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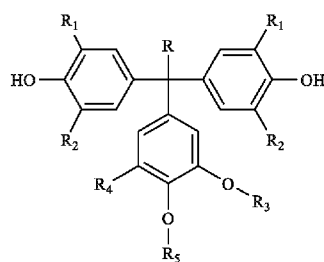
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(54) Title: BIO-BASED BISPHENOL MONOMERS, POLYPHENOLS AND THEIR POLYMERS, A PROCESS OF PREPARATION AND APPLICATIONS THEREOF



Formula I

(57) Abstract: The present invention relates to bio-based bisphenol monomer of formula I and process of preparation thereof. Specifically, the present invention relates to bio-based bisphenol monomers of formula I containing multiple alkoxy groups, and polyphenols. The bisphenol monomers of formula I contain built-in methoxy groups, which represent latent phenolic hydroxyl groups and could conveniently be de-blocked to phenolic hydroxyl groups leading to formation of polyphenols containing catechol/phloroglucinol units with anti-oxidant properties and are potentially useful in various applications like cosmetics, polymer additives and so on. Further, the present invention relates to process of preparation of polymers using bisphenol monomer of formula I as valuable building blocks wherein the high performance thermoplastics are poly(ether sulfone)s, poly(ether ether ketone)s, polyesters, polycarbonates, polyphosphonates, etc. and thermosetting resins are epoxies, cyanate esters, phthalonitriles, propargyl ethers, etc.

**BIO-BASED BISPHENOL MONOMERS, POLYPHENOLS AND THEIR POLYMERS, A  
PROCESS OF PREPARATION AND APPLICATIONS THEREOF**

**FIELD OF THE INVENTION**

5 The present invention relates to a bio-based bisphenol monomer of formula I. Particularly, the present invention relates to a process for the preparation of bio-based bisphenol monomers of formula I containing multiple phenolic hydroxyl, alkoxy groups, and polyphenols. Further, the present invention relates to a process for the preparation of polymers using bio-based bisphenol monomers of formula I wherein the thermoplastics prepared are poly(ether sulfone)s (PSUs),  
10 poly(ether ether ketone)s (PEEKs), polycarbonates, polyesters, etc., while thermosetting polymers prepared are epoxies, cyanate esters, phthalonitriles, propargyl ethers, etc. and the applications of said polymers as anti-oxidant agents, anti-fouling agents, adhesion promoters, redox active agents in battery applications, etc.

**BACKGROUND AND PRIOR ART OF THE INVENTION**

15 Bisphenols are important class of bifunctional monomers that are widely used in the preparation of a host of high-performance polymers such as poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates, polyesters, epoxy resins, etc. A recent landscape study of bisphenol-A (BPA) monomer demonstrated that about 6.3 million tons/year (2023) were produced annually worldwide from petroleum-based chemicals. However, BPA has estrogen-mimicking, hormone-  
20 like properties, which causes hormone disruption upon consumption. Early investigations have suggested that BPA can accumulate in humans and this can eventually affect growth in reproductive, neurological and developmental problems, as well as thyroid hormone disruption, obesity and metabolic disease. As a result, BPA has been banned on a global platform and strict policies have been implemented on the uses of BPA-based products. For instance, the use of  
25 BPA in baby bottles has been banned in European Union and Canada and this movement has changed the scenario in the U.S. where public pressure has led to the virtual termination of the use of BPA in baby bottles and infant formula packaging (refer, Ga Won Jeon, Clin Exp Pediatr, 65(9), 2022; and European commission, Press release, 25 February 2011, [https://ec.europa.eu/commission/presscorner/detail/en/IP\\_11\\_229](https://ec.europa.eu/commission/presscorner/detail/en/IP_11_229)). Added to this, the raw  
30 materials in the synthesis of BPA are derived from petroleum sources, which also cause environmental pollution. Therefore, it is important to design monomers that can act as safer replacement for bisphenol-A, and to develop methods for their synthesis based on renewable bio-derived chemicals.

35 There are several approaches in the literature for the synthesis of (partially) bio-derived bisphenol-A-like molecules that are based on bio-based chemicals, such as lignin-derived aromatics, cashew nut shell liquid, terpenes, levulinic acid, etc. Of these raw materials, lignin is abundantly available. The worldwide production of lignin is approximately 100 million tons per

year (2024) generated as a waste product from paper and ethanol production. Lignin extraction from biomass (wheat straw, sugar cane bagasse, etc) can be carried out by a chemical delignification method, using either aqueous or organic solvent. Lignin is a natural phenolic polymer with high molecular weight, and complex composition, and is a non-edible biomass resource useful for production of value-added chemicals. Some of the most important lignin-derived aromatic chemicals are vanillin, syringaldehyde, syringol, guaiacol, vanillic acid, syringic acid, and ferulic acid.

References may be made to patent application WO2015140818A1, which reports bisphenol compounds with pendant furyl groups, useful for the preparation of polymers and a process for the synthesis of such bisphenols and polymers therefrom. The synthesized polymers contain pendant furyl groups which act as reactive sites for chemical modifications/crosslinking via click reaction with maleimides/bismaleimides.

References may be made to an article titled, "Partially bio-based aromatic poly(ether sulfone)s bearing pendant furyl groups: synthesis, characterization and thermo-reversible cross-linking with a bismaleimide", by Nagane et. al in *Polym. Chem.*, 2019, 10, 1089-1098, reported a fully bio-based bisphenol containing pendant furyl group, viz., 4,4'-(furan-2-ylmethylene)bis(2-methoxyphenol) (BPF) that was synthesized by base-catalyzed condensation of furfural with guaiacol. The partially bio-based (co)poly(ether sulfone)s were synthesized by aromatic nucleophilic substitution polycondensation of BPF and varying compositions of BPF and bisphenol-A (BPA) with bis(4-fluorophenyl) sulfone. The pendant furyl groups in (co)poly(ether sulfone)s provide reactive sites for modification and cross-linking via Diels–Alder reaction with maleimides and bismaleimides, respectively.

References may be made to an article entitled "Regioselective synthesis, isomerization, in vitro estrogenic activity, and copolymerization of bisguaiacol F (BGF) isomers", by Steven-Friso K. et. al in *Green Chem.*, 2019, 21, 6622 reported that bisguaiacol F (BGF), a potentially safer and renewable bisphenol A (BPA) replacement made from lignin derivable vanillyl alcohol (p-VA), is a promising building block for aromatic biopolymers. Another article by T. Periyasamy et. al entitled "Replacing bisphenol-A with bisguaiacol-F to synthesize polybenzoxazines for pollution-free environment" in *New J. Chem.*, 2016, 40, 9313-9319, reported the synthesis of BGF and BGF-based benzoxazines as an alternative to BPA and polybenzoxazines derived from BPA. A solvent-less method was adopted for the synthesis of BGF and the benzoxazine monomers.

Polyphenols- the compounds containing multiple phenolic hydroxyl groups- are important in various applications such as anti-oxidants, redox-active agents in battery applications and precursors to thermosettings.

References may be made to an article, ACS Sustainable Chem. Eng. 2018, 6, 7600–7608, in which a series of trisphenols containing methoxyl groups from lignin-derived chemicals such as guaiacol, vanillin and syringaldehyde, and demonstrated their use in preparation of epoxies is mentioned.

5 Thus, in view of above stated problems, there is a need to provide new bisphenol monomers that are largely bio-based and containing (latent) reactive sites. This is addressed by the inventors of present invention by providing novel bio-based bisphenol monomers which contain multiple alkoxy groups that could conveniently be de-blocked to phenolic hydroxyl groups “on demand”  
10 either in the monomer stage itself or *via* post-polymerization modification of the polymers derived therefrom. The phenolic hydroxyl reactive sites generated in the functionalized (co)polymer can be directly useful for certain applications or can be used for further chemical modifications. Moreover, the corresponding high-performance polymers are potentially applicable in various fields such as functional membranes with antifouling/antibacterial characteristics, redox-active agents for battery applications, adhesives, polymer coatings with inherent anti-oxidant  
15 characteristics, etc.

## OBJECTS OF THE INVENTION

Main objective of the present invention is to provide bisphenol monomer of formula I, which are based on bio-based chemicals.

20 Another objective of the present invention is to provide bisphenol monomers of formula I, reciting multiple phenolic hydroxyl or alkoxy groups, and polyphenols.

Yet another objective of the present invention is to provide a process of preparation of said bisphenol monomers of formula I.

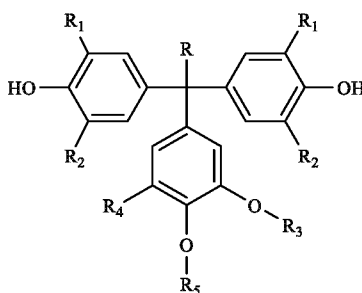
25 Yet another objective of the present invention is to provide a process of preparation of poly(ether sulfone)s (PSUs) as one of (co)polymers from said bisphenol monomers of formula I.

Yet another objective of the present invention is to provide a process of preparation of poly(ether ether ketone)s as one of (co)polymers from said bisphenol monomers of formula I.

Still another objective of the present invention is to provide a process of preparation of polyesters as one of (co)polymers from said bisphenol monomers formula I.

## 30 SUMMARY OF THE INVENTION

Accordingly in order to accomplish the set objectives, the present invention provides a bio-based bisphenol monomer of formula I



Formula I

wherein

R is hydrogen or alkyl,

5 R<sub>1</sub> is hydrogen, -O-alkyl or alkenyl,

R<sub>2</sub> is hydrogen or -O-alkyl,

R<sub>3</sub> is hydrogen, alkyl, alkenyl or alkynyl,

R<sub>4</sub> is hydrogen, O-alkyl, O-alkenyl or O-alkynyl, and

R<sub>5</sub> is hydrogen, alkyl, alkenyl or alkynyl.

10 In an embodiment of the present invention, wherein R is hydrogen or (C1-C5)alkyl, R<sub>1</sub> is hydrogen, -O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>2</sub> is -O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>3</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, R<sub>4</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, and R<sub>5</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl;

15 wherein the monomer of formula I recites 2 to 9 phenolic hydroxyl or alkoxy or methoxy groups; and

wherein the monomer of formula I recites at least four phenolic hydroxyl or alkoxy or methoxy groups.

In another embodiment of the present invention, said monomer is selected from

- 20 i. 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM)  
(monomer 1) and;
- ii. 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD)  
(monomer 2).

25 In yet another embodiment of the present invention, the bio-based bisphenol monomer of formula I reciting multiple phenolic hydroxyl or alkoxy groups, and polyphenols recite at least 2 to upto 9 hydroxyl groups.

In yet another embodiment, present invention provides a process of preparation of bio-based bisphenol monomers of formula I, the formula I comprising the steps of:

- a) stirring and dissolving a mixture of bio-based aldehyde and a phenolic compound in a container or reactor to obtain a solution;
- 5        b) adding condensing agent and Bronsted acid catalyst into said solution as obtained in step a) at temperature in the range of 40 to 50°C for time period in the range of 10 to 15 h under inert N<sub>2</sub> atmosphere to obtain crude product;
- c) washing the crude product as obtained in step b) with a solvent followed by evaporation and drying to obtain the bisphenol monomer compound of formula I; and
- 10       d) optionally purifying the bisphenol monomer compound of formula I as obtained in step c) to obtain pure bisphenol monomer compound of formula I.

In yet another embodiment of the present invention, the step a) is carried out at a temperature in the range of 25 to 35 °C without addition of a solvent;

15       In yet another embodiment of the present invention, the solvent used in step c) is a hot water having temperature of at least about 70 °C or a distilled water;

In yet another embodiment of the present invention, the evaporation of step c) is done using a rotary evaporator under reduced pressure in the range of 100 to 200 mm Hg at a temperature in the range of 120 to 160 °C;

20       In yet another embodiment of the present invention, the drying of step c) is done by placing said viscous liquid as obtained upon evaporation, in a vacuum oven at temperature in the range of 70 to 110 °C for time period of 10 to 14 hrs to obtain the monomer of formula I;

In yet another embodiment of the present invention, the bio-based aldehyde is selected from vanillin, syringaldehyde, and veratraldehyde; and

25       In yet another embodiment of the present invention, the phenolic compound is selected from syringol, and guaiacol.

