

THERMOPHOTOCHROMIC POLYMER AND METHOD OF PREPARING THERMOPHOTOCHROMIC POLYMER

5 TECHNICAL FIELD

The present disclosure relates broadly to a thermophotochromic polymer comprising two or more spiropyran units or derivatives thereof. The present disclosure also relates to a method of preparing said thermophotochromic
10 polymer.

BACKGROUND

Photochromism refers to light induced change of color. Typically, solutions
15 of photochromic compounds absorb electromagnetic radiation like ultraviolet (UV) light and undergo a transition from colorless or pale yellow to a colored form. This transition accompanies many changes in physico-chemical properties such as electric dipole moment, change in volume, difference in emission behavior, change in basicity and affinity to metal ions etc. Because of this nature,
20 photochromic compounds are proposed to be useful for various applications such as chemosensors, near-infrared (NIR) two photon fluorescent probe for living cancer cells, optical materials, optical information storage, cosmetics, optobioelectronic devices, chiroptical molecular switches, mechanochromic materials and many others. One of the advantages of photochromism is its non-
25 invasive nature as it operates in such a way that the stimuli i.e. the electromagnetic radiation is not in direct contact (e.g., physical contact) with the system undergoing changes.

In spite of this advantage, conventional photochromic compounds and/or
30 system have several limitations and are far from desirable. This is further elaborated below.

There have been discussions on alternative materials to replace conventional photochromic compounds. For example, crosslinkable units derived from mechanochromic compounds, thermally switchable photochromism in solid materials, coreshell capsules containing solutions of photochromic dyes in acidic phase change materials, and copolymers of difunctional photochromic compounds have been discussed. However, these studies are faced with various challenges. In particular, these currently available photochromic compounds are often either insoluble in water or hydrolytically unstable. Indeed, some of these currently available compounds decompose easily while some of these compounds hydrolyzed back to its starting materials upon solubilizing in water through host-guest interactions. Research and development are ongoing but to date, the search for suitable photochromic compounds remains futile.

Importantly, it is noted that the concept of thermophotochromism is rare. Reports on thermophotochromism are scarce or rather absent.

In view of the above, there is a need to address or at least ameliorate the above-mentioned problems. There is also a need to provide a thermophotochromic polymer and a method of preparing said thermophotochromic polymer that address or at least ameliorate the above-mentioned problems.

SUMMARY

In one aspect, there is provided a thermophotochromic polymer comprising two or more spiropyran units or derivatives thereof, wherein the polymer is configured to reversibly change its absorbance characteristics upon an application of thermal energy and/or ultraviolet light.

In one embodiment, an application of thermal energy facilitates a change in absorbance characteristics in a same direction as an application of ultraviolet light.

In one embodiment, an application of visible light facilitates a change in absorbance characteristics in an opposite direction as an application of thermal energy and/or ultraviolet light.

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In one embodiment, the polymer changes from a lighter colour to a darker colour upon application of thermal energy and/or UV light.

In one embodiment, the polymer is configured to further reversibly change its surface wettability characteristics upon an application of thermal energy and/or ultraviolet light.

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In one embodiment, an application of thermal energy and/or ultraviolet light result(s) in the ring opening of the spiropyran units or derivatives thereof in the polymer.

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In one embodiment, an application of visible light facilitates ring closing of the spiropyran units or derivatives thereof in the polymer.

In one embodiment, the polymer is present at a concentration of from 0.01 wt% to 50.0 wt% in solution.

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In one embodiment, the polymer is soluble in a solvent.

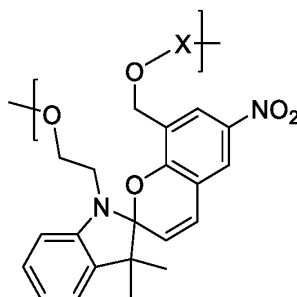
In one embodiment, the polymer comprises at least one of a polyester polymer, polyurethane polymer and combinations thereof.

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In one embodiment, the spiropyran units or derivatives thereof are coupled to at least one of carbamate/urethane linkage(s), ester linkage(s) and combinations thereof.

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In one embodiment, the polymer comprises at least one structural unit represented by Formula I:



Formula I

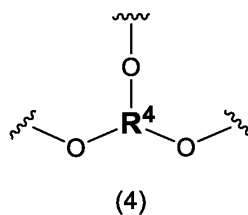
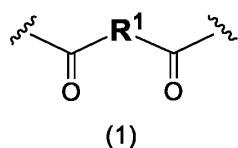
wherein

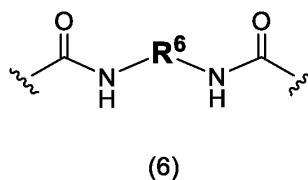
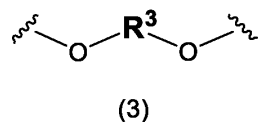
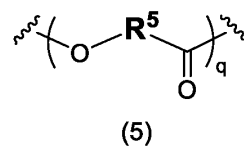
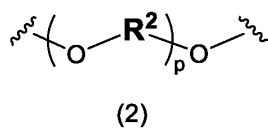
X comprises linear aliphatic, branched aliphatic, cyclic, aromatic hydrocarbons and combinations thereof;

one or more of the C atoms in the linear aliphatic, branched aliphatic, cyclic, aromatic hydrocarbons and combinations thereof is/are optionally replaced by $-O-$, $-C(=O)-$, $-C(=O)-O-$, $-O-C(=O)-$, $-NR^b-C(=O)-$ and/or $-C(=O)-NR^b-$; and

R^a and R^b are each independently selected from H, optionally substituted alkyl, optionally substituted alkenyl or optionally substituted alkynyl.

In one embodiment, X comprises one or more of the following general formula (1), (2), (3), (4), (5) and (6):





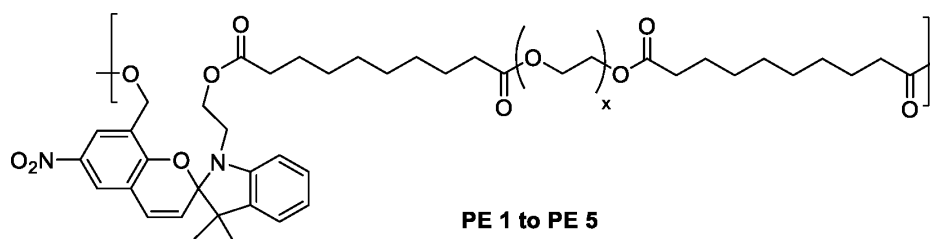
wherein

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkylcycloalkyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted aryl, optionally substituted alkylaryl, optionally substituted heteroaryl, optionally substituted alkylheteroaryl and combinations thereof;

$p \geq 1$; and $q \geq 1$.

