Abstract: In an embodiment, a catalyst comprises a sulfonated polymerization product of a monovinylaromatic monomer and less than 2.0 wt% of a polystyrene aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst. In another embodiment, a method of producing a bisphenol comprises reacting a phenolic compound with one or both of an aldehyde and a ketone in the presence of a catalyst to produce a bisphenol; wherein the catalyst is a sulfonated polymerization product of a monovinylaromatic monomer and less than 2.0 wt% of a polystyrene aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

Fig. 1

[Continued on next page]
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
AN ION-EXCHANGE RESIN CATALYST AND A METHOD OF MAKING AND FOR USING THE SAME IN THE PREPARATION OF A BISPHENOL

CROSS-REFERENCE


BACKGROUND

[0002] Bisphenols such as Bisphenol A (BPA) (4,4’-(propane)-2,2-diyl)diphenol or p,p’-BPA) are often used in the production of plastics such as polycarbonates, polyesters, and epoxy resins. BPA is commercially produced by the condensation reaction of acetone and two equivalents of phenol in the presence of a catalyst such as a strong acid or an ion-exchange resin (IER). The productivity of the catalyst is directly affected by the amount of crosslinking in the IER. Specifically, lower crosslinking levels result in increased productivity due to the improved swelling ability of the catalyst as the improved swelling ability results in and increased accessibility of the acid sites that catalyze the reaction. However, low crosslinking levels of IER resins also generally result in IER resins with increased compressibility values, which can contribute to an increased pressure drop through the catalyst bed in the reactor, and which ultimately limits the production of BPA.

[0003] An improved method for the production of bisphenols such as BPA using IER catalysts is therefore desirable.

BRIEF SUMMARY

[0004] Disclosed herein is a catalyst and a method of using the catalyst for producing a bisphenol.

[0005] In an embodiment, a catalyst comprises a sulfonated polymerization product of a monovinylaromatic monomer and less than 2.0 wt% of a polyvinyl aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

[0006] In another embodiment, a method of producing a bisphenol comprises reacting a phenolic compound with one or both of an aldehyde and a ketone in the presence of a catalyst to produce a bisphenol; wherein the catalyst is a sulfonated polymerization product
of a monovinylaromatic monomer and less than 2.0 wt% of a polyvinyl aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

[0007] In an embodiment, a method of producing a catalyst comprises reacting the monovinylaromatic monomer and less than 2.0 wt% of the polyvinyl aromatic monomer based on the total amount of monomer in the presence of an initiator, an optional stabilizer, and an optional aliphatic monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

[0008] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The following is a brief description of the drawings wherein like elements are numbered alike and which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

[0010] FIG. 1 is a graphical representation of BPA content (weight percent versus time) of Example 2;

[0011] FIG. 2 is a graphical representation of compressibility data of Example 3;

[0012] FIG. 3 is a graphical representation of totalized BPA (expressed in grams per gram dry catalyst) as a function of time of Example 4;

[0013] FIG. 4 is a graphical representation of BPA activity (expressed in terms of grams BPA/hr/gram dry catalyst) as a function of Totalized BPA of Example 4;

[0014] FIG. 5 is a bar graph comparing the amount of impurities in weight percent of the stream at WHSV = 1 of Example 9; and

[0015] FIG. 6 is a bar graph comparing the amount of impurities in weight percent of the stream at WHSV = 2 of Example 9.

DETAILED DESCRIPTION

[0016] Bisphenols such as BPA can be produced by the condensation reaction of an aldehyde or ketone such as acetone and two equivalents of a phenolic compound catalyzed by an ion-exchange resin (IER) catalyst, where the catalyst is generally a sulfonated copolymer such as a polystyrene-divinylbenzene copolymer. The productivity, as determined by one or both of the selectivity and the conversion, of the catalyst can be greatly affected by the
percentage of crosslinking of the copolymer as the crosslinking of the copolymer directly affects the swelling nature of the catalyst and thus the accessibility of the active site. A catalyst with 2 weight percent (wt%) crosslinking in the polystyrene matrix, for example, can offer better accessibility of the acidic sites that catalyze the reaction as compared to a catalyst with 4 wt% crosslinking. However, the same catalyst with 4 wt% crosslinking can have a decreased compressibility. A decreased compressibility can be desirable, in view of bisphenol reactor conditions such as stream viscosity and reactor pressure. For example, for commercial-size bisphenol reactors, a compressibility (volume divided by initial volume) \((V/V_o)\) value greater than or equal to 0.6 is desirable (for example, 0.6 to 1), greater than or equal to 0.8 (for example, 0.8 to 1) is more desirable when the volume \((V)\) is measured at a specific applied stress of 20 pounds per square inch \((\text{lb/inch}^2)\) (138 kiloPascal \((\text{kPa})\)).

[0017] It was surprisingly found that an IER catalyst comprising a sulfonated copolymer product of a monovinyl aromatic monomer and a polyvinyl aromatic monomer, having less than 2 wt% crosslinking, and 0.1 to 1.0 millimoles \((\text{mmol})\), specifically, 0.4 to 0.6 mmol of sulfone bridges per gram of dry catalyst can provide one or more of a conversion of greater than or equal to 88 wt%, a selectivity of greater than or equal to 92 wt%, and a compressibility \((V/V_o)\) value greater than or equal to 0.6 \(V/V_o\) at 20 lb/inch\(^2\) in the manufacture of bisphenols such as BPA. As used herein the term "dry catalyst" can refer to a catalyst with a water content of less than or equal to 1 wt%, specifically, less than or equal to 0.1 wt%, more specifically, 0 to 0.1 wt% of water based on the total weight of the catalyst.

[0018] The IER catalyst can be formed by suspending a reaction mixture comprising a monovinyl aromatic monomer, a polyvinyl aromatic monomer, an initiator, and an optional aliphatic crosslinking monomer in an aqueous liquid to form a crosslinked copolymer. The monovinyl aromatic monomer can comprise one or both of styrene and a substituted styrene such as alpha-methyl styrene, vinyl toluene, ethyl vinyl benzene, vinyl naphthalene, and the like, or a combination comprising at least one of the foregoing. The polyvinyl aromatic monomer can comprise divinyl benzene, divinyl toluene, trivinyl benzene, divinyl chloro benzene, diallyl phthalate, divinyl naphthalene, divinyl xylene, divinyl ethyl benzene, trivinyl naphthalene, polyvinyl anthracene, and the like, or a combination comprising at least one of the foregoing. The polyvinyl aromatic monomer can comprise divinyl benzene. The aliphatic crosslinking monomer can comprise trivinyl cyclohexane, a di- or polyacrylate, and a di-or poly methacrylate, e.g., trimethylol propane trimethacrylate, ethylene glycol dimethacrylate, ethylene glycol diacrylate, neopentyl glycol dimethacrylate, and
pentaerythritol tetra- and trimethacrylates, and the like, or a combination comprising at least one of the foregoing.

[0019] The percentage of crosslinking of IER catalysts formed by copolymerization of a monovinyl aromatic monomer and a polyvinyl aromatic monomer (such as sulfonated polystyrene-divinylbenzene copolymers) is based on the amount of crosslinker, i.e., polyvinyl aromatic monomer such as divinyl benzene and the optional aliphatic crosslinking monomer, present during manufacture of the catalyst. Advantageously, the IER catalysts herein can be manufactured using less than 2 wt% of the crosslinker, based on the total weight of the monomers. The polyvinyl aromatic monomer (VAM) can be present in an amount of 0.01 wt% to less than 2 wt% (0.01 wt% ≤ VAM < 2 wt%), or 0.1 to less than 2 wt% (0.1 wt% ≤ VAM < 2 wt%), or 0.5 to less than 2 wt% (0.5 wt% ≤ VAM < 2 wt%), for example, 1.0 to 1.8 wt% (1.0 wt% ≤ VAM ≤ 1.8 wt%), each based on the total weight of the monomers. The polyvinyl aromatic monomer can be present in an amount of 1.1 wt% to 1.15 wt%, or 1.12 to 1.14 wt%, or 1.12 to 1.13 wt% each based on the total weight of the monomers. The foregoing amounts are particularly useful in the manufacture polystyrene-divinylbenzene copolymers.