In yet another embodiment of the present invention, the Bronsted acid catalyst is selected from p-toluene sulfonic acid (PTSA), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), acetic acid (CH<sub>3</sub>COOH), MeSO<sub>3</sub>H, acidic ion exchange resin, sulfated zirconia, and polyoxometalates (heteropolyacids); wherein the condensing agent is selected from zinc chloride, magnesium chloride (MgCl<sub>2</sub>), ferric chloride (FeCl<sub>3</sub>), and aluminum chloride (AlCl<sub>3</sub>).

30

In yet another embodiment of the present invention, the concentration of bio-based aldehyde is in range of 30 to 35 mol %.

In yet another embodiment of the present invention, the concentration of phenolic compound is in range of 66 to 70 mol %.

In yet another embodiment of the present invention, the concentration of condensing agent is in range of 0.1 to 1 mol %.

5 In yet another embodiment of the present invention, the concentration of Bronsted acid catalyst is in range of 0.1 to 1 mol %.

In yet another embodiment of the present invention, yield of the monomer of formula I is in range of 60 to 70 %.

10 In yet another embodiment of the present invention, selectivity of the monomer of formula I is in range of 70 to 75 % with a conversion rate of the bio-based aldehyde into said monomer of formula I is in range of 70 to 75%.

In yet another embodiment of the present invention, wherein said polymer is selected from poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates and polyester.

15 In yet another embodiment of the present invention, wherein said polymer comprises phenolic hydroxyl or alkoxyl or methoxyl groups, and polyphenols, with at least 2 to 9 hydroxyl groups.

In yet another embodiment, present invention provides a process for the preparation of a polymer comprising the steps of:

- a) dissolving and preparing a reaction mixture comprises the bisphenol monomer of formula I, a monomer, a catalyst and solvent in a container or reactor;
- 20 b) refluxing the reaction mixture as obtained in step, a) at temperature in the range of 120-140 °C with constant stirring in range of 500 to 1000 RPM for time period in the range of 1-2 h to obtain crude polymer product along with water;
- c) distilling out the water produced in step b) to obtain crude polymer which is further heated at temperature in the range of 140-155 °C for time period of 2-5 h to obtain  
25 viscous polymer solution; and
- d) precipitating the viscous polymer solution of step c) in a precipitating solvent followed by washing, reprecipitation, rewashing and drying under reduced pressure at 25 to 35 °C for time period of 12-24 h to obtain the desired polymer;

wherein said polymer is poly(ether sulfone) or poly(ether ether ketone).

30 In yet another embodiment of the present invention, the monomer is a sulfonyl monomer or ether ketone monomer.

In yet another embodiment of the present invention, the sulfonyl monomer is selected from bis(4-chlorophenyl)sulfone and bis(4-fluorophenyl)sulfone.

In yet another embodiment of the present invention, the ether ketone monomer is selected from 4,4'-difluorobenzophenone, 1,4-phenylenebis((4-fluorophenyl)methanone) and 1,3-phenylenebis((4-fluorophenyl)methanone).

In yet another embodiment of the present invention, the bisphenol monomer of formula I is 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) or 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD).

In yet another embodiment of the present invention, the catalyst used in step a) is selected from alkali metal hydroxide or alkali metal carbonate, wherein the alkali metal hydroxide is selected from NaOH, KOH, and LiOH; and the alkali metal carbonate is selected from Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and Mg<sub>2</sub>CO<sub>3</sub>.

In yet another embodiment of the present invention, the solvent used in step a) is selected from *N*, *N*-dimethylacetamide, toluene, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and/or mixture thereof.

In yet another embodiment of the present invention, the precipitating/precipitating solvent used at step d) is methanol.

In yet another embodiment of the present invention, said polymer is chemically modified to generate catechol moieties and phenolic hydroxyl groups.

In yet another embodiment of the present invention, the polymer is further chemically modified to introduce functional groups at hydroxyl group through alkylation, esterification and synthesis of graft co-polymers via 'grafting onto' or 'grafting from' approach.

In yet another embodiment of the present invention, said polymers exhibit adhesive, antioxidant, antimicrobial and redox activity in battery applications.

In yet another embodiment of the present invention, the present invention further provides processes of preparation of polymers using said monomer of formula I wherein the polymers are selected from poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonate, polyester, and so on.

In yet another embodiment of the present invention, the present invention provides a process of generating functional groups in said synthesized polymer(s) by simple de-protection reaction after polymerization. The reactive sites (OH groups) generated in the functionalized copolymer may be directly useful for certain applications or for further chemical modifications.

In yet another embodiment of the present invention, the present invention provides further chemical modification of said copolymers, selected from alkylation, esterification and synthesis of graft polymers, and since there is a presence of catechol/phloroglucinol moieties, it is anticipated to exhibit adhesion, antimicrobial, and antioxidant properties.

5 In yet another embodiment of the present invention, the present invention provides a catalyst for said de-protection reaction selected from the group of  $\text{BBr}_3$ , pyridine-HCl, trimethylsilyl iodide, HBr, HI and so on.

10 In yet another embodiment of the present invention, the present invention provides largely bio-based bisphenol monomers of formula I specifically 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) and/or 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD) that are synthesized by acid-catalyzed reaction of bio-based veratraldehyde which can also be obtained from vanillin, - with guaiacol or syringol. All of the reactants are derivable from lignin - the second most abundant source of aromatic chemicals on earth.

15 In yet another embodiment of the present invention, the bisphenol monomer of formula I may contain built-in methoxyl groups, which represent latent phenolic hydroxyl groups and could be conveniently de-blocked to phenolic hydroxyl groups leading to formation of polyphenols containing catechol/phloroglucinol units with anti-oxidant properties and are potentially useful in various applications such as cosmetics, polymer additives and so on. The methoxyl groups in the  
20 polymers could be conveniently de-blocked 'on-demand' to generate multiple hydroxyl groups in the constituent repeating units. Based on the number and location of methoxyl groups in the bisphenol monomers, catechol/phloroglucinol-type units are generated in the polymer backbone. The presence of these units confers interesting surface properties and characteristics such as anti-oxidant, adhesion to dissimilar surfaces, anti-fouling and anti-bacterial to the polymers which  
25 make these polymers interesting candidates for applications in membrane materials and coatings.

In yet another embodiment of the present invention, the bisphenol monomers of formula I represent valuable building blocks for synthesis of a range of high performance thermoplastics such as poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates, polyesters, and  
30 polyphosphonates.

In yet another embodiment of the present invention, the bisphenol monomers and polyphenols are interesting precursors for thermosetting resins such as multifunctional epoxies, cyanate esters, phthalonitriles and propargyl ethers.

35 **BRIEF DESCRIPTION OF THE DRAWINGS**

**Figure 1** illustrates a) DPPH radical discoloration due to the reaction with catechol-containing PSU-OH-3. The photo was taken 2 min after the addition of PSU-OH-3 to DPPH solution. [-] means no polymer was added, b) UV-vis spectra of DPPH before and after addition of PSU-OH-3, c) % inhibition of PSU-OH-3, PSU-OH-4 and PSU-OH-5 with five different concentrations.

5 **Figure 2** illustrates Bacterial inhibition zone of Gram-positive bacterium *Staphylococcus aureus* and Gram-negative bacterium *Escherichia coli* with various concentrations of PSU-OH-3.

**Figure 3** illustrates time-kill curves for *Staphylococcus aureus* (a Gram-positive bacterium) and *Escherichia coli* (a Gram-negative bacterium) with PSU-OH-3

10 **Figure 4** illustrates performance of PSU-OH-5 as an organic electrode in zinc-ion battery: a) CV graph at 0.5 mV sec<sup>-1</sup> scan rates, (b) rate capability data, (c) GCD profiles at various current densities (the 1st cycles of each current density and (d) cycling performance at 100 mA g<sup>-1</sup>.

**Figure 5** illustrates load vs extension curves of PSU-OMe-5 and PSU-OH-5

**Figure 6** illustrates lap shear strength of PSU-OMe-5 and PSU-OH-5 evaluated on aluminium substrates

15 **Figure 7** illustrates the synthesis of bisphenol of formula I.

**Figure 8** illustrates the synthesis of partially bio-based (co)poly(ether sulfone)s bearing pendent methoxyl groups.

**Figure 9** illustrates post-functional modifications of poly (ether sulfone)s.

20 **Figure 10** illustrates a plausible redox mechanism involving pendant catechol moieties in (co)poly(ether sulfone)s (indicated by wavy line).

## DETAILED DESCRIPTION OF THE INVENTION

“Alkyl” as used herein is collection of carbon atoms that are covalently linked together in normal, secondary, tertiary or cyclic arrangements, i.e., in linear, branched, cyclic arrangement or some combination thereof. An alkyl substituent to structure is chain of carbon atoms that is covalently attached to structure through sp<sup>3</sup> carbon of substituent. The alkyl substituents, as used herein, contain one or more saturated moieties or groups and may additionally contain unsaturated alkyl moieties or groups, i.e., substituent may comprise one, two, three or more independently selected double bonds or triple bonds and combination thereof, typically one double or one triple bond if such unsaturated alkyl moieties or groups are present. Unsaturated alkyl moieties or groups include moieties or groups as described below for alkenyl, alkynyl, cycloalkyl, and aryl moieties. Saturated alkyl moieties contain saturated carbon atoms (sp<sup>3</sup>) and no aromatic, sp<sup>2</sup> or sp carbon atoms. The number of carbon atoms in an alkyl moiety or group can vary and typically is 1 to about 50, e.g., about 1-30 or about 1-20, unless otherwise specified, e.g., C<sub>1-8</sub> alkyl or C<sub>1-8</sub> alkyl means an alkyl moiety containing 1, 2, 3, 4, 5, 6, 7 or 8 carbon atoms and C<sub>1-6</sub> alkyl or C<sub>1-6</sub> alkyl means an alkyl moiety containing 1, 2, 3, 4, 5 or 6 carbon atoms. When an alkyl

substituent, moiety or group is specified, species may include methyl, ethyl, 1-propyl (n-propyl), 2-propyl (iso-propyl,  $-\text{CH}(\text{CH}_3)_2$ ), 1-butyl (n-butyl), 2-methyl-1-propyl (iso-butyl,  $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2-butyl (sec-butyl,  $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ ), 2-methyl-2-propyl (t-butyl,  $-\text{C}(\text{CH}_3)_3$ ), amyl, isoamyl, sec-amyl and other linear, cyclic and branch chain alkyl moieties. Unless otherwise specified, alkyl groups can contain species and groups described below for cycloalkyl, alkenyl, alkynyl groups, aryl groups, arylalkyl groups, alkylaryl groups and the like.

