole % ethylene glycol, and

(iv) the nucleating agent,

10 in the presence of a catalyst at a temperature in the range of from about 150°C to about 250°C while removing water or methanol by-product to form a precondensation product; and

(b) polymerizing the precondensation product under vacuum at temperature in the range of from about 220°C to about 290°C while removing excess diol component to form a polyether ester having polytrimethylene ether terephthalate soft segment and polyethylene terephthalate hard segment.

15 18. The polyether ester elastomer of claim 16, prepared by the steps of:

(a) heating

(i) a polymeric ether glycol component comprising at least about 50 wt% of a polytrimethylene ether glycol,

(ii) terephthalic acid and/or dimethyl terephthalate, and

20 (iii) a molar excess of a diol component comprising at least about 75 mole % ethylene glycol,

in the presence of a catalyst at temperature in the range of from about 150°C to about 250°C while removing water and/or methanol by-product to form a precondensation product;

25 (b) adding the nucleating agent to the precondensation product,; and

(c) polymerizing the precondensation product under vacuum at a temperature in the range of from about 220°C to about 290°C while removing excess diol to form a

polyether ester having polytrimethylene ether terephthalate soft segment and polyethylene terephthalate hard segment.

19. A fiber made from the polyether ester elastomer composition of claim 1.
20. A flexible film made from the polyether elastomer composition of claim 1.