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(54) Title: POLYETHERESTER BLOCK COPOLYMER ELASTOMERS

(57) Abstract

A polyetherester block copolymer useful in molding applications is prepared from the polymerization of from 5-50 % by weight of polyether block segments and from 50-95 % by weight of polyester block segments. The polyether block segments are a poly(propylene oxide)glycol or an ethylene oxide-capped derivative produced using a double metal cyanide complex catalyst. The glycol contains lower levels of unsaturation, increased functionality and a narrower molecular weight distribution than that prepared using conventional basic catalysts.

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POLYETHERESTER BLOCK COPOLYMER ELASTOMERS

This invention relates generally to the production of polyetherester block copolymer elastomers and, more specifically to the production of polyetherester block copolymers made utilizing polyols having low ethylenic unsaturation and prepared using double metal cyanide catalysis. The copolymers exhibit excellent thermal properties and rubber-like elasticity.

Conventional polyetherester block copolymers are prepared by the transesterification of poly(tetramethylene glycol) (so-called "PTMEG") and 1,4-butanediol with dimethyl terephthalate, as disclosed, for example, in U.S. Patent 4,251,652. Replacing PTMEG by less expensive poly(propylene oxide) (so-called "PPG") of the same molecular weight and prepared by conventional basic catalysis tends to provide polymers having inferior physical properties. One apparent reason for this difference between the PTMEG and the PPG is that the secondary hydroxyl groups on the PPG are less reactive and thermally less stable.

Capping the PPG with ethylene oxide leads to a polyol (so-called "EOPPG") that mainly consists of PPG units; however, the end hydroxyl groups derived from EO are primary hydroxyls, like those in PTMEG. Polyesters made using EOPPG having the same molecular weight as comparison PTMEG also leads to copolyesters having inferior physical properties relative to the PTMEG. Moreover, the above-referenced '652 patent teaches that PTMEG having a very narrow molecular weight distribution can be utilized to form copolyesters having even further-enhanced physical properties.

Since PPG and EOPPG are considerably less expensive than PTMEG, new polyetherester block copolymer elastomers and processes for providing PPG- and EOPPG-based polyetherester block copolymer elastomers exhibiting comparable physical properties to those based upon PTMEG would be highly desired by the elastomer manufacturing community. The present invention provides one answer to this need.

In one aspect, the present invention provides an improved process for producing a polyetherester block copolymer elastomer comprising 50 to 95% of polyester block segments and 5% to 50% by weight of polyether block segments comprising a glycol selected from the group consisting of poly(propylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and combinations thereof, the improvement comprising fabricating said glycol using a double metal cyanide complex catalyst to provide a molecular weight for the glycol in the range of between about 400 and about 10,000 (preferably between 1000 and 10,000) and a low level of terminal ethylenic unsaturation that is generally less than 0.03, preferably less than 0.02, more preferably less than 0.015, milliequivalents per gram of polyol.

In another aspect, the present invention relates to a process for producing a polyetherester block copolymer elastomer comprising 50 to 95% of polyester block segments and 5% to 50% by weight of polyether block segments comprising:

(a) reacting at least one lower alcohol diester of a dicarboxylic acid component in a catalytic ester-interchange reaction with a diol component, said dicarboxylic acid component comprising at least 70 molar percent of at least one aromatic dicarboxylic acid having a molecular weight of 300 or less and containing at least 50 molar percent of terephthalic acid, and

(b) catalytically block polycondensing the ester-interchange reaction product from step (a) with a glycol selected from the group consisting of poly(propylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and combinations thereof, said glycol having been prepared using a double metal cyanide complex catalyst to provide a molecular weight for the glycol in the range of between about 400 and about 10,000 (preferably between 1000 and 10,000) and a low level of terminal ethylenic unsaturation that is generally less than 0.03, preferably less than 0.02, more preferably less than 0.015, milliequivalents per gram of polyol, to form said polyetherester block copolymer elastomer.

In another aspect, the present invention relates to a method of using a polyol prepared by double metal cyanide complex catalysis which comprises incorporating the polyol into a polyetherester block copolymer elastomer-forming composition during production of the elastomer, said polyol having a molecular weight in the range of between about 400 and about 10,000 (preferably between 1000 and 10,000) and a low level of terminal ethylenic unsaturation that is generally less than 0.03, preferably less than 0.02, more preferably less than 0.015, milliequivalents per gram of polyol.