**“Alkenyl”** as used herein means a substituent, moiety or group that comprises one or more double bond moieties (e.g.,  $-\text{CH}=\text{CH}-$ ) or 1, 2, 3, 4, 5 or 6 or more, typically 1, 2 or 3 such moieties and can include an aryl moiety or group such as benzene, and additionally comprises linked normal, secondary, tertiary or cyclic carbon atoms, i.e., linear, branched, cyclic or any combination thereof unless the alkenyl moiety is a vinyl moiety (e.g.,  $-\text{CH}=\text{CH}_2$ ). An alkenyl moiety, group or substituent with multiple double bonds may have the double bonds arranged contiguously (i.e., a 1, 3 butadienyl moiety) or non-contiguously with one or more intervening saturated carbon atoms or a combination thereof, provided that a cyclic, contiguous arrangement of double bonds do not form a cyclically conjugated system of  $4n+2$  electrons (i.e., aromatic). The number of carbon atoms in an alkenyl group or moiety can vary and typically is 2 to about 50, e.g., about 2-30 or about 2-20, unless otherwise specified, e.g.,  $\text{C}_{2-8}$  alkenyl or  $\text{C}_{2-8}$  alkenyl means an alkenyl moiety containing 2, 3, 4, 5, 6, 7 or 8 carbon atoms and  $\text{C}_{2-6}$  alkenyl or  $\text{C}_{2-6}$  alkenyl means an alkenyl moiety containing 2, 3, 4, 5 or 6 carbon atoms. Alkenyl moieties or groups will typically have 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms.

When an alkenyl moiety, group or substituent is specified, species include, by way of example and not limitation, any of the alkyl or cycloalkyl, groups moieties or substituents described herein that has one or more double bonds, methylene ( $=\text{CH}_2$ ), methylenemethylene ( $=\text{CH}-\text{CH}_3$ ), ethylenemethylene ( $=\text{CH}-\text{CH}_2-\text{CH}_3$ ),  $=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , vinyl ( $-\text{CH}=\text{CH}_2$ ), allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, cyclopentenyl, 1-methylcyclopentenyl, 1-hexenyl, 3-hexenyl, cyclohexenyl and other linear, cyclic and branched chained all carbon containing moieties containing at least one double bond. When alkenyl is used as a Markush group (i.e., a substituent) the alkenyl is attached to a Markush formula with which it is associated through an unsaturated carbon of a double bond of the alkenyl moiety or group unless specified otherwise.

**“Alkynyl”** as used herein means a substituent, moiety or group that comprises one or more triple bond moieties (i.e.,  $-\text{C}\equiv\text{C}-$ ), e.g., 1, 2, 3, 4, 5, 6 or more, typically 1 or 2 triple bonds, optionally comprising 1, 2, 3, 4, 5, 6 or more double bonds, with the remaining bonds (if present) being single bonds and comprising linked normal, secondary, tertiary or cyclic carbon atoms, i.e., linear, branched, cyclic or any combination thereof, unless the alkynyl moiety is ethynyl. The number of carbon atoms in an alkenyl moiety or group can vary and typically is 2 to about 50,

e.g., about 2-30 or about 2-20, unless otherwise specified, e.g., C<sub>2-8</sub>alkynyl or C<sub>2-8</sub> alkynyl means an alkynyl moiety containing 2, 3, 4, 5, 6, 7 or 8 carbon atoms. Alkynyl groups will typically have 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms.

When an alkynyl moiety or group is specified, species include, by way of example and not limitation, any of the alkyl moieties, groups or substituents described herein that has one or more double bonds, ethynyl, propynyl, butynyl, iso-butynyl, 3-methyl-2-butynyl, 1-pentynyl, cyclopentynyl, 1-methyl-cyclopentynyl, 1-hexynyl, 3-hexynyl, cyclohexynyl and other linear, cyclic and branched chained all carbon containing moieties containing at least one triple bond. When an alkynyl is used as a Markush group (i.e., a substituent) the alkynyl is attached to a Markush formula with which it is associated through one of the unsaturated carbons of the alkynyl functional group.

**Halogen” or “halo”** as used herein means fluorine, chlorine, bromine or iodine.

As used herein, the term **“alkylene”**, employed alone or in combination with other terms, refers to a divalent alkyl linking group. Examples of alkylene groups include, but are not limited to, ethan-1,2-diyl, propan-1,3-diyl, propan-1,2-diyl, butan-1,4-diyl, butan-1,3-diyl, butan-1,2-diyl, 2-methyl-propan-1,3-diyl, and the like.

As used herein, the term **“alkoxy”**, employed alone or in combination with other terms, refers to a group of formula —O-alkyl, wherein the alkyl group is as defined above. Examples of alkoxy groups include but not limited to methoxy, ethoxy, propoxy (e.g., n-propoxy and isopropoxy), t-butoxy, and the like.

The expressions, “ambient temperature” and “room temperature” or “rt” as used herein, are understood in the art, and refer generally to a temperature, e.g. a reaction temperature, that is about the temperature of the room in which the reaction is carried out, for example, a temperature from about 25 °C to about 35 °C.

The term “bio based-” used herein generally covers vanillin, veratraldehyde, guaiacol, syringaldehyde, eugenol, and others, which are obtained from Sigma Aldrich, a company based in the United States. There are some companies that manufacture chemicals directly from lignin as given here: Borregaard (Norway): Borregaard is a biorefinery company that produces lignin-based products, including lignin extraction, from wood-based raw materials; Domtar (Canada): Domtar is a pulp and paper company that also produces lignin as a byproduct of its operations; Stora Enso (Finland): Stora Enso is a renewable materials company that extracts lignin from wood pulp and uses it in various applications; Resolute Forest Products (Canada): Resolute Forest Products is a company involved in pulp and paper production and lignin extraction; West Fraser (Canada): West Fraser is a diversified wood products company with operations in pulp

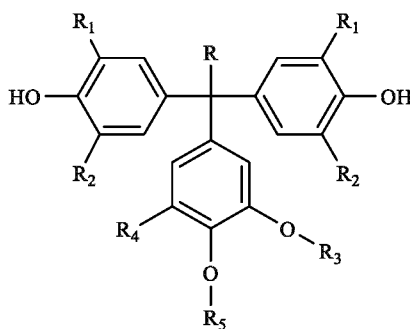
and lignin extraction; and Rayonier Advanced Materials (USA): Rayonier Advanced Materials produces specialty cellulose fibers and lignin from its pulp mills.

The present invention relates to bio-based bisphenol monomers of formula I which contain multiple alkoxy groups that could conveniently be de-blocked to phenolic hydroxyl groups “on demand” either in the monomer stage itself or *via* post-polymerization modification of the polymers derived therefrom. When de-blocked in the monomer stage, the derived polyphenols represent anti-oxidants and are potentially useful in various applications such as cosmetics, polymer additives and so on. The post-polymerization *via* de-blocking allows generation of a high density of hydroxyl functional groups in the polymer backbone. These hydroxyl groups provide reactive handle for further chemical modifications enabling the introduction of various functional groups and graft chains *via* the characteristic reactions of phenolic hydroxyl groups with appropriate reagents and pre-polymers. The modified polymers are potentially applicable in various fields such as functional membranes with antifouling/antibacterial characteristics, redox-active agents for battery applications, adhesives, polymer coatings with inherent anti-oxidant characteristics, etc.

The bisphenol monomers of formula I represent valuable building blocks for the synthesis of a range of high performance thermoplastics such as poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates, polyesters, and polyphosphonates. The alkoxy or methoxy groups in the polymers could be conveniently de-blocked ‘on-demand’ to generate multiple hydroxyl groups in the constituent repeating units. Based on the number and location of alkoxy or methoxy groups in the bisphenol monomers, catechol/ phloroglucinol -type units are generated in the polymer backbone. The presence of these units confers interesting surface properties and characteristics such as anti-oxidant, adhesion to dissimilar surfaces, anti-fouling and anti-bacterial to the polymers, which make these polymers interesting candidates for applications in membrane materials and coatings.

The bisphenol monomers and polyphenols are interesting precursors for thermosetting resins such as multifunctional epoxies, cyanate esters, phthalonitriles and propargyl ethers.

The present invention provides bio-based bisphenol monomer of formula I, wherein the formula I is represented by:



Formula I

wherein

R is hydrogen or alkyl,

R<sub>1</sub> is hydrogen, -O-alkyl, alkenyl

R<sub>2</sub> is hydrogen, -O-alkyl

5 R<sub>3</sub> is hydrogen, alkyl, alkenyl or alkynyl,

R<sub>4</sub> is hydrogen, O-alkyl, O-alkenyl or O-alkynyl, and

R<sub>5</sub> is hydrogen, alkyl, alkenyl or alkynyl.

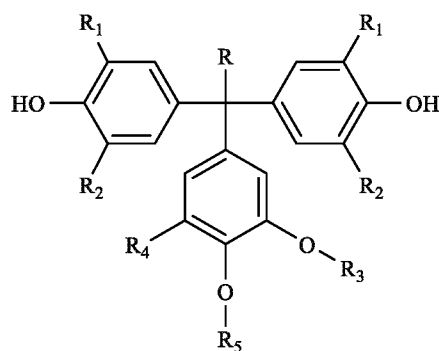
The phenol based monomer of formula I specifically recite one or more of: R being hydrogen or (C1-C5)alkyl, R<sub>1</sub> is hydrogen, -O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>2</sub> is -  
 10 O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>3</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, R<sub>4</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, and R<sub>5</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl.

The phenol based monomer of formula I recites 2 to 9 phenolic hydroxyl or alkoxy or methoxy groups.

15 The phenol based monomer of formula I recites at least four phenolic hydroxyl or alkoxy or methoxy groups.

The phenol based monomer of formula I is selected from 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) (monomer 1) and 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD) (monomer 2).

20 The present invention provides a process of preparation of bio-based bisphenol monomer of formula I, the formula I is represented by:



Formula I

wherein

25 R is hydrogen or alkyl,

R<sub>1</sub> is hydrogen, -O-alkyl, alkenyl

R<sub>2</sub> is hydrogen, -O-alkyl

R<sub>3</sub> is hydrogen, alkyl, alkenyl or alkynyl,

R<sub>4</sub> is hydrogen, O-alkyl, O-alkenyl or O-alkynyl, and

R<sub>5</sub> is hydrogen, alkyl, alkenyl or alkynyl.

The process comprising the steps of:

- a) stirring and dissolving a mixture of bio-based aldehyde and a phenolic compound in a container or reactor;
- 5        b) adding condensing agent and Bronsted acid catalyst into said solution of step a) at temperature in the range of 40 to 50 °C for time period of 10 to 15 h under inert N<sub>2</sub> atmosphere to obtain crude product;
- c) washing the crude product of step b) with solvent followed by evaporation and drying to obtain the bisphenol monomer compound of formula I; and
- 10       d) optionally, purifying the bisphenol monomer compound of formula I of step c) to obtain pure bisphenol monomer compound of formula I.

The bio-based aldehyde is selected from vanillin, syringaldehyde, veratraldehyde and so on.

The phenolic compound is selected from syringol, guaiacol, and so on.

- 15       The step a) is carried out within a temperature in the range of 25 to 35 °C (as room temperature) without addition of any solvent i.e., solvent-less or solvent-free step.

The Bronsted acid catalyst is selected from p-toluene sulfonic acid (PTSA), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), acetic acid (CH<sub>3</sub>COOH), MeSO<sub>3</sub>H, acidic ion exchange resin, sulfated zirconia, polyoxometalates (heteropolyacids) and so on.

- 20       The condensing agent is selected from zinc chloride, magnesium chloride (MgCl<sub>2</sub>), ferric chloride (FeCl<sub>3</sub>), aluminum chloride (AlCl<sub>3</sub>), and so on.

The amount/concentration of bio-based aldehyde is in range of 30 to 35 mol %.

The amount/concentration of phenolic compound is in range of 66 to 70 mol %.

The amount/concentration of condensing agent is in range of 0.1 to 1 mol %.

The amount/concentration of Bronsted acid catalyst is in range of 0.1 to 1 mol %.

- 25       The washing of step c) is done by at least three times with said solvent to remove the catalysts ZnCl<sub>2</sub> and PTSA.

The solvent used in step c) is hot water (having more than 70 °C of temperature) or distilled water.

The evaporation of step c) is done using a rotary evaporator under reduced pressure at temperature in the range of 120 to 160 °C to remove unreacted bio-based aldehyde and/or phenolic compound, and to obtain viscous liquid containing the crude product.