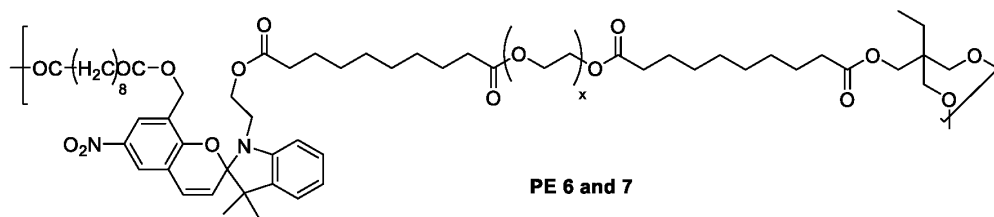
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In one embodiment, the polymer comprises at least one structural unit selected from the following:

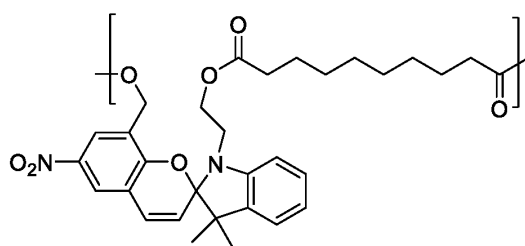
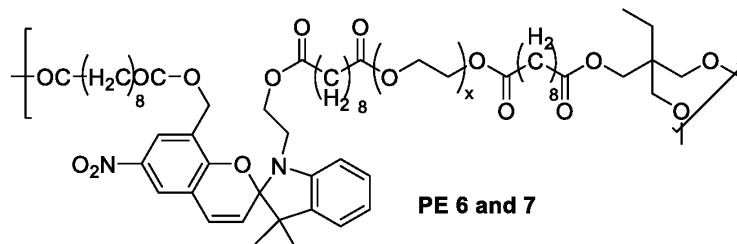


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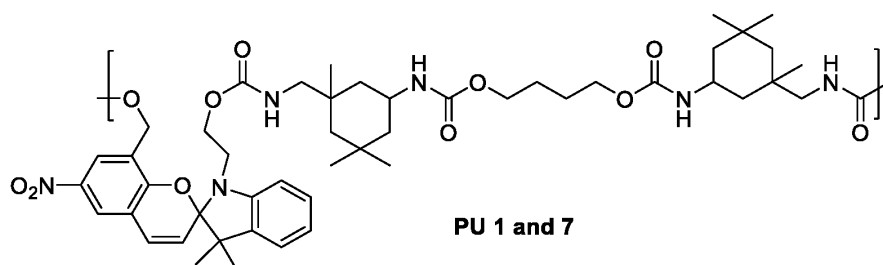
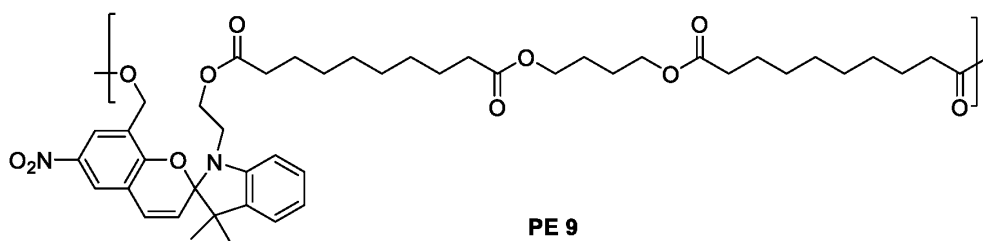
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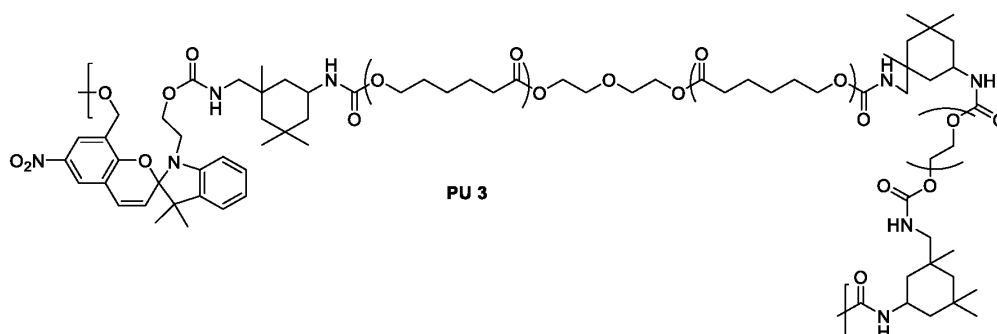
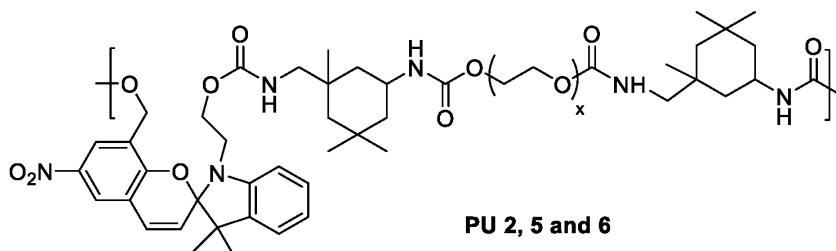


Or

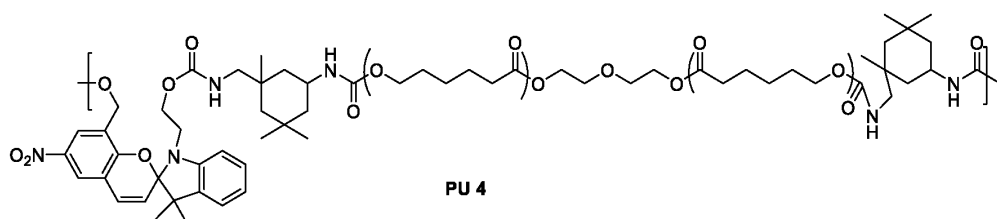


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In one aspect, there is provided a method of preparing the thermophotochromic polymer disclosed herein, the method comprising: reacting

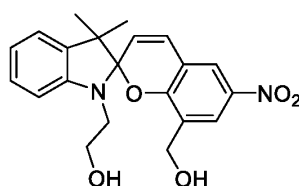
10 one or more spiropyran diol with one or more compounds selected from the group consisting of dicarboxylic acids, dicarboxylic acid derivatives, diacid chlorides, diisocyanates, diisocyanate derivatives, isocyanate derivatives, multifunctional carboxylic acids such as trifunctional carboxylic acids, polyfunctional carboxylic acids, monofunctional and multifunctional carboxylic acid derivatives such as

15 difunctional carboxylic acid derivatives, trifunctional carboxylic acid derivatives, polyfunctional carboxylic acid derivatives, multifunctional isocyanates and

multifunctional isocyanate derivatives, and optionally with one or more alcohols selected from dihydroxy, trihydroxy and polyhydroxy.