In yet another aspect, the present invention relates to the polyetherester block copolymer elastomers produced by the above-described processes.

These and other aspects will become apparent upon reading the following detailed description of the invention.

It is surprisingly found in accordance with the present invention that PPG- and EOPPG-based polyetherester block copolymer elastomers are provided which have physical properties comparable to those provided using PTMEG at a cost that is less than the cost of PTMEG-based elastomers.

Without wishing to be bound by any particular theory, it is believed by the present inventors that since PPG or EOPPG prepared using double metal cyanide complex (DMC) catalysts have lower levels of terminal unsaturation, increased functionality, and a narrower molecular weight distribution, as compared to the corresponding polyols made using conventional basic catalysts, the resulting polymers made using the DMC-catalyzed polyols exhibit enhanced physical properties.

The polyetherester block copolymers of the present invention suitably comprise a polyester portion preferably having both long chain ester moieties or units and short chain ester moieties or units. The term "long chain ester units" as used herein as applied to units in a polymer chain refers to the reaction product of a dicarboxylic acid with a long chain glycol. Such "long chain ester units," which are a repeating unit in the copolyesters of this invention, are represented by the following formula:

$$-OLO-C(O)-R-C(O)-$$

where L is a divalent radical remaining after removal of terminal hydroxyl groups from poly(alkylene oxide) glycols and R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight less than about 300. The long chain glycols are polymeric glycols having terminal (or as nearly terminal as possible) hydroxy groups and a molecular weight above about 400 and preferably from about 1000-10,000. The long chain glycols used to prepare the polyetherester of this invention are poly(alkylene oxide) glycols. Representative long chain glycols are poly(ethylene oxide) glycol, poly(1,2- and 1,3-propylene oxide) glycol, random or block copolymers of ethylene oxide and 1,2-propylene oxide, and random or block copolymers of tetrahydrofuran with minor amounts of a second monomer such as ethylene oxide and/or poly(1,2 propylene oxide).

Preferred polyol reactants are the polyether diols and combinations thereof. Suitable polyether diols include various polyoxyalkylene diols and combinations thereof preferably containing ethylene oxide ("EO") in an amount of between about 5 and about 40, more preferably between about 15 and about 30, weight percent based upon the weight of the polyol. Suitable diols preferably have a primary hydroxyl content of between about 30 and about 95%, more preferably between about 50 and about 95%. The ethylenic unsaturation level for the polyol is preferably no greater than 0.02, more preferably less than 0.015, milliequivalents per gram of polyol. It is preferred that any residual alkali metal catalyst in the polyol be no greater than 25 ppm, more preferably no greater than 8 ppm, most preferably no greater than 5 ppm. The potential adverse effects of residual alkali metal catalyst in the polyol can be overcome by neutralizing with an effective amount of an acid, such as phosphoric acid.

The polyols can be prepared, according to well-known methods, by condensing an alkylene oxide, or a mixture of alkylene oxides using random or step-wise addition, with a polyhydric initiator or mixture of initiators. Illustrative alkylene oxides include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, aralkylene oxides such as styrene oxide, and the halogenated alkylene oxides such as trichlorobutylene oxide and so forth. The most preferred alkylene oxide is propylene oxide or a mixture thereof with ethylene oxide using random or step-wise oxyalkylation.

The polyhydric initiator used in preparing the polyether diol reactant includes the following and mixtures thereof: ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, butane diols, pentane diols, water, combinations thereof, and the like.

The alkylene oxide-polyhydric initiator condensation reaction is preferably carried out in the presence of a double metal cyanide catalyst.

Without wishing to be bound by any particular theory, it is speculated by the present inventor that unsaturated end groups result in monofunctional species that act as chain stoppers in elastomer formation. In polyol synthesis with KOH catalysis, the unsaturation formed increases as a direct function of equivalent weight. Eventually conditions are established wherein further propylene oxide addition fails to increase the molecular weight. In other words, the use of alkali catalysts to produce high molecular weight, hydroxy terminated polyoxypropylene ethers results in a substantial loss in hydroxy functionality. With double metal cyanide catalysis, much less unsaturation is formed allowing higher equivalent weight polyols to be prepared.

The double metal cyanide complex class catalysts suitable for use and their preparation are described in Shell Chemical Company U.S. Patent Nos. 4,472,560 and 4,477,589 and The General Tire & Rubber Company U.S. Patent Nos. 3,941,849; 4,242,490 and 4,335,188.