Reduced pressure kept in step c) is in range of 100 to 200 mm Hg.

- 5 The drying of step c) is by placing said viscous liquid as obtained upon evaporation, in vacuum oven at temperature in the range of 70 to 110 °C for time period of 10 to 14 hrs to obtain the monomer of formula I.

The yield of monomer of formula I is in range of 60 to 70 %.

The selectivity of monomer of formula I is in range of 70 to 75 %.

- 10 The conversion of bio-based source into said monomer compound of formula I is in range of 70 to 75 %.

The present invention provides a bisphenol monomer with built-in functional groups (DMBM) (Scheme 1) which is used to prepare high performance polymers selected from poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates polyesters, epoxy resins, etc.

- 15 The present invention further provides processes of preparation of polymers using said monomer of formula I wherein the polymers are selected from poly (ether sulfone), poly (ether ether ketone), polyester, and so on.

- 20 The bio-based bisphenol monomer of formula I and polymers obtained therefrom may recite multiple phenolic hydroxyl or alkoxyl or methoxyl groups, and polyphenols, with at least 2 to upto 9 hydroxyl groups.

The present invention provides a process of preparation of polymer using said monomer compound of formula I wherein the polymer is poly (ether sulfone) (PSU); the process comprising steps of:

- 25 a) dissolving and preparing a reaction mixture comprises the bisphenol monomer of formula I, a monomer, a catalyst and solvent in a container or a reactor;
- b) refluxing the reaction mixture of step, a) at temperature in the range of 120-140 °C with constant stirring for time period of 1-2 h to obtain polymer product along with water;
- c) distilling out the water produced in step b) to obtain polymer which is further heated at temperature in the range of 140-155 °C for time period of 2-5 h to obtain viscous polymer solution; and
- 30

d) precipitating the viscous polymer solution of step c) in a precipitating solvent followed by washing, reprecipitation, rewashing and drying to obtain the desired polymer.

The monomer at step a) is selected from sulfonyl monomer and ether ketone monomer, wherein sulfonyl monomer is selected from bis(4-chlorophenyl)sulfone and bis(4-fluorophenyl)sulphone and ether ketone monomer is selected from 4,4'-difluorobenzophenone, 1,4-phenylenebis((4-fluorophenyl)methanone) and 1,3-phenylenebis((4-fluorophenyl)methanone).

The stirring speed kept in step b) is in range of 500 to 1000 RPM.

The catalyst used in step a) is selected from alkali metal hydroxide or alkali metal carbonate.

The alkali metal hydroxide is selected from NaOH, KOH, LiOH, and so on.

The alkali metal carbonate is selected from  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Mg}_2\text{CO}_3$ , and so on.

The solvent used in step a) is selected from *N, N*-dimethylacetamide, toluene, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and/or mixture thereof.

The distillation of water of step c) is done by the methods known in the art. Specifically, the distillation method is azeotropic distillation using toluene.

The precipitation of step d) is done by cooling and mixing the viscous polymer solution in methanol as precipitating solvent to precipitate out the polymer.

The washing of step d) is done by at least three time using water to remove metal impurity.

The reprecipitation of step d) is done by first dissolving the polymer in chloroform followed by methanol to precipitate out the particles of polymer.

The rewashing of step d) is done by using methanol.

The drying of step d) is done under reduced pressure at room temperature (25 to 35 °C) for time period of 12-24 h.

The mole ratio of bisphenol compound of formula I and bis(4-fluorophenyl)sulfone used in the process is 1:1.

The present invention provides a process of introducing functional groups in said synthesized polymer(s) by simple de-protection reaction after polymerization. The reactive sites (OH groups) generated in the functionalized copolymer may be directly useful for certain applications or for further chemical modifications.

In another aspect, the present invention provides further chemical modification of said copolymers, selected from alkylation, esterification and synthesis of graft polymers, and since there is a presence of catechol/phloroglucinol moieties, it exhibits adhesion, antimicrobial, and antioxidant properties.

- 5 In another aspect, the present invention provides a catalyst for said de-protection reaction selected from the group of  $\text{BBr}_3$ , pyridine-HCl, trimethylsilyl iodide, HBr, HI and so on.

Further, the inventors have used said prepared (co)poly(ether sulfone)s to prepare cast films. (PSU-1 to PSU-5). The results of synthesis of (co)poly(ether sulfone)s and their thermal properties are provided in Table 1 and 2, respectively.

Table 1

| (Co)poly(ether sulfone) code | DMBM (mol %) | BPA (mol %) | Observed DMBM <sup>a</sup> (mol %) | $\eta_{\text{inh}}^b$ (dL/g) | $M_n$ (g/mol) <sup>c</sup> | $\bar{D}$ |
|------------------------------|--------------|-------------|------------------------------------|------------------------------|----------------------------|-----------|
| PSU-OMe-1                    | 100          | 00          | —                                  | 0.80                         | 80800                      | 2.4       |
| PSU-OMe-2                    | 70           | 30          | 70                                 | 0.86                         | 93400                      | 2.5       |
| PSU-OMe-3                    | 50           | 50          | 50                                 | 0.91                         | 101600                     | 2.4       |
| PSU-OMe-4                    | 30           | 70          | 30                                 | 0.93                         | 107400                     | 2.3       |
| PSU-OMe-5                    | 10           | 90          | 09                                 | 1.04                         | 119700                     | 2.2       |
| PSU-BPA                      | 00           | 100         | —                                  | 1.28                         | 119000                     | 2.2       |

<sup>a</sup>Determined from  $^1\text{H}$  NMR spectra. <sup>b</sup> $\eta_{\text{inh}}$  was measured with 0.5% (w/v) solution in chloroform at  $30 \pm 1$  °C. <sup>c</sup>Measured by GPC in chloroform using polystyrenes as calibration standards.

Table 2:

| (Co)poly(ether sulfone) code | $T_{10}^a$ (°C) | Char Yield <sup>b</sup> (%) | $T_g^c$ (°C) |
|------------------------------|-----------------|-----------------------------|--------------|
| PSU-OMe-1                    | 382             | 41                          | 171          |
| PSU-OMe-2                    | 408             | 37                          | 173          |
| PSU-OMe-3                    | 420             | 32                          | 175          |
| PSU-OMe-4                    | 443             | 29                          | 178          |
| PSU-OMe-5                    | 478             | 27                          | 187          |
| PSU-BPA                      | 491             | 23                          | 190          |

<sup>a</sup>10 % weight loss on TG traces at a heating rate of  $10$  °C  $\text{min}^{-1}$  under nitrogen atmosphere. <sup>b</sup>% Char yield was measured at  $800$  °C. <sup>c</sup>Measured by DSC on second heating scan with a heating rate of  $10$  °C  $\text{min}^{-1}$  under nitrogen atmosphere.

In specific embodiment, the present invention provides largely bio-based bisphenol monomers selected from 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) and 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD), which are synthesized by

acid-catalyzed reaction of veratraldehyde which can also be obtained from vanillin, with guaiacol or syringol.

In another specific embodiment, the bisphenol monomers or polymers disclosed herein contain built-in methoxyl groups, which represent latent phenolic hydroxyl groups and could be conveniently de-blocked to phenolic hydroxyl groups leading to formation of polyphenols containing catechol/phloroglucinol units with anti-oxidant properties and are potentially useful in various applications such as cosmetics, polymer additives and so on.

In another specific embodiment, the bisphenol monomers disclosed herein provide valuable building blocks for the synthesis of a range of high performance thermoplastics such as poly(ether sulfone)s, poly(ether ether ketone)s polyesters, polycarbonates, and polyphosphonates. The methoxyl groups in the polymers could be conveniently de-blocked 'on-demand' to generate multiple hydroxyl groups in the constituent repeating units. Based on the number and location of methoxyl groups in the bisphenol monomers, catechol / phloroglucinol - type units are generated in the polymer backbone. The presence of these units confers interesting surface properties and characteristics such as anti-oxidant, adhesion to dissimilar surfaces, anti-fouling and anti-bacterial to the polymers which make these polymers interesting candidates for applications in membrane materials and coatings.

The bisphenol monomers and polyphenols disclosed herein are interesting precursors for thermosetting resins such as multifunctional epoxies, cyanate esters, phthalonitriles and propargyl ethers.

In an embodiment, the present invention provides that (co)poly(ether sulfone)s bearing pendant catechol moieties and phenolic hydroxyl groups show antioxidant properties.

When integrated into polymeric materials, such as coatings or biomaterials, the catechol groups enhance the ability of material to scavenge free radicals, thus protecting surfaces or organs from oxidative damage. In this context, the antioxidant potential of PSU-OH is assessed using 1,1-diphenyl-2-picrylhydrazyl (DPPH) method. The assessment of antioxidant activity of three samples of PSU-OH differing in the mol % content of phenolic moieties is conducted by observing changes in the color of DPPH solution from purple to yellow (**Figure 1a**). For comparison, parent (co)poly(ether sulfone) bearing methoxyl pendant groups is also evaluated. Blank DPPH solution shows absorption peak at a wavelength of 517 nm (**Figure 1b**). Upon addition of PSU-OH the absorption peak corresponding to DPPH disappears, which was also evident visually. These results are suggestive of radical scavenging activity of PSU-OH demonstrating strong antioxidant qualities while the parent (co)poly(ether sulfone) bearing methoxyl pendant was inactive under the stated conditions.

Each of the three PSU-OH samples was evaluated at five different concentrations in the range 100-500 µg/mL. The quantification of the radical scavenging activity (RSA) can be determined using Formula 1, utilizing the absorbance value.

$$RSA = \frac{S_{\text{control}} - S_{\text{sample}}}{S_{\text{control}}} \times 100 \quad (1)$$

At varying concentrations (100 to 500 µg/mL), DPPH free radical scavenging for PSU-OH-3, PSU-OH-4, and PSU-OH-5 was evaluated by taking ascorbic acid as the standard. The results obtained are shown in **Table 3** and **Figure 1c**. As expected, higher activity was observed with increase in the weight % for all the three samples tested. At a given concentration PSU-OH containing highest mol % of catechol and -OH groups exhibited highest antioxidant activity. The inherent antioxidant characteristics of (co)poly(ether sulfone)s imparted by bound catechol moieties could be a significant advantage in potential applications such as antifouling membranes, biomedical devices, etc.

**Table-3: Percentage inhibition of (co)poly(ether sulfone)s bearing phenolic hydroxyl and catechol moieties based on DPPH**

| Polymer Code | Percentage inhibition for different concentration |           |           |           |           |
|--------------|---------------------------------------------------|-----------|-----------|-----------|-----------|
|              | 100 µg/mL                                         | 200 µg/mL | 300 µg/mL | 400 µg/mL | 500 µg/mL |
| PSU-OH-3     | 25.05                                             | 36.52     | 48.48     | 63.58     | 72.83     |
| PSU-OH-4     | 12.57                                             | 25.91     | 36.36     | 52.55     | 64.46     |
| PSU-OH-5     | 5.79                                              | 18.64     | 26.49     | 31.42     | 35.96     |

In another embodiment, the present invention provides that a (co)poly(ether sulfone)s bearing pendant catechol moieties and phenolic hydroxyl groups show antimicrobial activity. Catechol-bearing polymeric materials effectively inhibit microbial colonization presenting a promising application in medical devices, coatings, etc. As a representative example, PSU-OH-3 is evaluated for its antimicrobial properties. **Figure 2** illustrates results obtained using varying concentrations (0.05 to 50 mg/mL) of PSU-OH-3. The findings indicate a 23mm inhibition zone against the Gram-positive bacterium *Staphylococcus aureus* NCIM 5257 and an 18mm inhibition zone against the Gram-negative bacterium *Escherichia coli* NCIM 2065, showcasing the efficacy of PSU-OH against these microbial strains. The antimicrobial effectiveness is also assessed by measuring optical density at different time intervals (**Figure 3**).