[0020] The initiator can be a free radical initiator. The free radical initiator can comprise an oil-soluble initiator (such as benzoyl peroxide, lauroyl peroxide, t-butyl peroctoate, t-butyl peroxy benzoate, t-butyl peroxy pivalate, t-butylperoxy-2-ethylhexanoate, bis(4-t-butyl cyclohexyl) peroxy dicarbonate), an azo compound (such as azo bis(isobutrylonitrite), azobis(dimethyl valeronitrile), and the like), or a combination comprising one or more of the foregoing initiators.

[0021] The reaction mixture can further comprise a stabilizer that stabilizes monomer droplets prior to polymerization. The stabilizer can comprise gelatin, starch, carboxymethylcellulose, poly(acrylic acid), poly(vinyl alcohol), a water-insoluble inorganic stabilizer in particulate form (such as bentonite, magnesium hydroxide, and the like), or a combination comprising one or more of the foregoing.

[0022] The temperature of the reaction mixture can be increased to a polymerization temperature that is greater than or equal to an activation temperature of the initiator in order to initiate the polymerization reaction. For example, the polymerization temperature can be 40 to 100 degrees Celsius (°C), specifically, 50 to 90°C. The reaction can occur under agitation to produce a catalyst in the form of spherical beads. The spherical beads can have an average diameter of 20 micrometers to 1 millimeter.
[0023] After polymerization, the crosslinked copolymer can be separated from the suspending medium (for example, by gravity, centrifugal flow, hydraulic separation, or filtration), dried, and functionalized.

[0024] To form the IER catalyst, the crosslinked copolymer is functionalized with a sulfonating reagent composition and a sulfone crosslinker. The sulfonating reagent composition can comprise chlorosulfonic acid, sulfur trioxide, sulfuric acid, or a combination comprising one or more of the foregoing. The sulfonating reagent composition can further comprise a boron compound such as boric acid and boron oxide. The sulfonating reagent composition and reaction conditions can be selected to form sulfone bridges between two aromatic rings and to form sulfonic acid groups on the aromatic rings. For example, a sulfuric acid/SO$_3$ mixture can have an acid concentration of 101 to 104.5% in order to introduce both sulfone bridging groups and an average of at least one sulfonic acid group per aromatic nucleus.

[0025] The number of sulfone bridges in the IER catalyst can be determined by subtracting the millimoles (mmol) of sulfonic acid groups per gram of dry catalyst, determined by titration of the sulfonic acid groups, from the mmol of total sulfur determined by elemental analysis. The number of sulfone bridges can be 0.1 to 1.0 mmol, specifically, 0.4 to 0.6 mmol of sulfone bridges per gram of dry catalyst.

[0026] The IER catalyst can be used as a fixed-bed catalyst in condensation reactions, for example, the condensation of a phenolic compound with ketones or aldehydes to produce bisphenols. The IER catalyst can be exposed to a feed comprising a condensation mixture comprising the phenolic compound and one or both of a ketone and an aldehyde. The feed can comprise less than or equal to 5 wt%, or 0 to 5 wt%, or 0 to 2 wt% of water based on the total weight of the feed.

[0027] A wide variety of phenolic compounds can be used, which, as used herein means an aromatic compound substituted with a single hydroxyl group. The aromatic compound can be monocyclic or polycyclic, and can be substituted with up to 5 substituents, provided that such substituents do not substantially adversely affect the reaction or reaction product. The bisphenol can be of the formula (2) or of the formula (3) as described below.

[0028] The ketone can have the formula $R^{k1}$-(C=0)-R$^{k2}$, wherein $R^{k1}$ and $R^{k2}$ can each independently be a C$_{1-18}$ specifically, C$_{1-6}$ aliphatic group and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous provided that such substituents do not substantially adversely affect the reaction or reaction product. $R^{k1}$
and R$^k$ can together form a C5-18 cycloalkyl group (such as cyclohexanone or methylcyclohexanone) or a C5-18 cycloalkylene group. The aldehyde can have the formula R$^k$-(C=O)-H, wherein R$^k$ can be that described above or hydrogen.

[0029] The IER catalyst can be used as a fixed-bed catalyst in the condensation of cyclohexanone and o-cresol to produce 1,1-bis(4-hydroxy-3-methylphenyl) cyclohexane (DMBPC). The IER catalyst can be used as a fixed-bed catalyst in the condensation of acetone and phenol to produce BPA.

[0030] The reaction of the phenolic compound and the aldehyde or ketone can occur in a stoichiometric amount or in a molar excess of the phenolic compound. For example, the molar ratio of the phenolic compound to the aldehyde or ketone can be 20:1 to 2:1.

[0031] The reaction can occur at a temperature of 40 to 100°C with, for example, 1 to 40 wt% catalyst based on the weight of the phenolic compound and the aldehyde or ketone. The reaction can occur in the presence of a mercaptan reaction promoter (such as ethanethiol, 3-mercaptopropionic acid, amioethane thiol, dimethyl thiazolidine, and the like). Aminoethiol promoter can be ionically attached the catalyst.

[0032] The IER catalyst is particularly useful in large commercial reactors used to produce high volumes of bisphenols such as BPA. Due to the large size of fixed bed bisphenol reactors and the viscosity of the bisphenol reaction stream, bisphenol production rates are sensitive to pressure drops that can occur across the reactor. Pressure drops can be affected by catalyst particle size and particle uniformity, but also particle compressibility. The IER catalyst herein can have a combination of low crosslinking and low compressibility, which can allow for greater productivity (higher selectivity and/or higher acetone conversion), together with decreased pressure drop across the reactor. In particular, the IER catalyst can have a compressibility (V/V$_0$) value greater than or equal to 0.6 V/V$_0$, for example, of 0.6 to less than 1.0, or 0.6 to 0.9, or 0.6 to 0.8, or 0.6 to 0.7, or 0.7 to less than 1.0, or 0.7 to 0.9, or 0.7 to 0.8 at 20 lb/inch$^2$. The IER catalyst can provide one or more of an acetone conversion of greater than or equal to 88 wt%, or greater than or equal to 90 wt%, for example, 88 to 98 wt%, 90 to 98 wt%, 92 to 98 wt%, or 88 to 95 wt%, and a selectivity of greater than or equal to 92 wt%, for example, 92 to 100 wt%, or 92 to 98 wt%, or 92 to 96 wt%.

[0033] The bisphenols produced by this process can be used to manufacture a polycarbonate. A "polycarbonate" as used herein means compositions having repeating structural carbonate units of formula (1).
in which the $R^1$ groups contain aliphatic, alicyclic, and/or aromatic moieties (e.g., greater than or equal to 30 percent, specifically, greater than or equal to 60 percent, of the total number of $R^1$ groups can contain aromatic moieties and the balance thereof are aliphatic, alicyclic, or aromatic). Optionally, each $R^1$ can be a $C_{n\text{-}30}$ aromatic group, that is, can contain at least one aromatic moiety. $R^1$ can be derived from a bisphenol (also referred to herein as a dihydroxy compound) of the formula $HO-R^2OH$, in particular of formula (2)

$$HO-A^1 \cdot Y^1 \cdot A^2 OH \quad (2)$$

wherein each of $A^1$ and $A^2$ is a monocyclic divalent aromatic group and $Y^1$ is a single bond or a bridging group having one or more atoms that separate $A^1$ from $A^2$. One atom can separate $A^1$ from $A^2$. Specifically, each $R^1$ can be derived from a bisphenol compound of formula (3)

$$HO- \begin{array}{c} \text{Cyclic group} \\ \text{X}^a \end{array} - \begin{array}{c} \text{Cyclic group} \\ \text{Y}^a \end{array} OH \quad (3)$$