One double metal cyanide complex catalyst found particularly suitable for use is zinc hexacyanometallate of formula:

$$Zn_3[M(CN)_6]_2 \bullet xZnCl_2 \bullet yGLYME \bullet zH_2O$$

wherein M may be Co(III), or Cr(III) or Fe(lI) Fe(lII); x, y, and z may be fractional numbers, integers, or zero and vary depending on the exact method of preparation of the complex.

The term "short chain ester units" as applied to units in a polymer chain refers to low molecular weight compounds or polymer chain units having molecular weights less than about 550. They are made by reacting a low molecular weight diol (below about 250) with dicarboxylic acid to form ester units represented by the following structure:

-OSO-C(O)-R-C(O)-

where S is a divalent radical remaining after removal of hydroxyl groups from a low molecular weight diol having a molecular weight less than about 250 and R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having molecular weight less than about 300.

Included among the low molecular weight diols (other than 1,4-butanediol) which react to form short chain ester units are acyclic, alicyclic, and aromatic dihydroxy compounds. Diols with 2-15 carbon atoms are preferred including ethylene, propylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, and decamethylene glycols, dihydroxy cyclohexane, cyclohexane dimethanol, resorcinol, hydroquinone, 1,5-dihydroxy naphthalene, etc. Especially preferred are aliphatic diols containing 2-8 carbon atoms. The bisphenols which can be used include bis(p-hydroxy) diphenyl, bis(p-hydroxyphenyl) methane, and bis(p-hydroxyphenyl) propane. Ester-forming derivatives which are equivalent to diols are also useful (e.g., ethylene oxide or ethylene carbonate can be used in place of ethylene glycol). The term "low molecular weight diols" used herein should be construed to include such equivalent ester-forming derivatives: provided, however, that the molecular weight requirement pertains to the diol only and not to its derivatives.

Other than terephthalic acid employed in the process of the present invention, the dicarboxylic acids which are reacted with the foregoing long chain glycols and low molecular weight diols to produce the polyetheresters of this invention are aliphatic, cycloaliphatic, or aromatic dicarboxylic acids. They are low in molecular weight, i.e., having a molecular weight of less than about 300. The term "dicarboxylic acids" as used herein, includes equivalents of dicarboxylic acids having two functional carboxyl groups which perform substantially like dicarboxylic acids in reaction with glycols and diols in forming copolyester polymers. Esters and ester-forming derivatives, such as acid halides and anhydrides are included as these equivalents with the molecular weight requirement pertaining to the acid and not to its equivalent ester or ester-forming derivative. Thus, an ester of a dicarboxylic acid having a molecular weight greater than 300 or an acid equivalent of a dicarboxylic acid having a molecular weight greater than 300 are included provided the acid has a molecular weight below about 300. The dicarboxylic acids can contain any substituent groups or combinations which do not substantially interfere with the copolyester polymer formation and use of the polymer of this invention.

Aliphatic dicarboxylic acids refers to carboxylic acids having two carboxyl groups each attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and is in a ring, the acid is cycloaliphatic. Aliphatic or cycloaliphatic acids having conjugated unsaturation often cannot be used because of homopolymerization except that some unsaturated acids, such as maleic acid, can be used.

Aromatic dicarboxylic acids refers to carboxylic acids having two carboxyl groups attached to a carbon atom in an isolated or fused benzene ring. It is not necessary that both functional carboxyl groups be attached to the same aromatic ring and where more than one ring is present, they can be joined by aliphatic or aromatic divalent radicals or divalent radicals such as -O- or $-SO_2-$.

Representative examples of aliphatic and cycloaliphatic acids which can be used for this invention are sebacic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, adipic acid, glutaric acid, succinic acid, carbonic acid, oxalic acid, azelaic acid, diethyl-malonic acid, allylmalonic acid, 4-cyclohexene-1,2-dicarboxylic acid, 2 ethylsuberic acid, 2,2,3,3-tetramethylsuccinic acid, cyclo-penlanedicarboxylic acid, decahydro-1,5-naphthalene dicarboxylic acid, 4,4-bicyclohexyl dicarboxylic acid, deahydro-2,6-naphthalene dicarboxylic acid, 4,4′-methyl- enebis-(cyclohexane carboxylic acid), 3,4-furan dicarboxylic acid. and 1,1-cyclobutane dicarboxylic acid. Preferred aliphatic acids are cyclohexane-dicarboxylic acids and adipic acid.