The time-kill test, elucidates either time-dependent or concentration-dependent impact on antimicrobial activity. Incubation at different time intervals (0, 4, 6, 8, 10, 12, and 24 h) under suitable conditions is conducted. Upon introducing PSU-OH-3 into the broth, a noticeable reduction in cell optical density is observed compared to the control experiment, signifying the inhibitory property of the polymer. Given the well-established application of poly(ether sulfone)s

in kidney dialysis membranes and medical equipment, the accessibility to poly(ether sulfone)s with inherent antimicrobial properties is a prized asset.

In yet another embodiment, the present invention provides that (co) poly(ether sulfone)s bearing pendant catechol moieties and phenolic hydroxyl groups show redox activity in zinc-ion batteries. Organic compounds containing catechol and multiple phenolic hydroxyl groups are of interest as electrode materials in zinc-ion batteries on account of their comparatively higher operating voltage, environmental friendliness, and lower toxicity. Catechol, like hydroquinone, rapidly undergoes oxidation, forming ortho-quinone, which is recognized for its high potential and electrochemical kinetics. Nevertheless, low molecular weight organic compounds are prone to dissolution in aqueous electrolytes and their redox radical intermediates are known to be unstable. It is hypothesized that catechol moieties bound to a poly(ether sulfone) backbone would help counter these shortcomings. (Co)poly(ether sulfone) bearing catechol moieties, viz. PSU-OH-5 was tested as organic electrode for zinc-ion battery. CV measurements were carried out at a voltage window of 0.2-1.8 V with a scan rate of 0.5 mV sec<sup>-1</sup>. **Figure 4a** illustrates a broad redox peak for PSU-OH-5, which is the characteristic feature associated with the catechol redox center. **Figure 4b** shows the rate performance data with a maximum discharge capacity of 65.2 mAhg<sup>-1</sup> achieved at a current density of 100 mA g<sup>-1</sup>. The GCD profiles of PSU-OH-5 at higher current densities of 0.1, 0.2, 0.3, 0.5 and 1 Ag<sup>-1</sup> result in 65.2, 54, 39, 28 and 17 mAhg<sup>-1</sup> of discharge capacities (**Figure 4c**). The cycling performance of PSU-OH-5 was carried out at 100 mA g<sup>-1</sup>, showing capacity retention of 69 % for 200 cycles (**Figure 4d**).

It is known that during the initial charge-discharge process the hydroxyl groups in the polymers can undergo oxidation transforming into carbonyl groups. A similar phenomenon is presumed to be operative in (co)poly(ether sulfone) bearing catechol moieties, as indicated in **Scheme 4**, ensuring an ample supply of active redox sites for accommodating zinc ions. The generated data supported the potential utility of (co)poly(ether sulfone) containing catechol moieties as organic polymer electrode in zinc-ion batteries with a better efficacy as evidenced from good cyclability and retention of superior capacity. These characteristics pave an entry for catechol-functionalized (co)poly(ether sulfone)s into battery applications.

In yet another embodiment, the present invention provides that (co)poly(ether sulfone)s bearing pendant catechol moieties and phenolic hydroxyl groups show adhesive performance.

Inspired by the well-established practical utility of catechol and gallol unit-containing small molecules and polymers as adhesives, (co)poly(ether sulfone)s containing phenolic hydroxyls and catechol units are tested for their adhesive performance.

Lap shear measurements on aluminium substrates were conducted using single lap joints following the ASTM D1002 standard. As indicated in **Figure 5**, methoxyl-functionalized polyether

sulfone (PSU-OMe-5) exhibited low adhesive strength of 0.025 MPa only which could be attributed to the lack of interactions of methoxyl groups and poly(ether sulfone) backbone with aluminium substrate. On the other hand, PSU-OH-5 demonstrated a lap shear strength of 2.40 MPa (**Figure 6**) and this dramatic increase could clearly be attributed to the presence of pendent catechol moieties which are well-known for their strong adhesive properties due to their ability to engage in multiple hydrogen bonds and metal ion coordination. Along with adhesive strength measurements, the type of adhesive failure was also assessed through visual inspection of the samples. For PSU-OMe-5, adhesive failure was observed, whereas PSU-OH-5 exhibited cohesive failure as shown in inset in **Figures 5a** and **5b**. The cohesive force in PSU-OH was observed to be dominant over adhesive strength between PSU-OH and aluminium substrate.

## EXAMPLES

Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

### Procurement details

veratraldehyde (> 98 %, Sigma Aldrich USA), guaiacol (> 99 %, Sigma Aldrich USA), *p*-toluenesulfonic acid monohydrate (99 %, Nice Chemicals, India), zinc chloride ( $\geq$  98%, Loba Chemie India), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), methyl methacrylate (MMA) were used as received. Bisphenol-A (BPA) (Sigma Aldrich) was sublimed under reduced pressure before use. Bis(4-fluorophenyl) sulfone and 4,4'-difluorobenzophenone were purchased from Sigma-Aldrich, India and were recrystallized from toluene. Calcium hydride, sodium sulfate, potassium carbonate, and sodium hydroxide were obtained from Thomas Baker Ltd. Mumbai and were used as received. Chloroform, triethylamine (TEA), methanol, *N,N*-dimethyl acetamide (DMAc) and toluene were obtained from Thomas Baker Ltd. Mumbai and were purified according to the standard procedures.

#### **Example 1: Synthesis of bio-based bisphenol monomer [4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (monomer compound 1) (DMBM)]**

Under magnetic stirring, veratraldehyde (1 mol) and guaiacol (5 mol) were charged into a 100 mL single-necked round-bottom flask. Upon complete dissolution of reactants, zinc chloride (0.1 mol) and *p*-toluenesulfonic acid (PTSA, 0.1 mol) were added. The mixture was kept under N<sub>2</sub> atm. at 50 °C for 24 h (**Figure 7**). The progress of the reaction was monitored by thin-layer chromatography (TLC). Next, the reaction mixture was washed with hot water (3 x 50 mL). The unreacted guaiacol was removed and recycled using a rotary evaporator under reduced pressure at 140 °C. The obtained viscous liquid was placed in vacuum oven at 90 °C for 12 h. The crude product was purified by column chromatography (solvent system ethyl acetate: pet ether, 10:90, v/v) followed by recrystallization from chloroform to obtain white powder with a yield of ~90 %.

M.P. 169.42 °C, <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ ppm 3.63 (4 H, s), 3.65 (7 H, s), 3.71 (4 H, s), 5.28 (1 H, s), 6.45 (3 H, d, *J*=8.01 Hz), 6.54 - 6.58 (1 H, m), 6.67 (4 H, s), 6.69 - 6.72 (2 H, m), 6.85 (1 H, d, *J*=8.01 Hz), 8.78 (2 H, s), <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ ppm 148.55 (s, 1 C) 147.42 (s, 1 C) 147.22 (s, 1 C) 144.90 (s, 1 C) 137.49 (s, 1 C) 135.65 (s, 1 C) 121.37 (s, 1 C) 121.05 (s, 1 C) 115.31 (s, 1 C) 113.46 (s, 1 C) 113.12 (s, 1 C) 111.71 (s, 1 C) 55.77 (s, 1 C) 55.61 (s, 1 C) 54.78 (s, 1 C) 40.26 (s, 1 C) 40.18 (s, 1 C) 40.09 (s, 1 C) 40.01 (s, 1 C) 39.93 (s, 1 C) 39.84 (s, 1 C) 39.68 (s, 1 C) 39.34 (s, 1 C) 39.18 (s, 1 C)

**Example 2: Synthesis of partially bio-based copoly(ether sulfone) bearing pendent methoxyl groups (PSU-OCH<sub>3</sub>)**

Into a 50 mL two-necked round bottom flask equipped with a nitrogen inlet and a Dean–Stark trap fitted with a reflux condenser were charged DMBM (1 mmol), bis(4-fluorophenyl)sulfone (1 mmol), anhydrous potassium carbonate (1.5 mmol), *N,N*-dimethylacetamide (10 mL) and toluene (10 mL). The reaction mixture was heated at 140 °C with constant stirring for 2 h and water was removed by azeotropic distillation with toluene. Toluene was removed by distillation and the reaction mixture was further heated at 155 °C for 5 h to obtain viscous polymer solution. The reaction mixture was cooled to room temperature and poured into methanol (100 mL). The precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and reprecipitated into methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature for 24 h.

<sup>1</sup>H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 7.81 (d, *J*=8.83 Hz, 5 H) 6.97 (d, *J*=8.20 Hz, 2 H) 6.93 (d, *J*=8.83 Hz, 4 H) 6.84 (d, *J*=8.20 Hz, 1 H) 6.79 - 6.81 (m, 2 H) 6.68 - 6.71 (m, 3 H) 6.65 (d, *J*=8.20 Hz, 1 H) 5.50 (s, 1 H) 3.88 (s, 3 H) 3.81 (s, 3 H) 3.67 (s, 7 H)

**Example 2A: Synthesis of copoly(ether sulfone) bearing pendent phenolic hydroxyl groups (PSU-OH) via demethylation of PSU-OCH<sub>3</sub>**

PSU-OCH<sub>3</sub> (0.3 g) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) were added into a 250 mL round bottom flask. Then, BBr<sub>3</sub> (1.951 g, 0.0077 mol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise and the reaction mixture was heated at 40 °C for 6 h. The reaction mixture was poured into ice-water and the separated solid was filtered. Polymer was dried at 60 °C for 36 h. Yield: 98 %.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 7.85 (br. s., 4 H) 7.24 (br. s., 4 H) 6.84 - 7.14 (m, 8 H) 6.75-6.40 (br. m., 1H) 5.31 (s., 0.09H) 1.60 (br. s., 6 H)

**Example 2B: Synthesis of PSU macroinitiator fitted with ATRP initiating sites from PSU-OH**

Into a 50 mL two necked round bottom flask equipped with a nitrogen inlet were placed *N,N*-dimethylformamide (50 mL), poly(ether sulfone) bearing pendent phenolic hydroxyl groups (PSU-OH) (0.3 g, 0.65 mmol) and TEA (0.46 mL, 3.28 mmol). 2-Bromoisobutyryl bromide (1 mL, 7.88 mmol) dissolved in *N,N*-dimethylformamide (10 mL) was added dropwise to the reaction mixture. The reaction was allowed to proceed at room temperature for 6 h. The reaction mixture

was poured in to water and polymer was extracted with dichloromethane. The dichloromethane solution was concentrated and poured into methanol to precipitate the polymer. The solid polymer was isolated by filtration and dried under reduce pressure at 60 °C for 12 h. Yield: 98 %.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 7.77 (d, *J*=8.76 Hz, 4 H) 7.09 - 7.24 (m, 4 H) 6.77 - 7.06 (m, 8 H) 5.51(s, 0.09H) 1.71 (s, 1 H) 1.62 (s, 6 H).

#### Example 2C: Synthesis of poly(ether sulfone)-graft-poly(methyl methacrylate)

PSU macroinitiator (0.20 g, 1.62 mmol) was dissolved in THF (15 mL) in a single-necked round bottom flask (50 mL) at room temperature and then transferred to a 100 mL nitrogen-filled Schlenk flask. MMA (0.48 g, 4.86) mmol, CuBr (70 mg, 4.86 mmol) and PMDETA (1.69 mg, 9.72 mmol) were added to the reaction mixture. The Schlenk flask was sealed with rubber septum, and argon gas was bubbled through the reaction mixture for 30 min while the reaction mixture was stirred magnetically. The reaction mixture was degassed by three freeze–pump–thaw cycles. The reaction flask was placed into an oil bath preheated to 90 °C, and the reaction was allowed to proceed for 20 h. The resultant copolymer was precipitated into a mixture of methanol and deionized water (1:4, in v/v) and isolated by filtration. Copolymer was dissolved in THF and re-precipitated into a mixture (1:1, v/v) of methanol: water (50 mL). The solid polymer was isolated by filtration and dried under reduce pressure at 40 °C for 24 h. Yield: 98 %.