In one embodiment, the spiropyran diol is reacted with the compounds in
5 a molar ratio of from 1:1 to 1:30, and optionally with the alcohols in a molar ratio of from 1:1 to 1:30.

In one embodiment, the spiropyran diol is represented by Formula II:



Formula II

In one embodiment, the one or more alcohols is/are present and is/are selected from the group consisting of C₂ to C₁₀ diol, oligomeric and polymeric ethylene, propylene glycols and combinations thereof.

In one embodiment, the method comprises reacting one or more spiropyran diol with one or more diisocyanates selected from the group consisting of hexamethylene diisocyanate, tetramethylene diisocyanate, cyclohexane diisocyanate, tetramethylxylene diisocyanate, dodecylene diisocyanate, tolylene
20 2,4-diisocyanate, tolylene 2,6-diisocyanate, isophorone diisocyanate, their derivatives thereof and combinations thereof.

In one embodiment, the method comprises reacting one or more spiropyran diol with one or more diacid chlorides selected from the group
25 consisting of adipoyl chloride, dodecanedioyl chloride, succinyl chloride, sebacoyl chloride, heptanedioyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesyl chloride and combinations thereof.

DEFINITIONS

The term "polymer" as used herein refers to a chemical compound comprising repeating units and is created through a process of polymerization.

- 5 The units composing the polymer are typically derived from monomers and/or macromonomers. A polymer typically comprises repetition of a number of constitutional units.

- 10 The terms "monomer" or "macromonomer" as used herein refer to a chemical entity that may be covalently linked to one or more of such entities to form a polymer.

- 15 The term "ultraviolet light" as used herein refers to irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths. The ultraviolet light may have a wavelength of from about 10 nm to about 400 nm, or about 365 nm. The ultraviolet light may be obtained from a light source (e.g., a mercury lamp) having a power of from about 1 W to about 100 W, about 2 W, about 3 W, about 4 W, about 5 W, about 6 W, about 7 W, about 8 W, about 9 W, about 10 W, about 20 W, about 30 W, about 40 W, about 50 W or about 60 W.

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- The term "visible light" as used herein refers to visible light (e.g. irradiation by electromagnetic waves in the visible light spectrum/wavelengths). The terms "visible light", "white light" and "sunlight" may be used interchangeably. The visible light may have a wavelength of from about 400 nm to about 700 nm. The visible light may be obtained from a light source having a power of from about 1 W to about 100 W, about 2 W, about 3 W, about 4 W, about 5 W, about 6 W, about 7 W, about 8 W, about 9 W, about 10 W, about 20 W, about 30 W, about 40 W, about 50 W or about 60 W.

- 30 The term "bond" refers to a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

The term "aliphatic" as used herein encompasses, but is not limited to, "alkyl", "alkenyl", "alkynyl", "cycloalkyl", "cycloalkenyl" and the like.

The term "alkyl" as a group or part of a group refers to a straight or
5 branched aliphatic hydrocarbon group having 1 to 20 carbon atoms, 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Examples of suitable straight and branched alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-
10 dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-
15 dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl and the like. The group may be a terminal group or a bridging group.

The term "alkenyl" as a group or part of a group denotes an aliphatic
20 hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched having 2 to 20 carbon atoms, 2 to 10 carbon atoms, 2 to 6 carbon atoms, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms in the chain. The group may contain a plurality of double bonds and the orientation about each double bond is independently E or Z.
25 Exemplary alkenyl groups include, but are not limited to, ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-
30 hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 2-octenyl, 3-octenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 2-decenyl, 3-decenyl and the like. The group may be a terminal group or a bridging group.

The term "alkynyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon triple bond and which may be straight or branched having 2 to 20 carbon atoms, 2 to 10 carbon atoms, 5 2 to 6 carbon atoms, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms in the chain. The group may contain a plurality of triple bonds. Exemplary alkynyl groups include, but are not limited to, acetylenyl, propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-pentynyl, 2-pentynyl, 3-methyl-1-butynyl, 4-pentynyl, 1-hexynyl, 2-hexynyl, 5-hexynyl, 1-heptynyl, 2-heptynyl, 6-heptynyl, 1-10 octynyl, 2-octynyl, 7-octynyl, 1-nonyl, 2-nonyl, 8-nonyl, 1-decynyl, 2-decynyl, 9-decynyl and the like. The group may be a terminal group or a bridging group.

The term "cyclic" as used herein broadly refers to a structure where 15 one or more series of atoms are connected to form at least one ring. The term includes, but is not limited to, both saturated and unsaturated 5-membered and saturated and unsaturated 6-membered rings. Examples of groups having a cyclic structure include, but are not limited to, cyclopentane, cyclopentene, cyclohexane, cyclohexene, benzene and the like. The term 20 "cyclic" as used herein includes "heterocyclic".

The term "heterocyclic" as used herein broadly refers to a structure where two or more different kinds of atoms are connected to form at least one ring. For example, a heterocyclic ring may be formed by carbon atoms and at least another 25 atom (i.e. heteroatom) selected from oxygen (O), nitrogen (N) or (NR) and sulfur (S), where R is independently a hydrogen or an organic group. The term also includes, but is not limited to, saturated and unsaturated 5-membered, and saturated and unsaturated 6-membered rings. Examples of groups having a heterocyclic structure include, but are not limited to furan, thiophene, 1H-pyrrole, 30 2H-pyrrole, 1-pyrroline, 2-pyrroline, 3-pyrroline, 1-pyrazoline, 2-pyrazoline, 3-pyrazoline, 2-imidazoline, 3-imidazoline, 4-imidazoline, pyrazole, imidazole, oxazole, isoxazole, thiazole, isothiazole, 1,2,3-triazole, 1,2,4-triazole, 1,2,3-

oxadiazole, disubstituted 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, tetrahydrofuran, tetrahydrothiophene, pyrrolidine, 1,3-dioxolane, 1,2-oxathiolane, 1,3-oxathiolane, pyrazolidine, imidazolidine, pyridine, pyridazine, pyrimidine, 5 pyrazine, 1,2-oxazine, 1,3-oxazine, 1,4-oxazine, thiazine, 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine, 2H-pyran, 4H-pyran, 2-pyrone, 4-pyrone, 1,4-dioxin, 2H-thiopyran, 4H-thiopyran, tetrahydropyran, thiane, piperidine, 1,4-dioxane, 1,2-dithiane, 1,3-dithiane, 1,4-dithiane, 1,3,5-trithiane, piperazine, morpholine, thiomorpholine and the like.