Representative examples of aromatic dicarboxylic acids which can be used include phthalic and isophthalic acids, bibenzoic acid, substituted dicarboxy compounds with two benzene nuclei such as bis(p-carboxyphenyl)-methane, p-oxy(p-carboxyphenyl) benzoic acid, ethylene-bis(p-oxybenzoic acid), 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, phenanthrene dicarboxylic acid, anthracene dicarboxylic acid, 4,4′-sulfonyl dibenzoic acid, and C1-C12 alkyl and ring substitution derivatives thereof, such as halo, alkoxy, and aryl derivatives. Hydroxyl acids such as p(beta-hydroxyethoxy) benzoic acid can also be used providing an aromatic dicarboxylic acid is also present.

Aromatic dicarboxylic acids are a preferred class for preparing the copolyester polymers of this invention. Among the aromatic acids, those with 8-16 carbon atoms are preferred, particularly the phenylene dicarboxylic acids, i.e., phthalic and isophthalic acids.

Polyetheresters containing mixed short chain ester units, i.e., polymers made from more than one kind of dicarboxylic acid and/or more than one kind of low molecular weight diol, are soluble in many partially halogenated aliphatic hydrocarbon solvents such as chloroform and 1,1,2-trichloroethane. This solubility is useful in solvent coating applications. In contrast, polyetherester based only on butylene terephthalate short chain units are usually insoluble in such solvents.

The polyetherester of this invention contain about 50-95% by weight of short chain ester units, the remainder being long chain ester units. Polyetheresters containing less than about 50% by weight of short chain units exhibit lower initial modulus and reduced resistance toward solvents while polyetherester containing more then about 95 weight percent of short chain units have poor low temperature resistance and no longer exhibit elastomeric characteristics. The preferred range of short chain ester content is at 70-90% by weight based upon the total weight of the copolyester.

Preferred polyetherester of this invention are those prepared from dimethyl terephthalate, 1,4-butanediol, and poly(propylene oxide) glycol or poly(propylene oxide) glycol capped with 15-30% ethylene oxide, having a molecular weight of about 1000-4000. Optionally, up to about 30 mole percent and preferably 5-25 mole percent of the dimethyl terephthalate in these polymers can be replaced by dimethyl phthalate or dimethyl isophthalate or butanediol can be replaced with neopentyl glycol until up to about 30% and preferably 10-25% of the short chain ester units are derived from neopentyl glycol in these poly(propylene oxide) glycol or poly(ethylenepropylene oxide)glycol polymers.

The dicarboxylic acids or their derivatives and the polymeric glycol are incorporated into the final product in the same molar proportions as are present in the reaction mixture. The amount of low molecular weight diol actually incorporated corresponds to the difference between the moles of diacid and polymeric glycol present in the reaction mixture. When mixtures of low molecular weight diols are employed, the amounts of each diol incorporated is largely a function of the amounts of the diols present, their boiling points, and relative reactivities. The total amount of glycol incorporated is still the difference between moles of diacid and polymeric glycol.

The polymers described are conveniently made by a conventional ester interchange reaction. A preferred procedure involves heating the dimethyl ester of terephthalic acid with a long chain glycol and a molar excess of 1,4-butanediol in the presence of a catalyst at 150-260°C. while distilling off methanol formed by the ester interchange. Depending on temperature, catalyst, glycol excess, and equipment, this reaction can be completed within few minutes to a few hours. This procedure results in the preparation of a low molecular weight prepolymer which can be carried to a high molecular weight copolyester of this invention by the procedure described below. Such prepolymers can also be prepared by number of alternate esterification or ester interchange processes; for example, the long chain glycol can be reacted with a high or low molecular weight short chain ester homopolymer or copolymer in the presence of catalyst until randomization occurs. The short chain ester homopolymer or copolymer can be prepared by ester interchange from either the dimethyl esters and low molecular weight diols, as above, or from the free acids with the diol acetates. Alternatively, the short chain ester copolymer can be prepared by direct esterification from appropriate acids, anhydrides, or acid chlorides, for example, with diols or by other processes such as reaction of the acids with cyclic ethers or carbonates. Obviously, the prepolymer might also be prepared by running these processes in the presence of the long chain glycol.