<sup>1</sup>H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 7.85 (d, *J*=7.75 Hz, 4 H) 7.24 (d, *J*=8.00 Hz, 6 H) 7.01 (d, *J*=7.50 Hz, 4 H) 6.94 (d, *J*=7.38 Hz, 4 H) 5.57 (br. s., 1 H) 3.61 (br. s., 20 H) 1.76 - 2.18 (m, 13 H) 1.70 (br. s., 9 H) 1.26 (br. s., 8 H) 0.93 - 1.13 (m, 8 H) 0.85 (br. s., 14 H).

#### Example 3: Synthesis of (co)polyester bearing pendent methoxyl groups

The interfacial polycondensation reactions were carried out in a 100 mL two-necked round bottom flask equipped with a mechanical stirrer. In a typical copolymerization reaction, 4,4'-((3,4-dimethoxyphenyl)methylene)bis(2-methoxyphenol) (1.0 g, 2.52 mmol) and bisphenol A (BPA) (0.575 g, 2.52 mmol) were dissolved in 1M aqueous solution of sodium hydroxide (9.8 mL). The mixture was stirred for 1 h at 10 °C. Next, benzyltriethylammonium chloride (68.63 mg) was added to the reaction mixture and stirring was continued. After 30 min, the solution of isophthaloyl chloride (IPC) (1.024 g, 5.044 mmol) in dichloromethane (20 mL) was added to the reaction mixture and the mixture was stirred vigorously at 2000 rpm for 1.5 h. The reaction mixture was poured into water; the precipitated polymer was filtered and washed several times with water. The polymer was dissolved in chloroform and reprecipitated into methanol. The fibrous polymer obtained was filtered, washed with methanol, and dried under reduced pressure at room temperature for 24 h. Yield: 98 %.

<sup>1</sup>H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 1.74 (s, 3 H) 3.70 - 3.77 (m, 3 H) 3.79 - 3.85 (m, 2 H) 3.86 - 3.91 (m, 2 H) 5.55 (s, 1 H) 6.67 (d, *J*=7.25 Hz, 1 H) 6.71 - 6.77 (m, 1 H) 6.83 (br. s., 2

H) 7.07 - 7.20 (m, 4 H) 7.33 (d,  $J=8.39$  Hz, 2 H) 7.68 (t,  $J=7.25$  Hz, 1 H) 8.36 - 8.52 (m, 2 H) 8.95 - 9.10 (m, 1 H)

#### Example 4: Synthesis of bio-based (co)poly(ether ether ketone)s bearing pendant methoxyl groups

A 50 mL three-necked round bottom flask equipped with a nitrogen inlet, a Dean–Stark trap fitted with a reflux condenser and a magnetic stirring bar was charged with DMBM (1.0 g, 2.52 mmol), 4,4'-difluorobenzophenone (0.54 g, 2.52 mmol), anhydrous potassium carbonate (0.64 g, 4.60 mmol), *N,N*-dimethylacetamide (10 mL) and toluene (10 mL). The reaction mixture was heated at 140 °C with stirring for 2 h and water was removed by azeotropic distillation with toluene. Toluene was removed by distillation, and the reaction mixture was heated at 155 °C for 7 h. The reaction mixture was cooled to room temperature and was poured into methanol (100 mL). The precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and re-precipitated into methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature for 24 h. Yield: 98 %.  $^1\text{H}$  NMR (500 MHz, CHLOROFORM- $d$ )  $\delta$  ppm 7.79 (br. s., 4 H) 7.19 - 7.24 (m, 1 H) 6.96 - 7.11 (m, 7 H) 6.92 (br. s., 1 H) 6.84 (br. s., 1 H) 5.54 (br. S., 0.09H) 3.73 (br. s., 1 H) 1.72 (br. s., 6 H)

#### Example 4A: Synthesis of poly(ether ether ketone)s bearing pendent phenolic hydroxyl groups (PEEK-OH) via demethylation of PEEK-OCH<sub>3</sub>

PEEK-OCH<sub>3</sub> (0.3 g) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) were added into a 250 mL round bottom flask. Then, BBr<sub>3</sub> (0.88 g, 3.5 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise and the reaction mixture was heated at 40 °C for 6 h. The reaction mixture was poured into ice-water and the separated solid was filtered. Polymer was dried at 60 °C for 36 h. Yield: 98 %.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm 7.67 (br. s., 4 H) 7.22 (br. s., 4 H) 6.95 (br. s., 6 H) 5.49 (s, 0.09 H) 1.63 (br. s., 5.54 H)

#### Example 5: Synthesis of ((3,4-dimethoxyphenyl)methylene)bis(2-methoxy-4,1-phenylene) bis(2-bromo-2-methylpropanoate) (Br-DMBM-Br macroinitiator)

Into a 50 mL two necked round bottom flask equipped with a nitrogen inlet were placed *N,N*-dimethylformamide (50 mL), DMBM (1 g, 2.52 mmol) and TEA (1.02g, 10.08 mmol). 2-Bromoisobutyryl bromide (2.319 g, 10.08 mmol) dissolved in *N,N*-dimethylformamide (10 mL) was added dropwise to the reaction mixture. The reaction was allowed to proceed at room temperature for 6 h. The reaction mixture was poured in to water and product was extracted with dichloromethane. The crude product purified by column chromatography (solvent system ethyl acetate: pet ether, 20:80, v/v) to obtain white powder with a yield of ~98 %.

<sup>1</sup>H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 6.99 (d, *J*=8.13 Hz, 2 H) 6.71 - 6.82 (m, 3 H) 6.54 - 6.69 (m, 4 H) 5.48 (s, 1 H) 3.87 (s, 3 H) 3.78 (s, 3 H) 3.71 (s, 6 H) 2.04 - 2.09 (m, 13 H).

**Example 6: Synthesis of 4, 4', 4''-methanetriyltris(benzene-1,2-diol)**

DMBM (1 g, 2.52 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) were added into a 250 mL round bottom flask. Then, BBr<sub>3</sub> (2.90 mL, 35 mol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added dropwise and the reaction mixture was heated at 40 °C for 6 h. The reaction mixture was poured into ice-water and the separated solid was filtered. The product was dried at 60 °C for 36 h. Yield: 98 %. *M<sub>w</sub>* ~340.04.

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ ppm 8.76 (br. s., 5 H) 6.62 (d, *J*=8.08 Hz, 4 H) 6.44 - 6.48 (m, 4 H) 6.30 - 6.35 (m, 4 H) 5.00 (s, 1 H)

**Example 7: Synthesis of ((4-((2-bromo-2-methylpropanoyl)oxy)-3-((2-bromo-2-methylpropanoyl)oxy)phenyl)methylene)bis(benzene-4,1,2-triyl) tetrakis(2-bromo-2-methylpropanoate)**

Into a 50 mL two necked round bottom flask equipped with a nitrogen inlet were placed *N,N*-dimethylformamide (50 mL) 4,4',4''-methanetriyltris(benzene-1,2-diol) (1g, 2.94 mmol) and TEA (4.36 mL, 3.52 mmol). 2-Bromoisobutyryl bromide (4.36 mL, 3.52 mmol) dissolved in *N,N*-dimethylformamide (10 mL) was added dropwise to the reaction mixture. The reaction was allowed to proceed at room temperature for 6 h. The reaction mixture was poured in to water and product was extracted with dichloromethane. The crude product was purified by column chromatography (solvent system ethyl acetate: pet ether, 20:80, v/v) to obtain white powder with a yield of ~98 %. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 7.21 (d, *J*=8.00 Hz, 3 H) 6.99 - 7.04 (m, 6 H) 5.59 (s, 1 H) 2.05 (d, *J*=7.00 Hz, 37 H)

**Example 8: Synthesis of six-arm poly(methyl methacrylate) by Atom Transfer Radical Polymerization using ((4-((2-bromo-2-methylpropanoyl)oxy)-3-((2-bromo-2-methylpropanoyl)oxy)phenyl)methylene)bis(benzene-4,1,2-triyl) tetrakis(2-bromo-2-methylpropanoate) as the initiator**

((4-((2-Bromo-2-methylpropanoyl)oxy)-3-((2-bromo-2-methylpropanoyl)oxy)phenyl)methylene)bis(benzene-4,1,2-triyl) tetrakis(2-bromo-2-methylpropanoate) (0.30 g, 0.243 mmol) was dissolved in THF (15 mL) in a single-necked round bottom flask (50 mL) at room temperature and then transferred to a 100 mL nitrogen-filled Schlenk flask. MMA (7.29 g, 72.91 mmol) mmol, CuBr (1g, 7.29 mmol) and PMDETA (2.52 mg, 14.58 mmol) were added to the reaction mixture. The Schlenk flask was sealed with rubber septum, and argon gas was bubbled through the reaction mixture for 30 min while the reaction mixture was magnetically stirred. The reaction mixture was degassed by three freeze-pump-thaw cycles. The reaction flask was placed into an oil bath preheated to 70 °C, and the reaction was allowed to proceed for 20 h. The resultant polymer was precipitated into a mixture (1:4, v/v)

of methanol and deionized water (50 mL) and isolated by filtration. Copolymer was dissolved in THF and re-precipitated into a mixture 1:1, v/v) of methanol: water (50 mL). The solid polymer was isolated by filtration and dried under reduce pressure at 40 °C for 24 h.

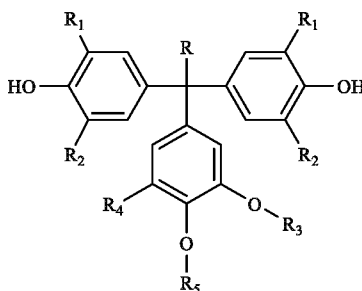
Similar procedure was followed for synthesis of poly(methyl methacrylate) using ((3,4-dimethoxyphenyl)methylene)bis(2-methoxy-4,1-phenylene) bis(2-bromo-2-methylpropanoate).

## ADVANTAGES OF THE INVENTION

- The present invention provides largely bio-based bisphenol monomers containing latent phenolic hydroxyl groups, useful as starting material for a range of high-performance polymers and as precursors for compounds with multiple phenolic hydroxyl groups.
- Provides novel lignin-derived monomers with multiple phenolic hydroxyl groups that exhibit properties such as anti-bacterial, anti-oxidant, etc.
- Provides high performance polymers (from said monomers) such as poly(ether sulfone)s, poly(ether ether ketone)s aromatic polyesters, polycarbonates, polyphosphonates and thermosetting resins such as epoxies, cyanate esters and -propargyl ethers containing latent functional groups that can be used for post-modification of the polymer as well as to exploit properties such as anti-bacterial, anti-oxidant, adhesives, etc. by simple deprotection.
- Provides a post-modification process of poly(ether sulfone)s with graft polymer chains.
- Uses bio-based, inexpensive, and easily available raw materials in a simple and economic process.
- Provides bisphenol containing built-in latent functional groups synthesized from lignin-derived compounds in a single step process.
- Polyphenols with as many as nine phenolic hydroxyl groups can be obtained in one step from the bisphenol compound.
- The designed bisphenol monomer contains at least four methoxy groups so that high density of functional groups can be introduced in the polymer.
- The corresponding high-performance polymers are potentially applicable in various fields such as functional membranes, adhesives, antifouling/antibacterial coatings and oil repellent polymer coatings with inherent antioxidant characteristics, etc.

**CLAIMS**

1. A bio-based bisphenol monomer of formula I



Formula I

wherein

R is hydrogen or alkyl,

R<sub>1</sub> is hydrogen, -O-alkyl or alkenyl,

R<sub>2</sub> is hydrogen or -O-alkyl,

R<sub>3</sub> is hydrogen, alkyl, alkenyl or alkynyl,

R<sub>4</sub> is hydrogen, O-alkyl, O-alkenyl or O-alkynyl, and

R<sub>5</sub> is hydrogen, alkyl, alkenyl or alkynyl.