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The term “aromatic” as used herein when referring to hydrocarbons, refers broadly to hydrocarbons having a ring-shaped or cyclic structure with delocalised electrons between carbon atoms. The term encompasses, but is not limited to, monovalent (“aryl”), divalent (“arylene”) monocyclic aromatic 15 groups having 5 to 6 atoms. Examples of such groups include, but are not limited to, benzene, furan, thiophene, pyrrole, pyrazole, imidazole, oxazole, thiazole, triazole, oxadiazole, thiadiazole, tetrazole, benzofuran, benzothiophene, benzopyrrole, benzodifuran, benzodithiophene, benzodipyrrole, pyridine, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 20 1,2,4-triazine, 1,3,5-triazine and the like.

The term “heteroaromatic” as used herein when referring to hydrocarbons, refers broadly to aromatic hydrocarbons that have one or more carbon atoms replaced by a heteroatom. The term encompasses, but is not 25 limited to, monovalent (“aryl”), divalent (“arylene”) monocyclic, polycyclic conjugated or fused aromatic groups having 5 to 14 atoms, where 1 to 6 atoms in each aromatic ring are heteroatoms selected from oxygen (O), nitrogen (N) or (NH) and sulfur (S). Examples of such groups include, but are not limited to, furan, thiophene, pyrrole, pyrazole, imidazole, oxazole, 30 thiazole, triazole, oxadiazole, thiadiazole, tetrazole, benzofuran, benzothiophene, benzopyrrole, benzodifuran, benzodithiophene,

benzodipyrrole, pyridine, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine and the like.

The term "optionally substituted," when used to describe a chemical structure or moiety, refers to the chemical structure or moiety wherein one or more of its hydrogen atoms is optionally substituted with a chemical moiety or functional group such as alcohol, alkoxy, alkanoyloxy, alkoxycarbonyl, alkenyl, alkyl (e.g., methyl, ethyl, propyl, t-butyl), alkynyl, alkylcarbonyloxy ($-\text{OC}(\text{O})\text{alkyl}$), amide ($-\text{C}(\text{O})\text{NH-alkyl-}$ or $-\text{alkylNHC}(\text{O})\text{alkyl}$), tertiary amine (such as alkylamino, arylamino, arylalkylamino), aryl, aryloxy, azo, carbamoyl ($-\text{NHC}(\text{O})\text{O-alkyl-}$ or $-\text{OC}(\text{O})\text{NH-alkyl}$), carbamyl (e.g., CONH_2 , as well as CONH-alkyl , CONH-aryl , and CONH-arylalkyl), carboxyl, carboxylic acid, carboxylic acid salt (e.g., $-\text{COO}^-\text{Na}^+$), cyano, ester, ether (e.g., methoxy, ethoxy), halo, haloalkyl (e.g., $-\text{CCl}_3$, $-\text{CF}_3$, $-\text{C}(\text{CF}_3)_3$), heteroalkyl, isocyanate, isothiocyanate, nitrile, nitro, phosphodiester, sulfide, sulfonamido (e.g., SO_2NH_2), sulfone, sulfonyl (including alkylsulfonyl, arylsulfonyl and arylalkylsulfonyl), sulfoxide, thiol (e.g., sulfhydryl, thioether) or urea ($-\text{NHCONH-alkyl-}$).

The term "carbamate" or "urethane" or the like is intended to broadly refer to a group containing $-\text{O}-\text{C}(=\text{O})\text{NR-}$, where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

The term "ester" or the like is intended to broadly refer to a group containing $-\text{O}-\text{C}(=\text{O})-$. The group may be a terminal group or a bridging group.

The term "alkoxy" as used herein refers to straight chain or branched alkyloxy groups. Examples include methoxy, ethoxy, n-propoxy, isopropoxy, tert-butoxy, and the like.

The term "alkoxyalkyl" as used herein is intended to broadly refer to a group containing $-R-O-R'$, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

5 The term "alkylcarbonyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

10 The term "alkylcarbonylalkyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-R'$, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

15 The term "carboxylalkyl" as used herein is intended to broadly refer to a group containing $-C(=O)-O-R$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

20 The term "oxycarbonylalkyl" as used herein is intended to broadly refer to a group containing $-O-C(=O)-R$, where R is alkyl as defined herein. The group may be a terminal group or a bridging group.

 The term "alkylcarboxylalkyl" as used herein is intended to broadly refer to a group containing $-R-C(=O)-O-R'$, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

25 The term "alkoxycarbonylalkyl" as used herein is intended to broadly refer to a group containing $-R-O-C(=O)-R'$, where R and R' are alkyl as defined herein. The group may be a terminal group or a bridging group.

30 The term "oxy" as used herein is intended to broadly refer to a group containing $-O-$.

The term "carbonyl" as used herein is intended to broadly refer to a group containing —C(=O)— .

The term "oxycarbonyl" as used herein is intended to broadly refer to a group containing —O—C(=O)— .

The term "carboxyl" as used herein is intended to broadly refer to a group containing —C(=O)—O—R , where R is hydrogen or an organic group.

The term "halogen" represents chlorine, fluorine, bromine or iodine. The term "halo" represents chloro, fluoro, bromo or iodo.

The term "amine group" or the like is intended to broadly refer to a group containing —NR_2 , where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

The term "amide group" or the like is intended to broadly refer to a group containing —C(=O)NR_2 , where R is independently a hydrogen or an organic group. The group may be a terminal group or a bridging group.

The term "micro" as used herein is to be interpreted broadly to include dimensions from about 1 micron to about 1000 microns.

The term "nano" as used herein is to be interpreted broadly to include dimensions less than about 1000 nm, less than about 500 nm, less than about 100 nm or less than about 50 nm.

The term "particle" as used herein broadly refers to a discrete entity or a discrete body. The particle described herein can include an organic, an inorganic or a biological particle. The particle used described herein may also be a macro-particle that is formed by an aggregate of a plurality of sub-particles or a fragment of a small object. The particle of the present disclosure may be spherical,

substantially spherical, or non-spherical, such as irregularly shaped particles or ellipsoidally shaped particles. The term "size" when used to refer to the particle broadly refers to the largest dimension of the particle. For example, when the particle is substantially spherical, the term "size" can refer to the diameter of the particle; or when the particle is substantially non-spherical, the term "size" can refer to the largest length of the particle.

The terms "coupled" or "connected" as used in this description are intended to cover both directly connected or connected through one or more intermediate means, unless otherwise stated.