The resulting prepolymer is then carried to high molecular weight by distillation of the excess of short chain diol. This process is known as "polycondensation." Additional ester interchange occurs during this distillation to increase the molecular weight and to randomize the arrangement of the copolyester units. Best results are usually obtained if this final distillation or polycondensation is run at less than 1 mm. pressure and 240-260°C. for less than 2 hours in the presence of anti-oxidants such as sym-di-beta-naphthyl-p-phenylenediamine and 1,3,5--trimethyl-2,4,6-tris[3,5-ditertiarybutyl-4-hydroxy-benzyl]benzene. Most practical polymerization techniques rely upon ester interchange to complete the polymerization reaction. In order to avoid excessive hold time at high temperatures with possible irreversible thermal degradation, a catalyst for the ester interchange reaction should be employed. While a wide variety of catalysts can be used, organic titanates such as tetrabutyl titanate used alone or in combination with magnesium or calcium acetates are preferred. Complex titanates, such as $Mg[HTi(OR)_6]_2$, derived from alkali or alkaline earth metal alkoxides and titanate esters are also very effective. Inorganic titanates, such as lanthanum titanate, calcium acetate/antimony trioxide mixtures and lithium and magnesium alkoxides are representative of other catalysts which can be used.

Ester interchange polymerizations are generally run in the melt without added solvent, but inert solvents can be used to facilitate removal of volatile components from the mass at low temperatures. This technique is especially valuable during prepolymer preparation, for example, by direct esterification. However, certain low molecular weight diols, for example, butanediol in terphenyl, are conveniently removed during high polymerization by azeotropic distillation. Other special polymerization techniques, for example, interfacial polymerization of bisphenol with bisacylhalides and bisacylhalide capped linear diols, may prove useful for preparation of specific polymers. Both batch and continuous methods can be used for any stage of copolyester polymer preparation. Polycondensation of prepolymer can also be accomplished in the solid phase by heating divided solid prepolymer in a vacuum or in stream of inert gas to remove liberated low molecular weight diol. This method has the advantage of reducing degradation because it must be used at temperatures below the softening point of the prepolymer.

Although the polyetherester possess many desirable properties, it is advisable to stabilize certain of the compositions to heat or radiation by ultraviolet light. This can be done by incorporating stabilizers in the polyester compositions.

Stabilizers include phenols and their derivatives, amines and their derivatives, compounds containing both hydroxyl and amine groups, hydroxyazines, oximes, polymeria phenolic esters and salts of multivalent metals in which the metal is in its lower valence state.

Representative phenol derivatives useful as stabilizers include 4,4'-bis(2,6-ditertiary-butylphenol), 1,3,5-trimethyl-2,4,6-tris[3,5-ditertiary-butyl-4-hydroxybenzyl]benzene and 4,4'-butylidene-bis(6-tertiary-butyl-m-cresol). Various inorganic metal salts or hydroxides can be used as well as organic complexes such as nickel dibutyl dithiocarbamate, manganous salicylate and copper 3-phenylsalicylate. Typical amine stabilizers include N,N'-bis(beta-naphthyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine and either phenyl-betanaphthyl amine or its reaction products with aldehydes. Mixtures of hindered phenols with esters of thiodipropionic acid, mercaptides, and phosphite esters are particularly useful. Additional stabilization to ultraviolet light can be obtained by compounding with various UV absorbers such as substituted benzophenones or benzotriazoles.

In general, the polyetherester elastomers of the present invention suitably have a hardness in the range between 80 Shore A and 80 Shore D. However, the properties of these polyetheresters can be modified by incorporation of various conventional inorganic fillers such as carbon black, silica gel, alumina, clays, and chopped fiber glass. In general, these additives have the effect of increasing the modulus of the material at various elongations. Compounds having a range of hardness values can be obtained by blending hard and soft polyesters of this invention.

The polyetherester of this invention have an outstanding balance of properties. In spite of their relatively low concentration of long chain ester units, the polyetherester have surprisingly good low temperature properties. At the same time, the polyetherester have useful tensile properties at temperatures as high as 200°C. In addition, the polyetherester of this invention retain their strength after extended exposure to a variety of organic fluids (including hydraulic fluids) at temperatures as high as 120-150°C. Similar advantages are provided by the polyetherester in heat aging.