2. The monomer as claimed in claim 1, wherein R is hydrogen or (C1-C5)alkyl, R<sub>1</sub> is hydrogen, -O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>2</sub> is -O-(C1-C5)alkyl, -O-(C1-C5)alkenyl or -O-(C1-C5)alkynyl, R<sub>3</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, R<sub>4</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl, and R<sub>5</sub> is hydrogen, (C1-C5)alkyl, (C1-C5)alkenyl or (C1-C5)alkynyl;

wherein the monomer of formula I recites 2 to 9 phenolic hydroxyl or alkoxy or methoxy groups; and

wherein the monomer of formula I recites at least four phenolic hydroxyl or alkoxy or methoxy groups.

3. The monomer of formula I as claimed in claim 1, wherein said monomer is selected from

- i. 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) (monomer 1) and;
- ii. 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD) (monomer 2).

4. A process for the preparation of bio-based bisphenol monomer of formula I as claimed in claim 1, wherein said process comprising the steps of:

a) stirring and dissolving a mixture of bio-based aldehyde and a phenolic compound in a container or reactor to obtain a solution;

b) adding condensing agent and Bronsted acid catalyst into said solution as obtained in step a) at temperature in the range of 40 to 50°C for time period in the range of 10 to 15 h under inert N<sub>2</sub> atmosphere to obtain crude product;

c) washing the crude product as obtained in step b) with a solvent followed by evaporation and drying to obtain the bisphenol monomer compound of formula I; and

d) optionally purifying the bisphenol monomer compound of formula I as obtained in step c) to obtain pure bisphenol monomer compound of formula I.

5. The process as claimed in claim 4, wherein

a) the step a) is carried out at a temperature in the range of 25 to 35 °C without addition of a solvent;

b) the solvent used in step c) is a hot water having temperature of at least about 70 °C or a distilled water;

c) the evaporation of step c) is done using a rotary evaporator under reduced pressure in the range of 100 to 200 mm Hg at a temperature in the range of 120 to 160 °C;

d) the drying of step c) is done by placing said viscous liquid as obtained upon evaporation, in a vacuum oven at temperature in the range of 70 to 110 °C for time period of 10 to 14 hrs to obtain the monomer of formula I;

e) the bio-based aldehyde is selected from vanillin, syringaldehyde, and veratraldehyde; and

f) the phenolic compound is selected from syringol, and guaiacol.

6. The process as claimed in claim 4, wherein the Bronsted acid catalyst is selected from p-toluene sulfonic acid (PTSA), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), acetic acid (CH<sub>3</sub>COOH), MeSO<sub>3</sub>H, acidic ion exchange resin, sulfated zirconia, and polyoxometalates (heteropolyacids);

7. The process as claimed in claim 4, wherein the condensing agent is selected from zinc chloride, magnesium chloride (MgCl<sub>2</sub>), ferric chloride (FeCl<sub>3</sub>), and aluminum chloride (AlCl<sub>3</sub>).

8. The process as claimed in claim 4, wherein the concentration of bio-based aldehyde is in range of 30 to 35 mol %, the concentration of phenolic compound is in range of 66 to 70 mol %, the concentration of condensing agent is in range of 0.1 to 1 mol %, and the concentration of Bronsted acid catalyst is in range of 0.1 to 1 mol %.

9. The process as claimed in claim 4, wherein yield of the monomer of formula I is in range of 60 to 70 %, and a selectivity of the monomer of formula I is in range of 70 to 75 %, with a conversion rate of the bio-based aldehyde into said monomer of formula I is in range of 70 to 75 %.

10. A polymer comprises the bio-based bisphenol monomer of formula I as claimed in claim 1, wherein said polymer is selected from poly(ether sulfone)s, poly(ether ether ketone)s, polycarbonates and polyester, ; wherein said polymer comprises phenolic hydroxyl or alkoxyl or methoxyl groups, and polyphenols, with at least 2 to 9 hydroxyl groups.

11. A process for the preparation of a polymer as claimed in claim 10, wherein said process comprises the steps of:

a) dissolving and preparing a reaction mixture comprises the bisphenol monomer of formula I, a monomer, a catalyst and solvent in a container or reactor;

b) refluxing the reaction mixture as obtained in step, a) at temperature in the range of 120-140 °C with constant stirring in range of 500 to 1000 RPM for time period in the range of 1-2 h to obtain crude polymer product along with water;

c) distilling out the water produced in step b) to obtain crude polymer which is further heated at temperature in the range of 140-155 °C for time period of 2-5 h to obtain viscous polymer solution; and

d) precipitating the viscous polymer solution of step c) in a precipitating solvent followed by washing, reprecipitation, rewashing and drying under reduced pressure at 25 to 35 °C for time period of 12-24 h to obtain the desired polymer;

wherein said polymer is poly(ether sulfone) or poly(ether ether ketone).

12. The process for the preparation of polymer as claimed in claim 11, wherein

a) the monomer is a sulfonyl monomer or ether ketone monomer;

b) the sulfonyl monomer is selected from bis(4-chlorophenyl)sulfone and bis(4-fluorophenyl)sulfone;

c) the ether ketone monomer is selected from 4,4'-difluorobenzophenone, 1,4-phenylenebis((4-fluorophenyl)methanone) and 1,3-phenylenebis((4-fluorophenyl)methanone);

5 d) the bisphenol monomer of formula I is 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2-methoxyphenol) (DMBM) or 4,4'-((3,4-dimethoxyphenyl)methylene)-bis(2,6-dimethoxyphenol) (DMBD);

e) the catalyst used in step a) is selected from alkali metal hydroxide or alkali metal carbonate, wherein the alkali metal hydroxide is selected from NaOH, KOH, and LiOH; and the alkali metal carbonate is selected from Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and Mg<sub>2</sub>CO<sub>3</sub>;

10 f) the solvent used in step a) is selected from *N,N*-dimethylacetamide, toluene, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and/or mixture thereof; and

g) the precipitating/reprecipitating solvent used at step d) is methanol.

13. The polymer as claimed in claim 10, wherein said polymer is chemically modified to  
15 generate catechol moieties and phenolic hydroxyl groups.

14. The polymer as claimed in claim 13 is further chemically modified to introduce functional groups at hydroxyl group through alkylation, esterification and synthesis of graft co-polymers via 'grafting onto' or 'grafting from' approach.

15. The polymer as claimed in claim 13, wherein said polymers exhibit adhesive, antioxidant,  
20 antimicrobial and redox activity in battery applications.