The term "associated with", used herein when referring to two elements refers to a broad relationship between the two elements. The relationship includes, but is not limited to a physical, a chemical or a biological relationship. For example, when element A is associated with element B, elements A and B may be directly or indirectly attached to each other or element A may contain element B or vice versa.

The term "adjacent" used herein when referring to two elements refers to one element being in close proximity to another element and may be but is not limited to the elements contacting each other or may further include the elements being separated by one or more further elements disposed therebetween.

The term "and/or", e.g., "X and/or Y" is understood to mean either "X and Y" or "X or Y" and should be taken to provide explicit support for both meanings or for either meaning.

Further, in the description herein, the word "substantially" whenever used is understood to include, but not restricted to, "entirely" or "completely" and the like. In addition, terms such as "comprising", "comprise", and the like whenever used, are intended to be non-restricting descriptive language in that they broadly include elements/components recited after such terms, in addition to other

components not explicitly recited. For example, when "comprising" is used, reference to a "one" feature is also intended to be a reference to "at least one" of that feature. Terms such as "consisting", "consist", and the like, may in the appropriate context, be considered as a subset of terms such as "comprising", "comprise", and the like. Therefore, in embodiments disclosed herein using the terms such as "comprising", "comprise", and the like, it will be appreciated that these embodiments provide teaching for corresponding embodiments using terms such as "consisting", "consist", and the like. Further, terms such as "about", "approximately" and the like whenever used, typically means a reasonable variation, for example a variation of +/- 5% of the disclosed value, or a variance of 4% of the disclosed value, or a variance of 3% of the disclosed value, a variance of 2% of the disclosed value or a variance of 1% of the disclosed value.

Furthermore, in the description herein, certain values may be disclosed in a range. The values showing the end points of a range are intended to illustrate a preferred range. Whenever a range has been described, it is intended that the range covers and teaches all possible sub-ranges as well as individual numerical values within that range. That is, the end points of a range should not be interpreted as inflexible limitations. For example, a description of a range of 1% to 5% is intended to have specifically disclosed sub-ranges 1% to 2%, 1% to 3%, 1% to 4%, 2% to 3% etc., as well as individually, values within that range such as 1%, 2%, 3%, 4% and 5%. It is to be appreciated that the individual numerical values within the range also include integers, fractions and decimals. Furthermore, whenever a range has been described, it is also intended that the range covers and teaches values of up to 2 additional decimal places or significant figures (where appropriate) from the shown numerical end points. For example, a description of a range of 1% to 5% is intended to have specifically disclosed the ranges 1.00% to 5.00% and also 1.0% to 5.0% and all their intermediate values (such as 1.01%, 1.02% ... 4.98%, 4.99%, 5.00% and 1.1%, 1.2% ... 4.8%, 4.9%, 5.0% etc.,) spanning the ranges. The intention of the above specific disclosure is applicable to any depth/breadth of a range.

Additionally, when describing some embodiments, the disclosure may have disclosed a method and/or process as a particular sequence of steps. However, unless otherwise required, it will be appreciated that the method or process should not be limited to the particular sequence of steps disclosed. Other
5 sequences of steps may be possible. The particular order of the steps disclosed herein should not be construed as undue limitations. Unless otherwise required, a method and/or process disclosed herein should not be limited to the steps being carried out in the order written. The sequence of steps may be varied and still remain within the scope of the disclosure. Unless otherwise stated or required,
10 one or more steps may also be omitted or removed in certain embodiments and these embodiments are understood to be still within the scope of the disclosure.

Furthermore, it will be appreciated that while the present disclosure provides embodiments having one or more of the features/characteristics
15 discussed herein, one or more of these features/characteristics may also be disclaimed in other alternative embodiments and the present disclosure provides support for such disclaimers and these associated alternative embodiments.

DESCRIPTION OF EMBODIMENTS

20

Exemplary, non-limiting embodiments of a thermophotochromic polymer comprising two or more spiropyran units or derivatives thereof, and a method of preparing said thermophotochromic polymer are disclosed hereinafter.

25 There is provided a polymer comprising thermophotochromic or photothermochromic properties, functions, units and/or groups. The polymer may be a thermophotochromic polymer or a photothermochromic polymer. In various embodiments, the terms "thermophotochromic" and "photothermochromic" may be used interchangeably. Similarly, the terms "thermophotochromism" and
30 "photothermochromism" may also be used interchangeably.

In various embodiments, the polymer is suitable for, capable of, adapted to or configured to reversibly change one or more of its properties upon an application of a stimulus. Such stimulus may include thermal energy (e.g., heat), ultraviolet light (e.g. irradiation by electromagnetic waves in the ultraviolet spectrum/wavelengths), visible light (e.g. irradiation by electromagnetic waves in the visible light spectrum/wavelengths), natural light, artificial light, pressure (e.g., mechanical pressure), ion addition, electric current, vibration, ultrasound and the like and combinations thereof. The one or more properties may be selected from the group consisting of absorption spectra characteristics, emission spectra characteristics, physico-chemical characteristics, refractive index characteristics, dielectric constant characteristics, electrochemical (e.g., electric conductivity) characteristics, phase transition characteristics, solubility characteristics, viscosity characteristics, surface wettability characteristics, photomechanical, conformation, polarity characteristics and the like and combinations thereof. In various embodiments, the reversibility in changing one or more of its properties upon an application of a stimulus is intended to mean that the change in one or more properties in one direction (a first direction) may be reversed such that a change in one or more of the same properties in the opposite direction (second opposite direction) may also be achieved, for example when the stimulus that causes the change in the first direction is removed and/or when a different stimulus is applied. Accordingly, in various embodiments, the reversibility in the change in the one or more properties may not necessarily mean that the one or more properties can completely revert to its initial/original unchanged state, although in some embodiments it may still be able to substantially achieve this. In other words, the change in one or more properties in the second opposite direction does not necessarily need to put the polymer back in a state as though the first direction change has not/never occurred. As an example, the polymer may change in a first direction from a lightest colour (e.g. colour A) to a darkest colour (e.g. colour C) upon applying a first stimulus (e.g. UV light) and change in a second opposite direction from a darkest colour (e.g. colour C) to a lighter colour (e.g. colour B) upon applying a second stimulus (e.g. visible light), where the lighter colour (e.g. colour B) is lighter than the darkest colour (e.g. colour C)

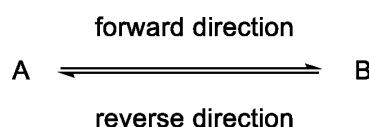
but still darker than the lightest colour (e.g. colour A). In such a situation, the colour change from a light colour to a dark colour may still be considered as reversible.