wherein $R^a$ and $R^b$ are each independently a halogen, $C_{1\text{-}12}$ alkoxy, or $C_{1\text{-}12}$ alkyl; and $p$ and $q$ are each independently integers of 0 to 4. It will be understood that $R^a$ is hydrogen when $p$ is 0, and likewise $R^b$ is hydrogen when $q$ is 0. Also in formula (3), $X^a$ is a bridging group connecting the two hydroxy-substituted aromatic groups, where the bridging group and the hydroxy substituent of each $C_6$ arylene group are disposed ortho, meta, or para (specifically, para) to each other on the $C_6$ arylene group. The bridging group $X^a$ can be single bond, -0-, -S-, -S(O)-, -S(O)\text{-}2-, -C(O)-, or a $C_{1\text{-}18}$ organic group. The $C_{1\text{-}18}$ organic bridging group can be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The $C_{1\text{-}18}$ organic group can be disposed such that the $C_6$ arylene groups connected thereto are each connected to a common alkylidene carbon or to different carbons of the $C_{1\text{-}18}$ organic bridging group. $p$ and $q$ can each be 1, and $R^a$ and $R^b$ are each a $C_{1\text{-}3}$ alkyl group, specifically, methyl, disposed meta to the hydroxy group on each arylene group.

[0034] $X^a$ can be a substituted or unsubstituted $C_{3\text{-}18}$ cycloalkylidene, a $C_{1\text{-}25}$ alkylidene of formula $-C(R^5)(R^d)$, wherein $R^5$ and $R^d$ are each independently hydrogen, $C_{1\text{-}12}$ alkyl, $C_{1\text{-}12}$ cycloalkyl, $C_{7\text{-}12}$ arylalkyl, $C_{1\text{-}12}$ heteroalkyl, or cyclic $C_{7\text{-}12}$ heteroarylalkyl, or a group of the formula $-C(=R^e)$, wherein $R^e$ is a divalent $C_{1\text{-}12}$ hydrocarbon group. Groups of this type include methylene, cyclohexymethylene, ethyldiene, neopentyldiene, and
isopropylidene, as well as 2-[2.2.1]-bicycloheptylidene, cyclohexylidene, cyclopentylidene, cyclododecylidene, and adamantylidene.

[0035] X^a can be a C\textsubscript{1-18} alkylene group, a C\textsubscript{3-18} cycloalkylene group, a fused C\textsubscript{6-18} cycloalkylene group, or a group of the formula \(-E^\text{a}\text{G}^\text{b}\text{B}^\text{c}\) wherein B\textsuperscript{1} and B\textsuperscript{2} are the same or different C\textsubscript{1-6} alkylene group and G is a C\textsubscript{3-12} cycloalkylidene group, or a C\textsubscript{6-12} arylene group. For example, X^a can be a substituted C\textsubscript{3-18} cycloalkylidene of formula (4)

\[
[R^\text{a}]_i - (O)_{k} - [R^\text{i}]
\]

wherein R\textsuperscript{a}, R\textsuperscript{p}, R\textsuperscript{q}, and R\textsuperscript{i} are each independently hydrogen, halogen, oxygen, or C\textsubscript{1-12} hydrocarbon groups; Q is a direct bond, a carbon, or a valent oxygen, sulfur, or \(-N(Z)\)- where Z is hydrogen, halogen, hydroxyl, C\textsubscript{1-12} alkyl, C\textsubscript{1-12} alkoxy, or C\textsubscript{1-12} acyl; r is 0 to 2, t is 1 or 2, q is 0 or 1, and k is 0 to 3, with the proviso that at least two of R\textsuperscript{a}, R\textsuperscript{p}, R\textsuperscript{q}, and R\textsuperscript{i} taken together are a fused cycloaliphatic, aromatic, or heteroaromatic ring. It will be understood that where the fused ring is aromatic, the ring as shown in formula (4) will have an unsaturated carbon-carbon linkage where the ring is fused. When k is one and i is 0, the ring as shown in formula (4) contains 4 carbon atoms, when k is 2, the ring as shown in formula (4) contains 5 carbon atoms, and when k is 3, the ring contains 6 carbon atoms. Two adjacent groups (e.g., R\textsuperscript{q} and R\textsuperscript{i} taken together) can form an aromatic group or R\textsuperscript{q} and R\textsuperscript{i} taken together can form one aromatic group and R\textsuperscript{q} and R\textsuperscript{i} taken together form a second aromatic group. When R\textsuperscript{q} and R\textsuperscript{i} taken together form an aromatic group, R\textsuperscript{p} can be a double-bonded oxygen atom, i.e., a ketone.

[0036] Bisphenols wherein X^a is a cycloalkylidene of formula (4) can be used in the manufacture of polycarbonates containing phthalimidine carbonate units of formula (4a)

\[
(R^\text{a}) - (R^\text{b})_p - (R^\text{b})_q
\]

wherein R\textsuperscript{a}, R\textsuperscript{b}, p, and q are as in formula (4), R\textsuperscript{3} is each independently a C\textsubscript{1-6} alkyl group, j is 0 to 4, and R\textsuperscript{4} is a C\textsubscript{1-6} alkyl, phenyl, or phenyl substituted with up to five C\textsubscript{1-6} alkyl groups. The phthalimidine carbonate units can be of formula (4b)
wherein $R^5$ is hydrogen or a C$_i$-alkyl. $R^5$ can be hydrogen. Carbonate units (4a) wherein $R^5$ is hydrogen can be derived from 2-phenyl-3,3'-bis(4-hydroxyphenyl)phthalimidine (also known as N-phenyl phenolphthalein bisphenol, or "PPPBP") (also known as 3,3-bis(4-hydroxyphenyl)-2-phenylisoindolin-1-one).

[0037] Other bisphenol carbonate repeating units of this type are the isatin carbonate units of formula (lc) and (Id)

wherein $R^a$ and $R^b$ are each independently C$_{1-12}$ alkyl, $p$ and $q$ are each independently 0 to 4, and $R^1$ is C$_{1-12}$ alkyl, phenyl, optionally substituted with 1 to 5 C$_{1-10}$ alkyl, or benzyl optionally substituted with 1 to 5 C$_{1-10}$ alkyl. $R^a$ and $R^b$ can each be methyl, $p$ and $q$ can each independently be 0 or 1, and $R^1$ can be C$_{1-4}$ alkyl or phenyl.

[0038] Other examples of bisphenol carbonate units derived from bisphenols (3) wherein $X^a$ is a substituted or unsubstituted C$_{3-18}$ cycloalkylidene (4) include the cyclohexylidene-bridged, alkyl-substituted bisphenol of formula (4e)

wherein $R^a$ and $R^b$ are each independently C$_{1-12}$ alkyl, $R^g$ is C$_{1-12}$ alkyl, $p$ and $q$ are each independently 0 to 4, and $t$ is 0 to 10. At least one of each of $R^a$ and $R^b$ can be disposed meta to the cyclohexylidene bridging group. $R^a$ and $R^b$ can each independently be C$_{1-4}$ alkyl, $R^g$ can be C$_{1-4}$ alkyl, $p$ and $q$ can each be 0 or 1, and $t$ is 0 to 5. $R^a$, $R^b$, and $R^g$ can be each methyl, $r$ and $s$ can be each 0 or 1, and $t$ can be 0 or 3, specifically, 0.
Examples of other bisphenol carbonate units derived from bisphenol (3) wherein X is a substituted or unsubstituted \( \text{C}_{3-18} \) cycloalkylidene include adamantyl units of formula (4f) and fluorenyl units of formula (4g)

\[
(R^a)_p \text{O} \text{C} \text{O} \text{O} \text{C} \text{O} \text{O} \text{C} \text{O} \text{O} \text{C} \text{O} \text{O} (4f) \]

\[
(R^b)_q \text{O} \text{C} \text{O} \text{C} (4g) \]

wherein \( R^a \) and \( R^b \) are each independently \( \text{C}_{1-12} \) alkyl, and \( p \) and \( q \) are each independently 1 to 4. At least one of each of \( R^a \) and \( R^b \) can be disposed meta to the cycloalkylidene bridging group. \( R^a \) and \( R^b \) can each independently be \( \text{C}_{1-3} \) alkyl, and \( p \) and \( q \) can be each 0 or 1. \( R^a \), \( R^b \) can be each methyl, \( p \) and \( q \) can be each 0 or 1. Carbonates containing units (4a) to (4g) are useful for making polycarbonates with high glass transition temperatures (Tg) and high heat distortion temperatures.