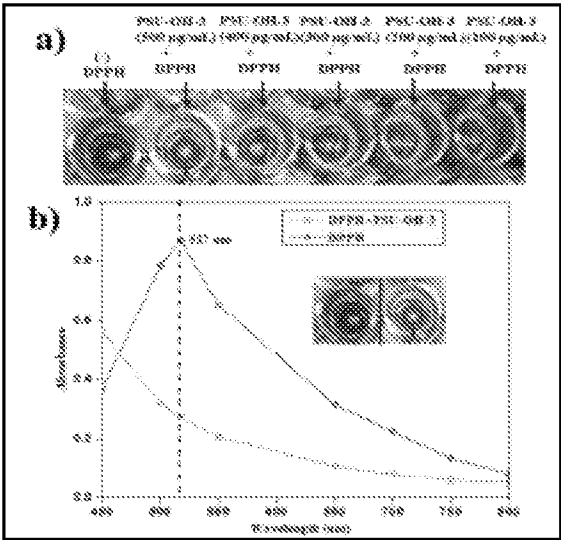


Figure 1a and 1b

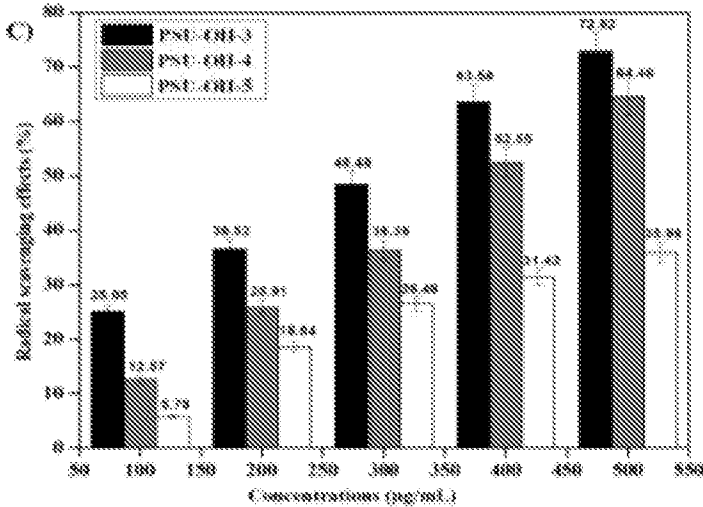


Figure 1c

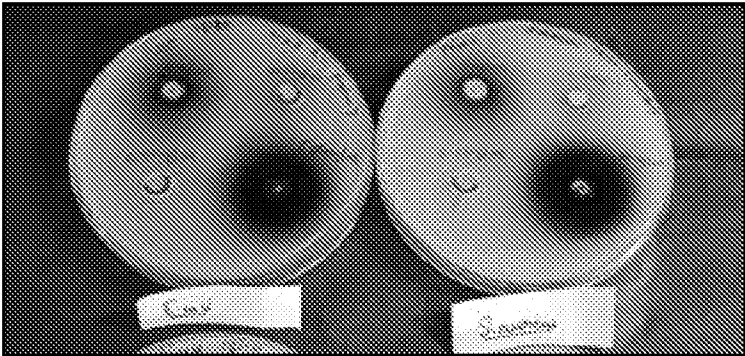


Figure 2

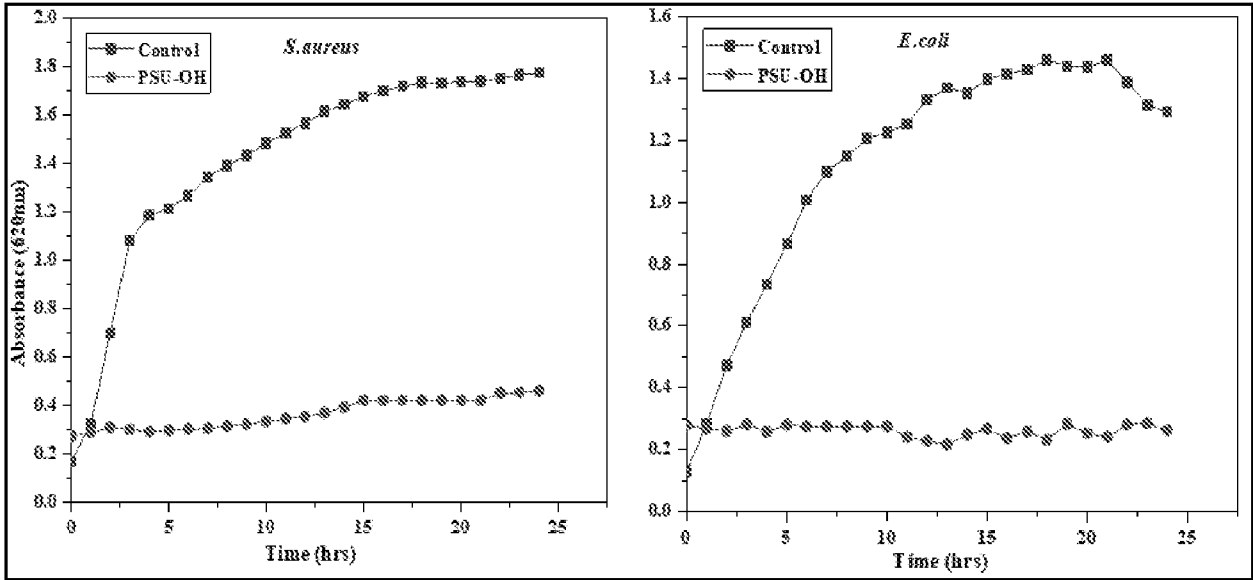


Figure 3

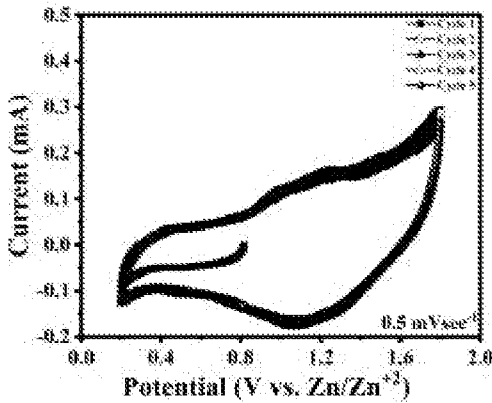


Figure 4a

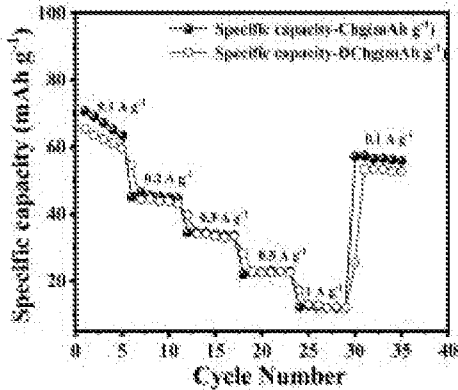


Figure 4b

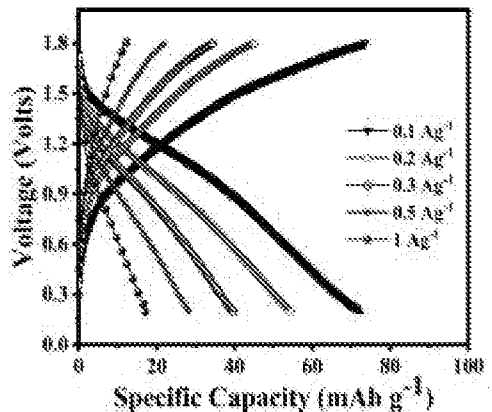


Figure 4c

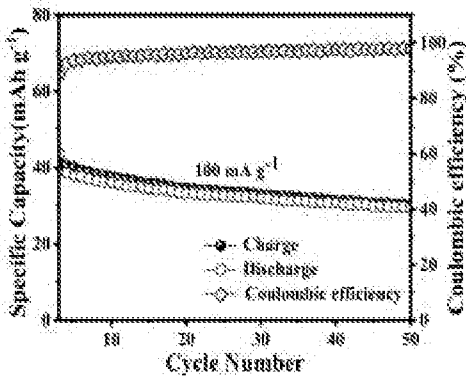


Figure 4d

3/4

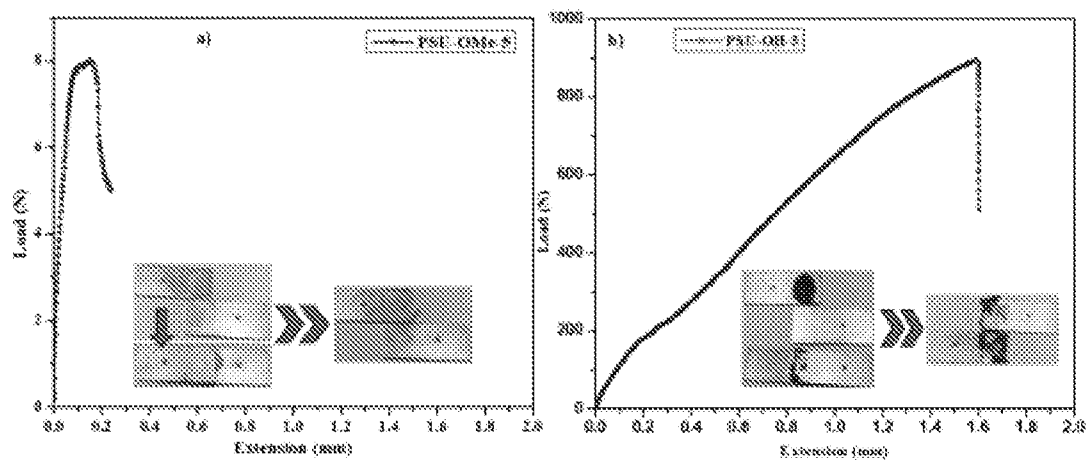


Figure 5a and 5b

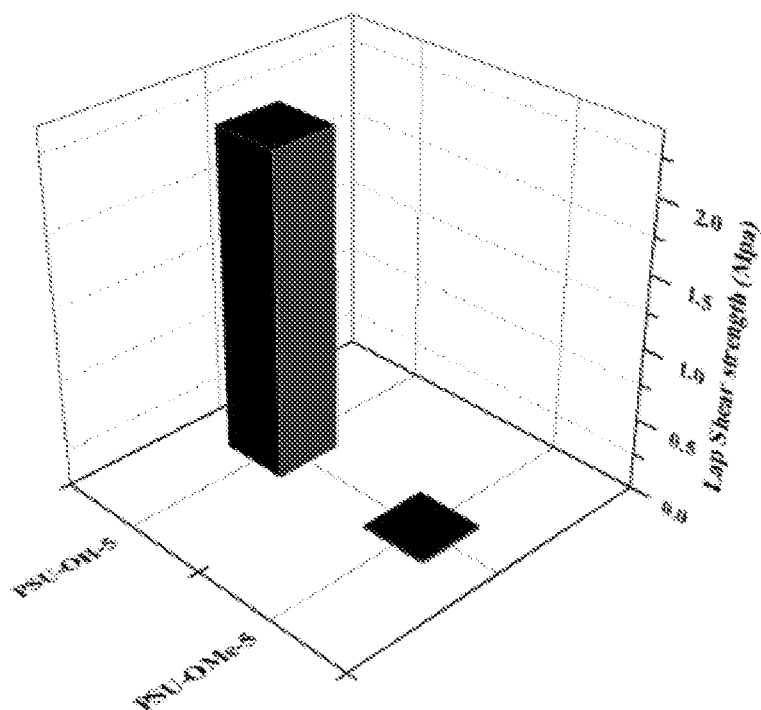


Figure 6

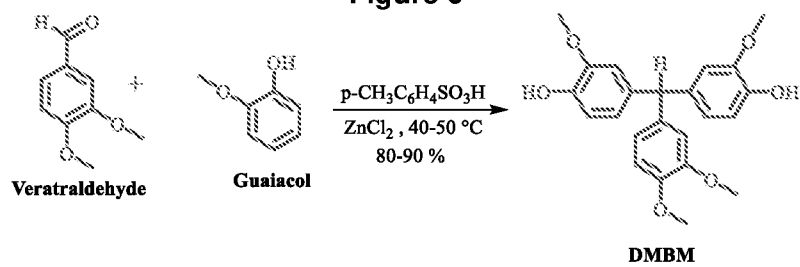


Figure 7

4/4

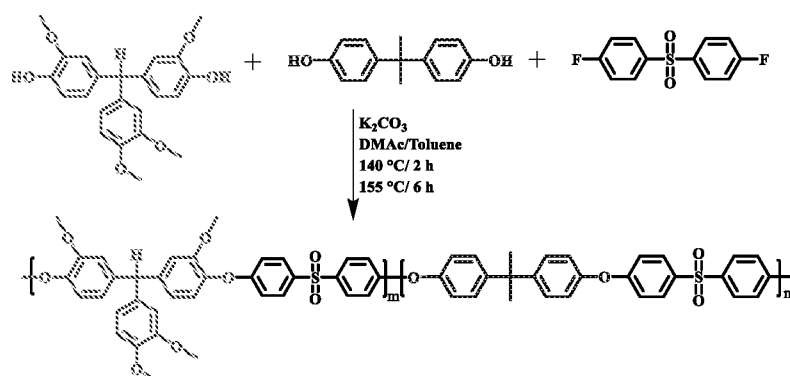


Figure 8

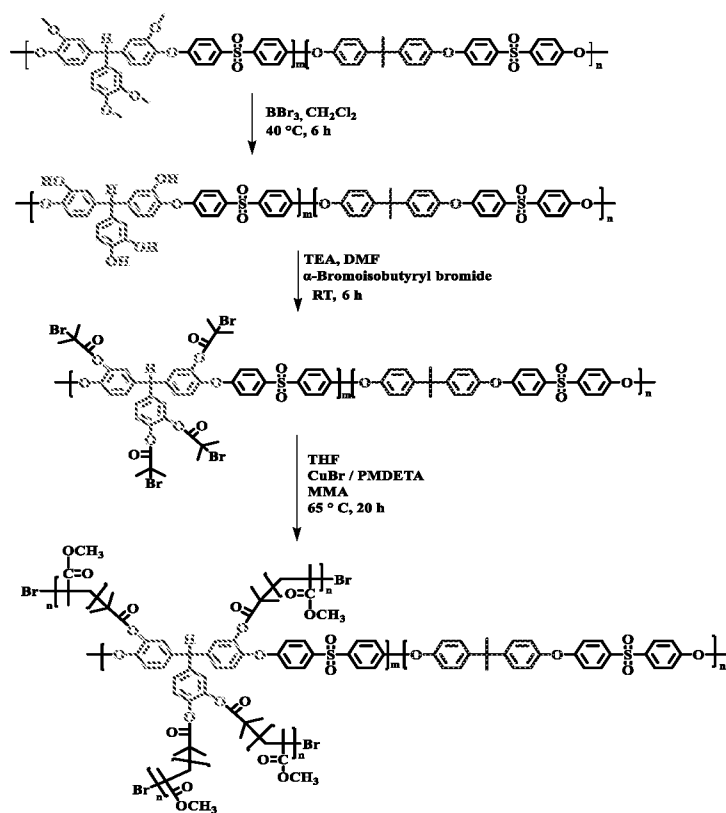


Figure 9

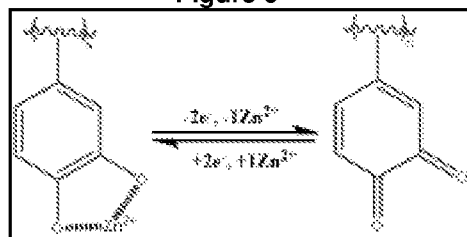


Figure 10

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IN2024/051953

## A. CLASSIFICATION OF SUBJECT MATTER

C07C39/16, C07C37/20, C07C43/23, C07C2/66 Version=2025.01

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)

C07C

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

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

PatSeer, IPO Internal Database

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                     | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | CN104370712A (UNIV CHANGZHOU) 25 FEBRUARY 2015<br>(25.02.2015) abstract, claims 1-4, para.<br>[0006]–[0013]            | 1–15                  |
| Y         | CN110809570B (UNIV LEUVEN KATH) 23 JUNE 2023<br>(23.06.2023) abstract, claims 6–7, 24, para.<br>[0005], [0068], [0157] | 1–15                  |

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

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“I” 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

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Date of the actual completion of the international search

28-01-2025

Date of mailing of the international search report

28-01-2025

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Authorized officer

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INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.  
PCT/IN2024/051953

| Citation       | Pub.Date   | Family           | Pub.Date   |
|----------------|------------|------------------|------------|
| CN 110809570 B | 23-06-2023 | CN 110809570 A   | 18-02-2020 |
|                |            | EP 3645492 A1    | 06-05-2020 |
|                |            | US 2020123315 A1 | 23-04-2020 |
|                |            | WO 2019002503 A1 | 03-01-2019 |