5 In various embodiments, the polymer is designed such that an application of thermal energy (e.g. heat) facilitates (or results in) a change in one or more of its properties in a same direction as an application of ultraviolet light (e.g. irradiation by electromagnetic waves in the ultraviolet wavelength). In various
10 embodiments therefore, the polymer is capable of responding to heat and ultraviolet (UV) light synonymously. Exposing the polymer to heat and UV light may produce/obtain same/similar/identical results/effects/outcomes.

 In various embodiments, the polymer is designed such that an application of visible light (e.g. irradiation by electromagnetic waves in the visible light
15 spectrum/wavelengths) facilitates (or results in) a change in one or more of its properties in a opposite direction as an application of thermal energy and/or ultraviolet (UV) light. In various embodiments therefore, the polymer is capable of responding to visible light and heat antonymously, and/or responding to visible
20 light and UV light antonymously. Exposing the polymer to visible light as compared to heat may produce/obtain different results/effects/outcomes.

 In various embodiments, the polymer is designed to exist in the form of a structure A (e.g., ring-closed form) and/or a structure B (e.g., ring-opened form). As shown in Scheme 1, A may be transformed into B in a forward direction and
25 B may be reversibly transformed back into A in a reverse direction. B may be transformed into A in a reverse direction and A may be reversibly transformed back into B in a forward direction. The transformation from A into B or B into A may be about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about
30 7%, about 8%, about 9%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 90%, about

91%, about 92%, about 93%, about 94%, about 95%, about 96%, about 97%, about 98%, about 99%, or about 100%.



5 Scheme 1. Reversible transformation between structures A and B

In various embodiments, the polymer is further designed such that transformation can be achieved by either (i) applying a stimulus; and/or (ii) removing a stimulus (that causes change in the opposite direction). In various

10 embodiments, transformation from A to B in the forward direction can be achieved by applying heat and/or UV light. In various embodiments, transformation from A to B in the forward direction can also be achieved by removing visible light/sunlight. In various embodiments, transformation from B to A in the reverse

15 direction can be achieved by applying visible light/sunlight. For example, exposure to visible light helps/facilitates a transformation from B to A by >90%, more than about 90%, more than about 91%, more than about 92%, more than about 93%, more than about 94%, more than about 95%, more than about 96%, more than about 97%, more than about 98%, or more than about 99%. This may be more easily achieved when the stimulus (or stimuli) that drives the direction of

20 transformation from A to B is simultaneously removed. In various embodiments, transformation from B to A in the reverse direction can also be achieved by removing the stimulus (or stimuli) that drives the direction of transformation from A to B (e.g. heat and/or UV light). This may also be achieved in the absence of a stimuli (or stimulus) that drives the direction of transformation from B to A (e.g.

25 visible light). For example, in the absence of visible light, heat and UV light, the conversion from B (e.g., a coloured spiropyran form) to A (i.e. its colourless spiropyran form) may still occur but at a level of <90%, less than about 90%, less than about 89%, less than about 88%, less than about 87%, less than about 86%, less than about 85%, less than about 80%, less than about 75%, less than about

30 70%, less than about 65%, less than about 60%, less than about 55%, or less

than about 50%. That is, some structures may still remain in the form of B (e.g., ring opened merocyanine form) as indicated by the lightly coloured solution (e.g., light pink colour of the solution). For example, even in the absence of exposure to heat and/or UV light, a coloured form (e.g., ring opened merocyanine form) may still be present at low concentrations. Accordingly, in various embodiments, it will be appreciated that providing visible light may not be required to initiate reversal of the process (i.e. drive the reaction towards the reverse direction).

In various embodiments, both A and B exist in equilibrium. For example, the polymer may comprise spiropyran ring(s), and both ring closing and ring opening forms may be in equilibrium. That is, both ring closed and ring opened forms of the spiropyran rings may be present simultaneously although their relative degree/amounts may be different. In various embodiments, the position of the equilibrium (e.g., whether the forward or the reverse direction is favoured; or whether the formation of A or B is favoured) is dependent on factors such as the presence and/or intensity of the dominating stimulus and stability of the polymer forms. For example, in the presence of many stimuli (e.g., heat, UV light and visible light), the position of the equilibrium lies towards the direction of the dominating stimulus and the net outcome depends on whichever is the dominant stimulus. The position of the equilibrium may also lie towards the direction of a more stabilized polymer form. In various embodiments, visible light has a dominating effect over heat. For example, in the presence of two opposing stimuli namely, heat and visible light, a reverse direction may be favoured towards the formation of A due to the dominating visible light stimulus. For example, through experiments performed inside a laboratory, it was observed that warm solutions (having a temperature of <50 °C) immediately changed colour when they were exposed to sunlight even while being warm. Without being bound by theory, it is believed that visible light has a dominating effect over heat.

In various embodiments, the dominating light/radiation of sunlight is visible light/radiation when sunlight is allowed to pass through a UV light absorbing substrate (e.g. a transparent or substantially transparent UV light absorbing

substrate). For example, without being bound by theory, it is believed that when sunlight passes through a transparent substrate such as a glass window, at least part of the UV light in the sunlight may have been absorbed by the window. Accordingly, in various embodiments, in the presence of sunlight indoors, the reverse direction (i.e. transformation from B to A) is favoured indoors due to the dominating visible light stimulus in sunlight that has passed through a UV light absorbing substrate (e.g. glass window). It will be appreciated that the position of the equilibrium is also dependent on the stability of the polymer form (e.g., stabilizing effect provided by water to merocyanine (i.e. ring opened form) may also determine the outcome). Thus, despite the dominating visible light stimulus, the position of the equilibrium may be shifted slightly to the forward direction (e.g., towards the stabilized ring-opened form B), showing that under ambient conditions (about 25 °C), some degree of colour (approx. 10%) may be present even under direct sunlight. That is, both ring closed and ring opened forms of the polymer (e.g. spiropyran rings) may be present simultaneously although their relative degree/amounts may be different. Since in various embodiments, the closed ring forms of the polymer (e.g. spiropyran rings) are substantially colourless, the presence of a small degree of opened ring forms of the polymer (e.g. spiropyran rings) may be sufficient to elicit a visible colour, albeit light or faint colour.

In various embodiments, the thermophotochromic polymer is suitable for, capable of, adapted to or configured to reversibly change its absorbance characteristics upon an application of a stimulus selected from the group consisting of thermal energy, ultraviolet light, and visible light. Absorbance characteristics (or colour) may be changed or tuned by alternating exposure between thermal energy, ultraviolet light, and/or visible light.