Other possible dihydroxy compounds of the formula \( \text{HO-R^a-OH} \) include compounds of formula (6)

\[
(R^b)_n \text{O} \text{C} \text{O} \text{C} \text{OH}_2 \text{O} \text{C} \text{O} \text{C} \text{OH}_2 \text{OH}_2 (6) \]

wherein each \( R^b \) is independently a halogen atom, a \( \text{C}_{1-10} \) hydrocarbyl such as a \( \text{C}_{1-10} \) alkyl group, a halogen-substituted \( \text{C}_{1-10} \) alkyl group, a \( \text{C}_{6-10} \) aryl group, or a halogen-substituted \( \text{C}_{6-10} \) aryl group, and \( n \) is 0 to 4. The halogen is usually bromine.

Some illustrative examples of specific dihydroxy compounds include the following: 4,4'-dihydroxybiphenyl, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)diphenylmethane, bis(4-hydroxyphenyl)-1-naphthylmethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2-(4-hydroxyphenyl)-2-(3-hydroxyphenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)isobutene, 1,1-bis(4-hydroxyphenyl)cyclododecane, trans-2,3-bis(4-hydroxyphenyl)-2-butene, 2,2-bis(4-hydroxyphenyl)adamantane, alpha, alpha'-bis(4-hydroxyphenyl)toluene, bis(4-hydroxyphenyl)acetonitrile, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-ethyl-4-hydroxyphenyl)propane, 2,2-bis(3-n-propyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(3-sec-butyl-
4-hydroxyphenyl)propane, 2,2-bis(3-t-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 2,2-bis(3-allyl-4-hydroxyphenyl)propane, 2,2-bis(3-methoxy-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dibromo-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dichloro-2,2-bis(5-phenoxy-4-hydroxyphenyl)ethylene, 4,4'-dihydroxybenzophenone, 3,3-bis(4-hydroxyphenyl)-2-butanone, 1,6-bis(4-hydroxyphenyl)-1,6-hexanediione, ethylene glycol bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfone, 9,9-bis(4-hydroxyphenyl)fluorine, 2,7-dihydroxypyrene, 6,6'-dihydroxy-3,3',3'-tetramethylspiro(bis)indane ("spirobiindane bisphenol"), 3,3-bis(4-hydroxyphenyl)phthalimide, 2,6-dihydroxydibenzo-p-dioxin, 2,6-dihydroxythianthrene, 2,7-dihydroxyphenoxathin, 2,7-dihydroxy-9,10-dimethylphenazine, 3,6-dihydroxydibenzofuran, 3,6-dihydroxydibenzothiophene, 2,7-dihydroxycarbazole, resorcinol, substituted resorcinol compounds such as 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, 5-butyl resorcinol, 5-t-butyl resorcinol, 5-phenyl resorcinol, 5-cumyl resorcinol, 2,4,5,6-tetrafluoro resorcinol, 2,4,5,6-tetrabromo resorcinol, or the like; catechol; hydroquinone; substituted hydroquinones such as 2-methyl hydroquinone, 2-ethyl hydroquinone, 2-propyl hydroquinone, 2-butyl hydroquinone, 2-t-butyl hydroquinone, 2-phenyl hydroquinone, 2-cumyl hydroquinone, 2,3,5,6-tetramethyl hydroquinone, 2,3,5,6-tetra-t-butyl hydroquinone, 2,3,5,6-tetrafluoro hydroquinone, 2,3,5,6-tetrabromo hydroquinone, or the like, or combinations comprising at least one of the foregoing dihydroxy compounds.

[0042] Specific examples of bisphenol compounds of formula (3) include 1,1-bis(4-hydroxyphenyl) methane, 1,1-bis(4-hydroxyphenyl) ethane, 2,2-bis(4-hydroxyphenyl) propane (hereinafter "bisphenol A" or "BPA"), 2,2-bis(4-hydroxyphenyl) butane, 2,2-bis(4-hydroxyphenyl) octane, 1,1-bis(4-hydroxyphenyl) propane, 1,1-bis(4-hydroxyphenyl) n-butane, 2,2-bis(4-hydroxy-2-methylphenyl) propane, 1,1-bis(4-hydroxy-t-butylphenyl) propane, 3,3-bis(4-hydroxyphenyl) phthalimidimine, 2-phenyl-3,3-bis(4-hydroxyphenyl) phthalimidimine (PPPBP), and 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane (DMBPC). Combinations comprising at least one of the foregoing dihydroxy compounds can also be used. The polycarbonate can be a linear homopolymer derived from bisphenol A, in which each of A1 and A2 can be p-phenylene, and Y1 can be isopropylidene in formula (3). Alternatively, the polycarbonate can be a copolymer comprising units derived from BPA and units derived from other dihydroxy compounds as described above.
"Polycarbonate" as used herein includes homopolycarbonates (wherein each
R₁ in the polymer is the same), copolymers comprising different R₁ moieties in the carbonate
("copolycarbonates"), copolymers comprising carbonate units and other types of polymer
units, such as ester units, and combinations comprising at least one of homopolycarbonates
and/or copolycarbonates.

The polycarbonate can be made by an interfacial polymerization process or in
a melt polymerization process, which can be a continuous melt process. Although the
reaction conditions for interfacial polymerization can vary, an exemplary process generally
involves dissolving or dispersing a dihydric phenol reactant in aqueous caustic soda or
potash, adding the resulting mixture to a water-immiscible solvent medium, and contacting
the reactants with a carbonate precursor in the presence of a catalyst such as, for example, a
tertiary amine or a phase transfer catalyst, under controlled pH conditions, e.g., 8 to 10. The
water immiscible solvent can be, for example, methylene chloride, ethylene dichloride, 1,2-
dichloroethane, chlorobenzene, toluene, and the like.

Among tertiary amines that can be used in interfacial polymerization are
aliphatic tertiary amines such as triethylamine and tributylamine, cycloaliphatic tertiary
amines such as N,N-diethyl-cyclohexylamine, and aromatic tertiary amines such as N,N-
dimethylaniline. Among the phase transfer catalysts that can be used are catalysts of the
formula (R³)₄Q⁺X, wherein each R³ is the same or different, and is a C₁₋₁₀ alkyl group; Q is a
nitrogen or phosphorus atom; and X is a halogen atom or a C₆₋₁₈ alkoxy group or C₆₋₁₈ aryloxy
group. Examples of phase transfer catalysts include (CH₃(CH₂)₂)₄NX, (CH₃(CH₂)₃)₄PX,
(CH₃(CH₂)₃)₄NX, (CH₃(CH₂)₄)NX, (CH₃(CH₂)₅)₄NX, (CH₃(CH₂)₆)₄NX, and
CH₃(CH₃(CH₂)₂)₄NX, wherein X is Cl, Br⁻, a C₁₋₈ alkoxy group or a C₆₋₁₈ aryloxy group. An
effective amount of a phase transfer catalyst can be 0.1 to 10 weight percent (wt%), or 0.5 to
2 wt%, each based on the weight of bisphenol in the phosgenation mixture.