Because the polymers of this invention have relatively low melt viscosity, (particularly at low shear), excellent thermal stability at processing temperature, rapid hardening rates, good flow and mold wetting characteristics, and relative insensitivity to moisture, they may be processed by substantially all procedures which have been used for thermoplastics in general, and in many instances, they offer significant processing advantage over competitive thermoplastic polymers. They are especially effective in injection molding and high speed extrusion applications because of their rapid hardening rates. The materials can be injection, compression, transfer and blow molded to form articles which may include inserts, if desired, meeting close tolerances. Because of their melt viscosity and stability, they can be used for melt and puddle casting. They can be readily extruded to produce films (blown or unblown), tubing, other forms having complicated cross-sections, and cross-heat extruded for hose, wire, cable, and other substrate covers. They can be melt spun to form fibers and filaments. They can be readily calendered to produce films and sheeting or to produce calender-coat woven and non-woven fabrics and other substances.

In finely divided form, the polymers of this invention offer the above-mentioned processing advantages for procedures employing powdered thermoplastics. In addition, they can be used in crumb form. The unique flow characteristics of these polymers give excellent definition on molded surfaces and facilitate fusion bonding procedures such as rotational molding (either one or two axis methods), slush molding, and centrifugal molding as well as powder coating techniques such as fluidized bed, electrostatic spray, flame spray, flock coating, powder flow coating, cloud chamber, and heat fused coating (for flexible substrates).

The melt viscosity and stability characteristics of these polymers offer advantages for use in certain coating and adhesive procedures such as dip, transfer, roller, and knife coating and hot melt adhesives. These same advantages are useful in various combining and laminating operations such as hot roll, web, and flame laminating as well as other thermoplastic heat sealing processes. The low melt viscosity of these polymers permits the use of more delicate substrates in combining, laminating, and calendering operations and allows penetration into the substrate, if desired.

As used herein, the term "molecular weight" is intended to designate number average molecular weight.

While the invention has been described above with reference to specific embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

All parts, proportions, and percentages disclosed herein are by weight unless otherwise indicated. The following examples further illustrate the invention.

EXAMPLES

Catalyst Preparation:

To 200 ml of dry methanol is added 11.2 g. of anhydrous magnesium acetate and the mixture is refluxed for 2 hrs. The resulting solution is cooled to room temperature and 44.4 ml of tetrabutyl titanate and 150 ml of 1,4-butanediol are added with mixing.

Proposed Example 1

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

	Parts
Polypropylene glycol, number average molecular weight about 1000	11.8
(unsaturation level of no greater than 0.015 meq.g) 1,4-butanediol	25.7
Dimethyl terephthalate	31.2
Dimethyl isophthalate	7.8
Sym-di-beta-naphthyl-p-phenylenediamine	0.17
Catalyst	0.36

A stainless steel stirrer with a paddle cut to conform with the internal radius of the flask is positioned about 1/8" from the bottom of the flask and the agitation is started. The flask is placed in an oil bath at 160°C., agitated for five minutes and then the catalyst is added. Methanol distills from the reaction mixture as the temperature is slowly raised to 250°C. over a period of one hour. When the temperature reaches 250°C. the pressure is gradually reduced to 0.3 mm. Hg within 20 minutes. The polymerization mass is agitated at 255-260°C. and <0.1 mm. Hg for 90 minutes. The resulting viscous molten product is scrapped from the flask in a nitrogen (water and oxygen free) atmosphere and allowed to cool. The inherent viscosity of the product at a concentration of 0.1 g./dcl. in m-cresol at 30°C. is indicative of good molecular weight formation. Samples for physical testing are prepared by compression molding at about 240°C. for one minute and cooling rapidly in the press. The polymer has a Shore D hardness of about 55-60.

The physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

Proposed Example 2

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

	Parts
Polypropylene glycol, number average molecular weight about 1000 (unsaturation level of no greater than 0.015 meq/g)	11.7
1,4-butanediol	20.2
2,2-dimethyl-1,3-propanediol	5.9
Dimethyl terephthalate	38.7
Sym-di-beta-naphthyl-p-phenylenediamine	0.17
Catalyst	0.36

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties are also indicative of good molecular weight formation with the modulus and strength values slightly less than those of Example 1 by virtue of the incorporation of the second short chain diol.