In various embodiments, the thermophotochromic polymer is designed such that an application of thermal energy to the polymer facilitates (or results in) a change in its absorbance characteristics in a same direction as an application of UV light to the polymer. In various embodiments, thermal energy comprises

thermal energy available under or provided by ambient conditions (e.g., room temperature at about 20°C to 40°C). For example, exposing the thermophotochromic polymer to thermal energy and UV light may obtain a same/similar/identical colour change. Exposing the thermophotochromic polymer to thermal energy and UV light may also obtain a same/similar/identical chemical conformation/state/form of the polymer. Accordingly, in various embodiments, thermal energy may be used as a substitute for UV light. Advantageously, such a design allows same/similar/identical results/effects/outcomes to be achieved with thermal energy (or simply heat available under ambient conditions), thereby eliminating the need for a high energy/power UV source, making the thermophotochromic process an energy efficient and/or sustainable one. In various embodiments, the thermophotochromic polymer disclosed herein is different from conventional photochromic polymers/materials. It will be appreciated that in conventional photochromism, exposure to UV light and heat produce opposite results/effects/outcomes and therefore, thermal energy (e.g., heat) cannot be used as a substitute for UV light.

In various embodiments, the thermophotochromic polymer is designed such that increasing temperature of the polymer facilitates (or results in) a change in its absorbance characteristics in a same direction as an application of UV light to the polymer. For example, the intensity of absorption may increase with temperature. In various embodiments, effects of UV light (photo) and temperature (thermo) are synonymous.

In various embodiments, the thermophotochromic polymer is designed such that an application of visible light to the polymer facilitates (or results in) a change in its absorbance characteristics in an opposite direction as an application of thermal energy and/or ultraviolet light to the polymer. For example, exposing the thermophotochromic polymer to visible light as compared to thermal energy may obtain different colour change and/or different chemical conformation/state/form of the polymer. Advantageously, such a design allows a reversible transition between different colour changes and/or forms of the

polymer to be achieved by switching between visible light and thermal energy. In various embodiments, the thermophotochromic polymer disclosed herein is different from conventional photochromic polymers/materials. It will be appreciated that in conventional photochromism, exposure to visible light and heat produce same/similar/identical results/effects/outcomes and therefore a reversible transition between different results/effects/outcomes cannot be achieved by switching between visible light and thermal energy (e.g., heat).

In various embodiments, the thermophotochromic polymer is capable of exhibiting a colour change. In various embodiments, the thermophotochromic polymer exhibits a colour change upon an application of a stimulus. It will be appreciated that in various embodiments, the thermophotochromic polymer may also exhibit a colour change upon removal of a stimulus. The colour change may comprise any one of the following:

- (i) a change from a substantially colourless state to a coloured state;
- (ii) a change from a coloured state to a substantially colourless state;
- (iii) a change from a lighter coloured state to a darker coloured state; and /or
- (iv) a change from a darker coloured state to a lighter coloured state.

In various embodiments, an application of thermal energy and/or UV light to the polymer facilitates (or results in) colour change (i) or colour change (iii). In various embodiments, a removal of thermal energy and/or UV light from the polymer facilitates (or results in) colour change (ii) or colour change (iv). In various embodiments, an application of visible light to the polymer facilitates (or results in) colour change (ii) or colour change (iv). In various embodiments, a removal of visible light from the polymer facilitates (or results in) colour change (i) or colour change (iii).

In various embodiments, the polymer exhibits a reversible colour change in response to thermal energy (e.g., heat), UV light and/or visible light. In various embodiments, the polymer changes from colourless to coloured upon application

of thermal energy and/or UV light; and from coloured to colourless upon application of visible light. In various embodiments, the polymer changes from a lighter colour to a darker colour upon application of thermal energy and/or UV light; and from a darker colour to a lighter colour upon application of visible light.

5 In various embodiments, an application of thermal energy and/or ultraviolet light result(s) in the polymer becoming darker in colour (or more intense); and optionally wherein an application of visible light reversibly reverts the polymer to a lighter (or less intense) colour. In various embodiments, an application of visible light facilitates (or results in) the polymer becoming lighter in colour (or less

10 intense); and optionally wherein a removal of visible light reversibly reverts the polymer to a darker (or more intense) colour. For example, in the absence of visible light, the polymer may change from pale pink to a darker or more intense colour (e.g., to a pink or darker pink). Advantageously, such a reversibility design imparts dynamic functionality/ characteristic to the polymer disclosed herein by

15 allowing embodiments of the polymer to reversibly change its absorbance characteristics synchronized with day-night cycles. In various embodiments, such design allows the polymer to be used as or incorporated into surfaces synchronized with day-night cycles, forming a colourless form in/during the daytime (under direct sunlight/visible light) and forming a coloured form in/during

20 the night-time (induced by ambient temperature).

Accordingly, in various embodiments, there is also provided dynamic surfaces formed therefrom.

25 In various embodiments, the thermophotochromic polymer is capable of absorbing light. In various embodiments, the thermophotochromic polymer absorbs light with wavelengths ranging from about 300 nm to about 700 nm, from about 350 nm to about 650 nm, from about 400 nm to about 600 nm, from about 450 nm to about 500 nm, or about 550 nm. In various embodiments, the

30 absorption range of the polymer solution depends on the state/structure/form/ configuration of the polymer. For example, when the polymer is in the ring closed form, the absorption may range from about 210 to about 400 nm, from about 220

nm to about 390 nm, from about 230 nm to about 380 nm, from about 240 nm to about 370 nm, from about 250 nm to about 360 nm, from about 260 nm to about 350 nm, from about 270 nm to about 340 nm, from about 280 nm to about 330 nm, from about 290 nm to about 320 nm, or from about 300 to about 310 nm. For example, when the polymer is in the ring opened form, the absorption may range from about 450 nm to 650 nm, from about 460 nm to about 640 nm, from about 470 nm to 630 nm, from about 480 nm to about 620 nm, from about 490 nm to 610 nm, from about 500 nm to about 600 nm, from about 510 nm to 590 nm, from about 520 nm to about 580 nm, from about 530 nm to 570 nm, from about 540 nm to about 560 nm, or about 550 nm.

In various embodiments, the thermophotochromic polymer is suitable for, capable of, adapted to or configured to further reversibly change its surface wettability characteristics upon an application of a stimulus selected from the group consisting of thermal energy, ultraviolet light, and visible light. Surface wettability characteristics (expressed in terms of contact angle) may be changed or tuned by alternating exposure between thermal energy, ultraviolet light, and/or visible light.