In a melt polymerization process, polycarbonates can be prepared by co-
reacting, in a molten state, a dihydroxy reactant, and a carbonate compound (such as
phosgene or a diaryl carbonate (herein also referred to as a diaryl carbonate ester)). The
dihydroxy reactant and/or the carbonate compound ester can be added to the polymerization
unit as a mixture with acetone. In addition, transesterification catalyst(s) can be employed.
Transesterification catalysts used in the melt transesterification polymerization production of
polycarbonates can include alkali catalysts and/or quaternary catalysts. As used herein the
term alkali catalyst refers to a catalyst comprising a source of one or both of alkali ions and
alkali earth ions and the term quaternary catalyst refers to a catalyst comprising one or both of a quaternary ammonium catalyst and a quaternary phosphonium catalyst.

[0047] The alkali catalyst comprises a source of alkali or alkaline earth ions. The sources of these ions include alkaline earth hydroxides such as magnesium hydroxide and calcium hydroxide. Sources of alkali metal ions can include the alkali metal hydroxides such as illustrated by lithium hydroxide, sodium hydroxide, potassium hydroxide, and combinations comprising at least one of the foregoing. Examples of alkaline earth metal hydroxides are calcium hydroxide, magnesium hydroxide, and combinations comprising at least one of the foregoing. Of these, sodium hydroxide is particularly desirable. The alkali catalyst typically will be used in an amount sufficient to provide 1 x 10^{-2} to 1 x 10^{-8} moles, specifically, 1 x 10^{-5} to 1 x 10^{-7} moles of metal hydroxide per mole of the dihydroxy compounds employed. Other possible sources of alkaline earth and alkali metal ions include salts of carboxylic acids (such as sodium acetate) and derivatives of ethylene diamine tetraacetic acid (EDTA) (such as EDTA tetrasyodium salt, and EDTA magnesium disodium salt), as well as combinations comprising at least one of the foregoing. For example, the alkali catalyst can comprise alkali metal salt(s) of a carboxylic acid, alkaline earth metal salt(s) of a carboxylic acid, or a combination comprising at least one of the foregoing. In another example, the alkali catalyst comprises Na_2Mg EDTA or a salt thereof.

[0048] The alkali transesterification catalyst can also, or alternatively, comprise salt(s) of a non-volatile inorganic acid. For example, the alkali catalyst can comprise salt(s) of a non-volatile inorganic acid such as NaH_2P0_4, NaH_2P0_4, Na_2HP0_4, KH_2P0_4, CsH_2P0_4, Cs_2FIP0_4, and combinations comprising at least one of the foregoing. Alternatively, or in addition, the alkali catalyst can comprise mixed alkali metal salt(s) of phosphoric acid, such as NaKHP0_4, CsNaFIP0_4, CsKHP0_4, and combinations comprising at least one of the foregoing.

[0049] Possible quaternary catalysts comprise a quaternary ammonium compound, a quaternary phosphonium compound, or a combination comprising at least one of the foregoing. The quaternary ammonium compound can be a compound of the structure (R^4)_2N^+X^-, wherein each R^4 is the same or different, and is a C_{1-20} alkyl, a C_{4-6} cycloalkyl, or a C_{4-6} aryl; and X^- is an organic or inorganic anion, for example, a hydroxide, halide, carboxylate, sulfonate, sulfate, formate, carbonate, or bicarbonate. Examples of organic quaternary ammonium compounds include tetramethyl ammonium hydroxide, tetrabutyl ammonium hydroxide, tetramethyl ammonium acetate, tetramethyl ammonium formate,
tetrabutyl ammonium acetate, and combinations comprising at least one of the foregoing. Tetramethyl ammonium hydroxide is often used. The quaternary phosphonium compound can be a compound of the structure \((R^5)_4P^+X^-\), wherein each \(R^5\) is the same or different, and is a C1-20 alkyl, a C4-20 cycloalkyl, or a C4-20 aryl; and \(X^-\) is an organic or inorganic anion, for example, a hydroxide, phenoxide, halide, carboxylate such as acetate or formate, sulfonate, sulfate, formate, carbonate, or bicarbonate. Where \(X^-\) is a polyvalent anion such as carbonate or sulfate, it is understood that the positive and negative charges in the quaternary ammonium and phosphonium structures are properly balanced. For example, where \(R^{20}\) to \(R^{23}\) are each methyls and \(X^-\) is carbonate, it is understood that \(X^-\) represents \(2(CO_3)^{2-}\). Examples of organic quaternary phosphonium compounds include tetramethyl phosphonium hydroxide, tetramethyl phosphonium acetate, tetramethyl phosphonium formate, tetrabutyl phosphonium hydroxide, tetrabutyl phosphonium acetate (TBPA), tetraphenyl phosphonium acetate, tetraphenyl phosphonium phenoxide, and combinations comprising at least one of the foregoing. TBPA is often used.

[0050] The amount of quaternary catalyst employed is typically based upon the total number of moles of dihydroxy compound employed in the polymerization reaction. When referring to the ratio of quaternary catalyst, for example, phosphonium salt, to all dihydroxy compounds employed in the polymerization reaction, it is convenient to refer to moles of phosphonium salt per mole of the dihydroxy compound(s), meaning the number of moles of phosphonium salt divided by the sum of the moles of each individual dihydroxy compound present in the reaction mixture. The amount of quaternary catalyst (e.g., organic ammonium or phosphonium salts) employed typically will be \(1 \times 10^{-2}\) to \(1 \times 10^{-3}\), specifically, \(1 \times 10^{-3}\) to \(1 \times 10^{-4}\) moles per total mole of the dihydroxy compounds in the reaction mixture.

[0051] The following examples are provided to illustrate use of the catalyst to manufacture bisphenols. The examples are merely illustrative and are not intended to limit the claims with respect to the materials, conditions, or process parameters set forth therein.

EXAMPLES

Example 1: Ion-exchange resins/Catalysts 1-7

[0052] Seven IERs, A-G, were prepared for use as BPA catalysts. Catalysts 1-6 were prepared in wet form by Thermax India Ltd. and were washed with water to make them acid-free as was determined by litmus paper. The IERs were then stripped of water in a rotary evaporator at 100 revolutions per minute (rpm) for 180 minutes and then vacuum dried.
Comparative Catalyst 7 from Lanxess was prepared similarly. Catalysts 1-7 have 1.00 to 4.00% crosslinking as shown in Table 1, where the % crosslinking is the wt% of the crosslinked divinylbenzene in the monomer mixture used to form the catalysts. Catalysts 1-6 were further crosslinked through sulfone bridges, where the content of the sulfone bridges was 0.4 to 0.6 mmol per gram of the IER.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% crosslinking</td>
<td>1.00</td>
<td>1.13</td>
<td>1.25</td>
<td>1.50</td>
<td>2.00</td>
<td>4.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Sulfone bridge present</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Sulfone content (mmol/g)</td>
<td>0.40</td>
<td>0.42</td>
<td>0.52</td>
<td>0.50</td>
<td>0.54</td>
<td>not measured</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Example 2: Initial catalyst activity of Catalysts 1-7

[0053] The selectivity and conversion of Catalysts 1-7 were determined by adding 0.25 g of the respective catalysts to the reactor bed of a batch reactor. Then, 5 g of a feed mixture of recycled phenol, 4 wt% acetone, and 1,000 parts per million (ppm) by weight thiol were added to the reactor. The reaction was allowed to proceed for 1 hour (hr), where samples for analysis were periodically removed. The samples were analyzed for BPA content and results are shown in FIG. 1, where the solid diamonds, solid squares, solid triangles, diamonds, squares, circles, and triangles represent Catalysts 1-7, respectively.

[0054] FIG. 1 shows that increasing the wt% crosslinking of the divinyl benzene results in a reduction in the amount of BPA produced with time, where Catalysts 1-6 show decreasing amounts of BPA at almost every time point. FIG. 1 further shows that Catalysts 1-4 result in a higher production of BPA with time as compared to Comparative Catalyst 7 that did not comprise the additional sulfone crosslinking. The two lines on the graph in FIG. 1 are best fit lines for Catalyst 2 and Comparative Catalyst 7.