Proposed Example 3

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

	Parts
Polypropylene glycol, number average molecular weight about 2000 (unsaturation level of no greater than 0.015 meq.g)	25.0
1,4-butanediol	27.26
Dimethyl terephthalate	33.0
Dimethyl isophthalate	8.25
Sym-di-beta-naphthyl-p-phenylenediamine	0.21
Catalyst	0.44

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

Proposed Example 4

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

Polypropylene glycol end capped with about 24% ethylene oxide, number average molecular weight about 2000 OH No. 49.2 (percent primary OH 81.5) (unsaturation 0.008 meq/g)	25.0
1,4-butanediol	27.26
Dimethyl terephthalate	33.0
Dimethyl isophthalate	8.25
Sym-di-beta-naphthyl-p-phenylenediamine	0.21
Catalyst	0.44

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

Proposed Example 5

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

Polypropylene glycol end capped with about 24% ethylene oxide, number average molecular weight about 4000	50.0
OH No. 26.8 (percent primary OH 88.7) (unsaturation 0.011 meq.g)	
1,4-butanediol	27.2
Dimethyl terephthalate	33.0
Dimethyl isophthalate	8.25
Sym-di-beta-naphthyl-p-phenylenediamine	0.26
Catalyst	0.56

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

Proposed Example 6

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

Polypropylene glycol end capped with about 24% ethylene oxide, number average molecular weight about 2000 OH No. 49.2 (percent primary OH 81.5) (unsaturation 0.008 meq/g)	10.0
1,4-butanediol	21.80
Dimethyl terephthalate	25.63

Dimethyl isophthalate	6.41
Sym-di-beta-naphthyl-p-phenylenediamine	0.14
Catalyst	0.30

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

Proposed Example 7

A polyetherester copolymer is prepared by placing the following materials in an agitated flask fitted for distillation:

Polypropylene glycol end capped with about 24% ethylene oxide, number average molecular weight about 4000 OH No. 26.8 (percent primary OH 88.7) (unsaturation level of 0.011 meq.g)	10.0
1,4-butanediol	21.80
Dimethyl terephthalate	25.25
Dimethyl isophthalate	6.31
Sym-di-beta-naphthyl-p-phenylenediamine	0.14
Catalyst	0.30

The procedure of Example 1 is used to prepare the polymer. The polyetherester copolymer has an inherent viscosity indicative of good molecular weight formation and the physical properties such as modulus values at different elongations, ultimate tensile strength, split tear, and flexural modulus are very good and indicative of good molecular weight formation.

WHAT IS CLAIMED IS:

1. An improved process for producing a polyetherester block copolymer elastomer characterized by containing 50 to 95% of polyester block segments and 5% to 50% by weight of polyether block segments comprising a glycol selected from the group consisting of poly(propylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and combinations thereof, said process comprising fabricating said glycol using a double metal cyanide complex catalyst to provide a number average molecular weight for the glycol in the range of between about 400 and about 10,000 and a low level of terminal ethylenic unsaturation that is less than 0.03 milliequivalents per gram of polyol.

2. The process of claim 1 characterized in that said glycol has a molecular weight of between 1,000 and 10,000, and wherein said unsaturation is less than 0.02 milliequivalents per gram of polyol.

3. A process for producing a polyetherester block copolymer elastomer characterized by containing 50 to 95% of polyester block segments and 5% to 50% by weight of polyether block segments said process comprising:

(a) reacting at least one lower alcohol diester of a dicarboxylic acid component in a catalytic ester-interchange reaction with a diol component, said dicarboxylic acid component comprising at least 70 molar percent of at least one aromatic dicarboxylic acid having a number average molecular weight of 300 or less and containing at least 50 molar percent of terephthalic acid, and

(b) catalytically block polycondensing the ester-interchange reaction product form step (a) with a glycol selected from the group consisting of poly(propylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and combinations thereof, said glycol being been prepared using a double metal cyanide complex catalyst to provide a number average molecular weight for the glycol in the range of between about 400 and about 10,000 and a low level of terminal ethylenic unsaturation that is less than 0.03 milliequivalents per gram of polyol, to form said polyetherester block copolymer elastomer.

4. The process of claim 3 characterized in that said glycol has a molecular weight of between 1,000 and 10,000, and wherein said unsaturation is less than 0.02 milliequivalents per gram of polyol.