Example 3: Compressibility testing of Catalysts 1-4 and 7

[0055] The compressibility of Catalysts 1-4 and 7 was tested by determining the change in the catalyst by volume, $V/V_0$, where $V_0$ is the initial catalyst volume and $V$ is the volume at an applied pressure. Specifically, an IER catalyst (30 grams (g), dried) was charged to the compressibility glass reactor (60 centimeters (cm) length, 1 inch diameter) and treated with a feed comprising recycled phenol (comprising 16 to 18 wt% of BPA and BPA by-products) with 4.0 to 4.5 wt% acetone at a flow rate of 30 grams per hour (g/hr) for about
72 hours. A piston of known weight was then clamped onto the resin so that it would just touch the surface of the swelled resin. The piston was then released and the displacement due to the piston was recorded as 0 displacement. After every 2 hr, known weights were added onto the piston and the displacement was recorded using a linear potentiometer. The weight and displacement were translated into the applied stress, delta pressure (P), and the results are shown in FIG. 2.

[0056] FIG. 2 shows that relative to Comparative Catalyst 7, the compressibility of Catalysts 3 and 4 is improved, the compressibility of Catalyst 2 is similar, and the compressibility of Catalyst 1 is slightly reduced. However, as can be seen from FIG. 3 and FIG. 4, Catalyst 2 had far better performance in forming BPA than Catalyst 7.

Example 4: Accelerated lifetime behavior

[0057] A multiport reactor study of Catalysts 1-4 and 7, where the catalyst behavior as determined by BPA production with time at a weighted hourly space velocity ( WHHSV) of 40 was performed. As used herein, the WHSV refers to the grams of feed per grams of catalyst per hour. The test was performed for 500 or 800 hr per each catalyst sample and the results were obtained using high pressure liquid chromatography (HPLC). Specifically, a recycled phenol (comprising 16 to 18 wt% of BPA and BPA by-products) with approximately 6 wt% acetone and 1,000 to 1,100 ppm by weight thiol was charged to the reactor. 1.25 g of dried catalyst was charged into each of three reactors connected in a series. The feed composition as above was pumped up-flow through the reactors so that the flow rate was maintained at 50 g/hr at the exit of the last reactor. Sample ports were connected in-between the reactors so that samples could be drawn using a glass syringe. Samples were collected using a glass sample vial from the exit of the last reactor. These samples were analyzed using HPLC for BPA and by-products content. The results are shown in FIG. 3 and FIG. 4. FIG. 3 shows totalized BPA (expressed in grams per gram dry catalyst) as a function of time. FIG. 4 shows BPA activity (expressed in terms of grams BPA/hr/gram dry catalyst) as a function of Totalized BPA. A transfer function was then used to determine the 5-year lifetime behavior of each of the catalysts, where if the catalyst performs without significant deactivation for 500 hr, then the test implies that the catalyst will have a lifetime of at least 5 years.

[0058] FIG. 3 shows the multiport reactor study at a WHSV of 40, of the totalized BPA production (TBP, where TBP is the grams of BPA divided by the grams of dry catalyst)
with time. The results show that Catalyst 2 has the least amount of deactivation, even after 800 hr as compared to Catalyst 7, whereas Catalysts 1 and 3 show some increased deactivation relative to Catalyst 7. FIG. 4 shows the rate of BPA formation (BPA activity) expressed in terms of grams of BPA produced per hour per gram of IER catalyst (dry basis) as a function of TBP (as defined above). In FIG. 4 we see that IER catalyst 2 has the highest BPA activity and the least deactivation trend over the entire duration of BPA production under accelerated conditions (40 WHSV flowrate).

Examples 5-8: Performance testing of Catalysts 2 and 7

[0059] The performance of Catalysts 2 and 7 was determined in a single column reactor (SCR), where the catalyst was located in a fixed bed and a feed was continuously passed through the catalyst bed at a WHSV of either 1 or 2. Specifically, the experiments were performed by adding 5 g of dry catalyst to the catalyst bed and feeding a reactant mixture of a recycled phenol (comprising 16 to 18 wt% of BPA and BPA by-products) with approximately 4 wt% acetone and a 1,000 to 1,100 ppm by weight thiol at 75°C. The results as determined by HPLC are shown in Table 2, where the data is the average of 8 reaction samples collected after a steady state was achieved.

<table>
<thead>
<tr>
<th>Example</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>2</td>
<td>C7</td>
<td>2</td>
<td>C7</td>
</tr>
<tr>
<td>WHSV</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>p,p' BPA selectivity (wt%)</td>
<td>93.1</td>
<td>92.0</td>
<td>93.6</td>
<td>92.5</td>
</tr>
<tr>
<td>Acetone Conversion (wt%)</td>
<td>88.4</td>
<td>84.2</td>
<td>83.5</td>
<td>77.5</td>
</tr>
<tr>
<td>p,p'/o,p' ratio</td>
<td>30.2</td>
<td>30.6</td>
<td>31.3</td>
<td>33.8</td>
</tr>
<tr>
<td>Total BPA selectivity (wt%)</td>
<td>96.4</td>
<td>95.3</td>
<td>96.9</td>
<td>95.5</td>
</tr>
</tbody>
</table>

[0060] Table 2 shows that the acetone conversion for Catalyst 2 was about 4 to 5% greater for Catalyst 2 as compared to Catalyst 7 at both a WHSV of 1 and 2. Table 2 further shows that the selectivity for p,p'-BPA was also increased for Catalyst 2 relative to Catalyst 7.

Example 9: Impurity profiles of Catalysts 2 and 7

[0061] The impurity profiles of the effluent (in weight percent based on the total weight of the effluent) of Examples 5-9 were determined and are shown in FIG. 5 and FIG. 6 at a WHSV of 1 and 2, respectively, for Catalyst 2 (light bars on the left) and Catalyst 7 (dark bars on the right). In the figures, o,p'-BPA is ortho, para-bisphenol A, LD-1 is a linear
dimer, CD-I is cyclic dimer-1, CD-2 is cyclic dimer-2, BPX-1 is 2,4-bis-(p-hydroxyphenylisopropylidenyl)phenol, BPX-2 is 2,4-bis(dimethyl-4-hydroxybenzyl)phenol, SBI is (1,1-spirobis(3,3'-dimethylindanol-5), and DMX is 9,9'-dimethyl xanthene.

[0062] FIG. 5 and FIG. 6 show that Comparative Catalyst 7 resulted in a higher production of all impurities except for o,p'-BPA and BPX-1. It is noted though that while Catalyst 2 resulted in more o,p'-BPA and more BPX-1 relative to Comparative Catalyst 7, these compounds can be further isomerized to p,p'-BPA. It is further noted that neither o,p'-BPA and BPX-1 contribute to discoloration of a BPA polycarbonate.

Example 10: Particle size distribution of Catalysts 2 and 7

[0063] The particle size distribution was determined using optical microscopy imaging of wet form particles. The average particle size distribution (average particle diameter) for Catalyst 2 was 796 micrometers and the average particle size distribution (average particle diameter) for Catalyst 7 was 1,145 micrometers. These values are within acceptable particle size for use as BPA catalysts.

Example 11: Moisture holding capacity of Catalysts 2 and 7

[0064] The moisture holding capacity was determined by the percentage of weight loss during dehydration of wet resin.

[0065] Analysis showed that the moisture holding capacity of Catalysts 2 and 7 were 87.5 and 80 wt%, respectively. Without being bound by theory, it is believed that the increased moisture holding capacity of Catalyst 2 is likely due to the fact that there is a lower percentage of divinyl benzene crosslinking in Catalyst 2 as compared to Catalyst 7.