5. The process of claim 3 characterized in that said diol component additionally comprises a diol selected from the group consisting of ethylene diol, propylene diol, tetramethylene diol, pentamethylene diol, 2,2-dimethyltrimethylene diol, hexamethylene diol, decamethylene glycol, dihydroxy cyclohexane, cyclohexane dimethanol, resorcinol, hydroquinone, 1,5-dihydroxy naphthalene, bisphenol, and combinations thereof.

6. The process of claim 3 characterized in that said dicarboxylic acid component additionally comprises a dicarboxylic acid selected from the group consisting of: sebacic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, adipic acid, glutaric acid, succinic acid, carbonic acid, oxalic acid, azelaic acid, diethyl-malonic acid, allylmalonic acid, 4-cyclohexene-1,2-dicarboxylic acid, 2 ethylsuberic acid, 2,2,3,3-tetramethylsuccinic acid, cyclopenlanedicarboxylic acid, decahydro-1,5-naphthalene dicarboxylic acid, 4,4-bicyclohexyl dicarboxylic acid, deahydro-2,6-naphthalene dicarboxylic acid, 4,4′-methyl- enebis-(cyclohexane carboxylic acid), 3,4-furan dicarboxylic acid. and 1,1-cyclobutane dicarboxylic acid, phthalic acid, isophthalic acid, bibenzoic acid, substituted dicarboxy compounds having two benzene nuclei such as bis(p-carboxyphenyl)methane, p-oxy(p-carboxyphenyl) benzoic acid, ethylene-bis(p-oxybenzoic acid), 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, phenanthrene dicarboxylic acid, anthracene

dicarboxylic acid, 4,4'-sulfonyl dibenzoic acid, and C1-C12 alkyl and ring substitution derivatives thereof, and combinations thereof.

7. The elastomer produced by the process of claim 3 characterized in that said process has a number average molecular weight of between about 15,000 and about 100,000.

8. A composition which comprises the elastomer produced by the process of claim 3 and further characterized in that said composition contains a compounding ingredient selected from the group consisting of anti-oxidants, plasticizers, uv stabilizers, heat stablilizers, adhesion promoters, fillers and pigments and employed in an amount of between 0 and about 75 weight percent based upon the total weight of the composition.

9. A method of using a polyol prepared by double metal cyanide complex catalysis characterized by incorporating the polyol into a polyetherester block copolymer elastomer-forming composition during production of the elastomer, said polyol having a number average molecular weight in the range of between about 400 and about 10,000 and a low level of terminal ethylenic unsaturation that is less than 0.03 milliequivalents per gram of polyol.

10. The method of claim 9 characterized in that said polyol has a number average molecular weight of between 1,000 and 10,000, and wherein said unsaturation is less than 0.02 milliequivalents per gram of polyol.

11. The process of claim 1 characterized in that said glycol has a number average molecular weight of between 1,000 and 10,000, and wherein said unsaturation is less than 0.015 milliequivalents per gram of polyol.

INTERNATIONAL SEARCH REPORT

Inte :ional application No.
PCT/US94/06312

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08G 63/66
US CL :525/408
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/408

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,652,713 (OKAZAKI ET AL.) 28 March 1972, column 3, lines 58 and 69.	1-11
Y	US, A, 4,322,335 (NIELD) 30 March 1982, column 2, lines 34-37 and 42-43.	1-11
Y	US, A, 4,207,230 (BIER ET AL.) 10 June 1980, column 2, lines 21-33 and column 4, line 4.	1-11
Y	US, A, 4,315,882 (HIRATSUKA ET AL.) 16 February 1982, column 3, lines 15-27.	1-11
Y	AU, A, 83,665 (E. I. DU PONT DE NEMOURS AND COMPANY) 10 February 1977, page 4, lines 16-28.	1-11
Y	JP, A, 49-48195 (TOYO SPINNING CO LTD) 19 December 1974, see Abstract.	1-11

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

11 AUGUST 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Int ional application No.
PCT/US94/06312

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,242,490 (EMERSON ET AL.) 30 December 1980, column 2, lines 25-44.	1-11
Y	US, A, 4,472,560 (KUYPER ET AL.) 18 September 1984, column 5, lines 29-38.	1-11
Y	US, A, 4,477,589 (VAN DER HULST ET AL.) 16 October 1984, column 6, lines 36-41.	1-11
Y	US, A, 3,829,505 (HEROLD) 13 August 1974, column 17, Example 1.	1-11