Example 12: Acid content of Catalysts 2 and 7

[0066] The acid milliequivalent was determined by titration. In particular, 100 to 150 milligrams (mg) of dried IER was exchanged with 10 milliliters (mL) of a 2.5 Normal (N) solution of NaCl and the liberated HCl was titrated using 0.1 N sodium hydroxide solution using a Metrohm potentiometric titrator. Analysis showed that the acid milliequivalent of Catalysts 2 and 7 were 5.3 and 5.1 per gram of dry catalyst, respectively. The total sulfur content was determined by elemental analysis by combustion using a LECO analyzer. Analysis showed that the total sulfur content of Catalysts 2 and 7 was 18.2 and 16.2 wt%, respectively. Considering Catalyst 7, the total sulfur content corresponds to 5.0 milliequivalents of-SCHH groups per gram of catalyst. From the difference of the total
sulfur between total sulfur content determined by elemental analysis and acid milliequivalent by titration, the milliequivalent of the sulfone content of Catalyst 2 was determined to be 0.4 mmol per gram of dry catalyst.

Example 13: Bead integrity of Catalyst 2

[0067] Bead integrity of Catalyst 2 was determined by osmotic shock testing by subjecting the beads to extreme acidic and extreme alkaline conditions and then observing the beads using scanning electron microscopy for bead integrity. Specifically, 10.0 g of dry catalyst particles were placed on filter paper in a Buchner funnel. The following liquids were passed over the catalyst particles without suction to complete one cycle: 50 mL of deionized water, 50 mL of an aqueous solution of 15 volume percent (vol%) sulfuric acid, 50 mL of deionized water, 50 mL of an aqueous solution of 20 vol% sodium hydroxide, and 50 mL of deionized water. After a complete cycle, vacuum was applied to dry the particles and images were taken. The cycling was repeated until the beads lost their integrity or until 8 cycles were repeated without any sign of bead breakdown.

[0068] The bead integrity test of Catalyst 2 resulted in no cracks or bead breakdown after the 8 cycles of osmotic shock testing indicating that Catalyst 2 is robust to osmotic shock.

[0069] Set forth below are some embodiments of the catalyst and methods of making, and of using the same.

[0070] Embodiment 1: A catalyst comprising a sulfonated polymerization product of a monovinylaromatic monomer and less than 2.0 wt% of a polyvinyl aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

[0071] Embodiment 2: The catalyst of Embodiment 1, wherein a compressibility value of the catalyst is greater than or equal to 0.6 at an applied stress of 138 kPa.

[0072] Embodiment 3: The catalyst of any one of the preceding embodiments, wherein an average particle size of the catalyst is 500 to 1,500 micrometers at a moisture content of 85 to 90 wt%.

[0073] Embodiment 4: The catalyst of any one of the preceding embodiments, wherein the catalyst is the polymerization product of greater than 1.0 to less than 2.0 wt%, or greater than 1.0 to 1.5 wt%, or greater than 1.0 to 2.0 wt%, or greater than 1.0 to 1.25 wt%, or 1.1 to 1.15 wt%, or 1.12 to 1.14 wt% of the polyvinyl aromatic monomer.
[0074] Embodiment 5: The catalyst of any one of the preceding embodiments, wherein the catalyst is the polymerization product of 1.11 to 1.14 wt% of the polyvinyl aromatic monomer.

[0075] Embodiment 6: The catalyst of any one of the preceding embodiments, wherein the catalyst is the polymerization product of 1.12 to 1.14 wt% of the polyvinyl aromatic monomer.

[0076] Embodiment 7: The catalyst of any one of the preceding embodiments, wherein the catalyst is the polymerization product of 1.12 to 1.13 wt% of the polyvinyl aromatic monomer.

[0077] Embodiment 8: The catalyst of any one of the preceding embodiments, wherein the catalyst comprises 0.4 to 0.6 millimole of the sulfone bridges per gram of dry catalyst.

[0078] Embodiment 9: The catalyst of any one of the preceding embodiments, wherein the catalyst exhibits no cracks after 8 cycles of an osmotic shock test; wherein a cycle of the osmotic shock test comprises introducing the catalyst in the form of a plurality of particles to a Buchner funnel without applying a suction; adding to the Buchner funnel in the following order; 50 mL of a first deionized water, 50 mL of an aqueous solution comprising 15 vol% sulfuric acid, 50 mL of a second deionized water, 50 mL of an aqueous solution comprising 20 vol% sodium hydroxide, and 50 mL of a third deionized water; and drying the plurality of particles by applying suction to the Buchner funnel.

[0079] Embodiment 10: A method of producing a bisphenol comprising: reacting a phenolic compound with one or both of an aldehyde and a ketone in the presence of the catalyst of any one of the preceding embodiments to produce the bisphenol.

[0080] Embodiment 11: The method of Embodiment 10, wherein the catalyst has a lifetime of greater than or equal to 5 years, wherein during the five years of continuous use in producing the bisphenol, a bisphenol activity in grams of bisphenol per hour per gram of the catalyst does not decrease by greater than or equal to 20%, wherein the catalyst is exposed to a feed during the continuous use and the feed comprises a water content of less than 5 wt% based on the total weight of the feed.

[0081] Embodiment 12: The method of any one of Embodiments 10-11, wherein the monovinylnaromatic monomer comprises styrene and/or wherein the polyvinyl aromatic monomer comprises divinyl benzene.
Embody endoth [13]: The method of any one of Embodiments 10-12, wherein the phenolic compound comprises a monocyclic phenolic compound, a polycyclic phenolic compound, or a combination comprising at least one of the foregoing.

Embody endoth [14]: The method of Embodiment 13, wherein the monocyclic phenolic compound and/or the polycyclic phenolic compound is substituted with up to 5 substituents.

Embody endoth [15]: The method of any one of Embodiments 10-14, wherein the phenolic compound comprises phenol.

Embody endoth [16]: The method of any one of Embodiments 10-15, wherein the aldehyde is present and wherein the aldehyde comprises a compound of the formula R^k1-(C=0)-H, wherein R^k1 is hydrogen of a C1-18, specifically, C1-6 aliphatic group and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous.

Embody endoth [17]: The method of any one of Embodiments 10-16, wherein the ketone is present and wherein the ketone comprises a compound of the formula R^k1-(C=0)-R^k2, wherein R^k1 and R^k2 are each independently a C1-18, specifically, C1-6 aliphatic group that can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous; wherein R^k1 and R^k2 can together form a C5-18 cycloalkyl group (such as cyclohexanone or methylcyclohexanone) or a C5-18 cycloalkylene group.

Embody endoth [18]: The method of any one of Embodiments 10-17, wherein the one or both of the aldehyde and the ketone comprises acetone.

Embody endoth [19]: The method of any one of Embodiments 10-18, wherein the monovinylaromatic monomer comprises styrene, alpha-methyl styrene, vinyl toluene, ethyl vinyl benzene, vinyl naphthalene styrene, or a combination comprising at least one of the foregoing; specifically, the monovinylaromatic monomer comprises styrene.

Embody endoth [20]: The method of any one of Embodiments 10-19, wherein the polyvinyl aromatic monomer comprises divinyl benzene, divinyl toluene, trivinyl benzene, divinyl chloro benzene, diallyl phthalate, divinyl naphthalene, divinyl xylene, divinyl ethyl benzene, trivinyl naphthalene, polyvinyl anthracene, or a combination comprising at least one of the foregoing; specifically, the polyvinyl aromatic monomer comprises divinyl benzene.

Embody endoth [21]: The method of any one of Embodiments 10-20, wherein the bisphenol comprises bisphenol A.
[0091] Embodiment 22: The method of any one of Embodiments 10-21, wherein a ratio of the phenolic compound to the aldehyde or ketone is 20:1 to 2:1.

[0092] Embodiment 23: A method for the manufacture of a polycarbonate comprising: combining the bisphenol of any one of Embodiments 10-22 and a carbonate source; and polymerizing mixture comprising the bisphenol and the carbonate source in the presence of a catalyst to produce the polycarbonate.


[0095] Embodiment 26: A polycarbonate made by the method of any one of Embodiments 23-25.

[0096] Embodiment 27: A method of producing the catalyst of any one of Embodiments 1-9, comprising reacting the monovinylaromatic monomer and less than 2.0 wt% of the polyvinyl aromatic monomer based on the total amount of monomer in the presence of an initiator, an optional stabilizer, and an optional aliphatic monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

[0097] Embodiment 28: The method of Embodiment 27, wherein the reacting comprises forming a reaction mixture comprising a suspending media, the monovinylaromatic monomer, the polyvinyl aromatic monomer, the initiator, the optional stabilizer, and the optional aliphatic monomer; increasing the temperature of the reaction mixture to a polymerization temperature to form the catalyst; separating the catalyst from the suspending media; and functionalizing the catalyst with a sulfonating agent by introducing the catalyst to a sulfonating reagent composition to form the sulfone bridges.

[0098] Embodiment 29: The method of Embodiment 28, wherein the sulfonating reagent composition comprises chlorosulfonic acid, sulfur trioxide, sulfuric acid, or a combination comprising one or more of the foregoing and a boron compound.

[0099] Embodiment 30: The method of any one of Embodiments 28-29, wherein the polymerization temperature is 40 to 100°C.

[0100] Embodiment 31: The method of any one of Embodiments 27-30, wherein the catalyst has an average of at least one sulfonic acid group per aromatic nucleus.
In general, the methods or polycarbonates can alternatively comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The methods or polycarbonates can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present disclosure.

All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of "up to 25 wt%, or, more specifically, 5 wt% to 20 wt%", is inclusive of the endpoints and all intermediate values of the ranges of "5 wt% to 25 wt%," etc.). "Combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms "a" and "an" and "the" herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to "one embodiment," "another embodiment," "an embodiment," and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements can be combined in any suitable manner in the various embodiments. "Or" means "and/or" unless the context specifies otherwise.

While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to Applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

I/we claim:
CLAIMS

1. A catalyst comprising a sulfonated polymerization product of a monovinylaromatic monomer and less than 2.0 wt% of a polyvinyl aromatic monomer, based on the total amount of monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

2. The catalyst of Claim 1, wherein a compressibility value of the catalyst is greater than or equal to 0.6 at an applied stress of 138 kPa.

3. The catalyst of any one of the preceding claims, wherein an average particle size of the catalyst is 500 to 1,500 micrometers at a moisture content of 85 to 90 wt%.

4. The catalyst of any one of the preceding claims, wherein the catalyst is the polymerization product of greater than 1.0 to less than 2.0 wt%, or greater than 1.0 to 1.5 wt%, or greater than 1.0 to 1.2 wt%, or greater than 1.0 to 1.25 wt%, or greater than 1.1 to 1.15 wt%, or 1.12 to 1.14 wt% of the polyvinyl aromatic monomer.

5. The catalyst of any one of the preceding claims, wherein the catalyst comprises 0.4 to 0.6 millimole of the sulfone bridges per gram of dry catalyst.

6. The catalyst of any one of the preceding claims, wherein the catalyst exhibits no cracks after 8 cycles of an osmotic shock test; wherein a cycle of the osmotic shock test comprises introducing the catalyst in the form of a plurality of particles to a Buchner funnel without applying a suction;

adding to the Buchner funnel in the following order;

- 50 mL of a first deionized water,
- 50 mL of an aqueous solution comprising 15 vol% sulfuric acid,
- 50 mL of a second deionized water,
- 50 mL of an aqueous solution comprising 20 vol% sodium hydroxide, and
- 50 mL of a third deionized water; and

drying the plurality of particles by applying suction to the Buchner funnel.

7. A method of producing a bisphenol comprising:

reacting a phenolic compound with one or both of an aldehyde and a ketone in the presence of the catalyst of any one of the preceding claims to produce the bisphenol.

8. The method of Claim 7, wherein the catalyst has a lifetime of greater than or equal to 5 years, wherein during the five years of continuous use in producing the bisphenol, a bisphenol activity in grams of bisphenol per hour per gram of the catalyst does not decrease.
by greater than or equal to 20%, wherein the catalyst is exposed to a feed during the continuous use and the feed comprises a water content of less than 5 wt% based on the total weight of the feed.

9. The method of any one of Claims 7-8, wherein the monovinylaromatic monomer comprises styrene and/or wherein the polyvinyl aromatic monomer comprises divinyl benzene.

10. The method of any one of Claims 7-9, wherein the phenolic compound comprises a monocyclic phenolic compound, a polycyclic phenolic compound, or a combination comprising at least one of the foregoing; and wherein the monocyclic phenolic compound and/or the polycyclic phenolic compound is optionally substituted with up to 5 substituents.

11. The method of any one of Claims 7-10, wherein the phenolic compound comprises phenol, the aldehyde or a ketone comprises acetone, the monovinylaromatic monomer is styrene, and the polyvinyl aromatic monomer is divinyl benzene.

12. A method for the manufacture of a polycarbonate comprising: combining the bisphenol of any one of Claims 7-11 and a carbonate source; and polymerizing mixture comprising the bisphenol and the carbonate source in the presence of a catalyst to produce the polycarbonate.

13. The method of Claim 12, wherein the bisphenol comprises bisphenol A.

14. The method of any of Claims 12 to 13, wherein the carbonate source comprises diphenyl carbonate.

15. The method of any of Claims 12 to 13, wherein the carbonate source comprises phosgene.

16. A method of producing the catalyst of any one of Claims 1-15, comprising reacting the monovinylaromatic monomer and less than 2.0 wt% of the polyvinyl aromatic monomer based on the total amount of monomer in the presence of an initiator, an optional stabilizer, and an optional aliphatic monomer, and wherein the catalyst comprises 0.1 to 1.0 millimole of sulfone bridges per gram of dry catalyst.

17. The method of Claim 16, wherein the reacting comprises forming a reaction mixture comprising a suspending media, the monovinylaromatic monomer, the polyvinyl aromatic monomer, the initiator, the optional stabilizer, and the optional aliphatic monomer; increasing the temperature of the reaction mixture to a polymerization temperature to form the catalyst; separating the catalyst from the suspending media; and functionalizing the
catalyst with a sulfonating agent by introducing the catalyst to a sulfonating reagent composition to form the sulfone bridges.

18. The method of Claim 17, wherein the sulfonating reagent composition comprises chlorosulfonic acid, sulfur trioxide, sulfuric acid, or a combination comprising one or more of the foregoing and a boron compound.

19. The method of any one of Claims 17-18, wherein the polymerization temperature is 40 to 100°C.

20. The method of any one of Claims 16-19, wherein the catalyst has an average of at least one sulfonic acid group per aromatic nucleus.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**INV.** B01J31/10

**ADD.**

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)

B01J

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)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
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<td><strong>US 5 233 096 A (LUNDOQUIST ERIC G [US])</strong> 3 August 1993 (1993-08-03) example e 5</td>
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<td>A</td>
<td><strong>US 5 616 622 A (HARRIS WILLIAM I [US] ET AL) 1 April 1997 (1997-04-01) column 1, line 1 - line 29; claims 1, 6</strong></td>
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<td>A</td>
<td><strong>EP 1 201 303 AI (NI PPN STEEL CHEMICAL CO) 2 May 2002 (2002-05-02) paragraph [0016]</strong></td>
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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 of particular relevance
  - "E" earlier application or patent but 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
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "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
  - "Z" document member of the same patent family

**Date of the actual completion of the international search**

12 October 2016

**Date of mailing of the international search report**

12/12/2016

**Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016**

Authorized officer

Klaes, Daphne
### Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. □ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
   
   1-11, 16-20

**Remark on Protest**

□ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11, 16-20

   A catalyst based on a sulfonated polymer azation product of a monovinylnyl aromatic monomer and less than 2.0 wt% of a polyvinyl aromatic monomer bearing sulfone bridges, a method of producing Bisphenol A in the presence of said catalyst and a method to prepare said catalyst.

2. claims: 12-15

   A method for the manufacture of a polycarbonate
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<th>Publication date</th>
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