In various embodiments, the polymer exhibits a reversible change in surface wettability in response to thermal energy (e.g., heat), UV light and/or visible light. In various embodiments, the surface (e.g., glass) in which the polymer is incorporated into changes from having high wetting (or surface energy/interfacial tension) to low wetting (or surface energy/interfacial tension) upon application of thermal energy and/or UV light; and from low wetting (or surface energy/interfacial tension) to high wetting (or surface energy/interfacial tension) upon application of visible light. In various embodiments, a surface in which the polymer is incorporated has a contact angle of from about 55.0° to about 70.0° (e.g. in its original form before any stimulus has been applied). In various embodiments, upon application of thermal energy and/or UV light, the contact angle changes to from about 85.0° to about 95.0°; and changes to from about 70.0° to about 85.0° upon application of visible light. In various

embodiments, upon application of thermal energy and/or UV light, the contact angle increases from 10.0° to about 45.0°, 15.0° to about 40.0°, 20.0° to about 35.0° or 25.0° to about 30.0°; and upon application of visible light decreases from about 5.0° to about 20.0°, or 10.0° to about 15.0° upon application of visible light.

- 5 In various embodiments, the absolute value of contact angle depends on the composition of the polymer. Extent of change in the contact angle from its original value may also be influenced by the polymer composition. However, in various embodiments, the change in contact angle may be negligible (e.g., negligibly small) or does not show any change in the absence of a light responsive moiety.

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In various embodiments, the contact angle is determined using a goniometer. A drop of water may be placed on a coated surface with a syringe. The drop of water may be then viewed through a camera attached with the goniometer to determine the angle.

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In various embodiments, the thermophotochromic polymer comprises spiropyran units/groups or derivatives thereof in the backbone of the polymer chain. In various embodiments, the spiropyran units/groups or derivatives thereof act as chromophore(s) that absorb and/or emit light of different wavelengths to provide a colour change.

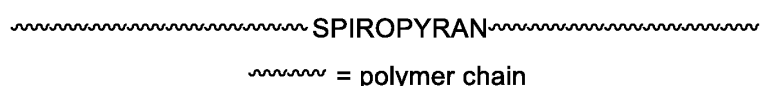
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- In various embodiments, the thermophotochromic polymer comprises two or more spiropyran units/groups or derivatives thereof in the backbone of the polymer chain. For example, the polymer may comprise at least 2, at least 3, at least 4, at least 5, at least 6, at least 7, at least 8, at least 9, at least 10, at least 15, at least 20, at least 25, at least 30, at least 35, at least 40, at least 45, at least 50, at least 60, at least 70, at least 80, at least 90, at least 100, at least 150, at least 200, at least 250, or at least 300 spiropyran units/groups or derivatives thereof in the backbone of the polymer chain. In various embodiments, the number of spiropyran units/groups or derivatives thereof present in the polymer can be altered as desired and/or designed according to the need or application the polymer is to be used for. Advantageously, the number of spiropyran

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units/groups or derivatives thereof is tunable and/or customizable, depending on the application the thermophotochromic polymer is to be used for. Even more advantageously, as the number of spiropyran units/groups or derivatives thereof in a polymer chain can be altered as desired, the concentration of the chromophores present in the polymer and consequently the thermophotochromic behavior/response of the polymer may also be tuned and adjusted as desired.

In various embodiments, the thermophotochromic polymer comprises two or more spiropyran units/groups or derivatives thereof in the backbone of the polymer and differs from an inferior comparative spiropyran polymer containing only one spiropyran unit per polymer chain (as shown in Scheme 2).



Scheme 2. Schematic representation of an example of an inferior spiropyran polymer

In various embodiments, spiropyran units/groups derivatives thereof include any spiropyran-containing units/groups that are or have been modified to gain or lose atom(s)/chemical group(s). For example, spiropyran derivatives thereof include a spiropyran diol that is or has been modified to lose two protons/H atoms.

In various embodiments, an application of thermal energy and/or ultraviolet light/visible light result(s) in a change of the open/close states of the ring in the spiropyran groups or derivatives thereof. For example, an application of thermal energy and/or ultraviolet light result(s) in the ring opening of the spiropyran groups or derivatives thereof in the polymer (e.g. resulting in a change in colour), optionally wherein an application of visible light facilitates (or results in) ring closing of the spiropyran groups or derivatives thereof in the polymer (e.g. resulting in a change in colour).

In various embodiments, the thermophotochromic polymer is present or used in a solid form (for e.g., film), as an aqueous solution, as an organic solution or in a gel form (for e.g., hydrogel).

5 In various embodiments, there is also provided a hydrogel comprising the polymer. In various embodiments, the hydrogel has a swelling ratio of from about 2 to about 5,000. In various embodiments, the hydrogel has a swelling ratio of about 2, about 5, about 10, about 20, about 30, about 40, about 50, about 100, about 150, about 200, about 250, about 300, about 350, about 400, about
10 450, about 500, about 1,000, about 1,500, about 2,000, about 2,500, about 3,000, about 3,500, about 4,000, about 4,500 or about 5,000.

In various embodiments, the thermophotochromic polymer is present at a concentration of from about 0.01 wt% to about 50.0 wt% in solution. The solution
15 may be organic solution or aqueous solution (e.g., aqueous medium or water). In various embodiments, the polymer is present at a concentration of from about 0.01 wt% to about 50.0 wt%, from about 0.02 wt% to about 45.0 wt%, from about 0.05 wt% to about 40.0 wt%, from about 0.10 wt% to about 35.0 wt%, from about 0.20 wt% to about 30.0 wt%, from about 0.30 wt% to about 25.0 wt%, from about
20 0.40 wt% to about 20.0 wt%, from about 0.50 wt% to about 15.0 wt%, from about 0.60 wt% to about 10.0 wt%, from about 0.70 wt% to about 9.0 wt%, from about 0.80 wt% to about 8.0 wt%, from about 0.90 wt% to about 7.0 wt%, from about 1.0 wt% to about 6.0 wt%, from about 2.0 wt% to about 5.0 wt%, or from about 3.0 wt% to about 4.0 wt% in solution. In various embodiments, higher viscosities
25 may be achieved by increasing the concentration of the polymer in the water/aqueous/organic solution (for e.g., up to 50 wt%).

In various embodiments, the thermophotochromic polymer is soluble in a solvent. The solvent may be aqueous (e.g., water/deionized water) or non-
30 aqueous (e.g., organic solvent). Any suitable solvent that effectively serves as a medium to contain the polymer may be used. In various embodiments, the solvent is an organic solvent. The organic solvent may be selected from but is not limited

to the group consisting of dimethylformamide (DMF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform, acetone, acetonitrile (ACN), dimethyl sulfoxide (DMSO), propylene carbonate (PC), dimethylcarbonate (DMC), dioxane, dioxolane, diglyme, methyl ethyl ketone (MEK), dimethylacetamide (DMAc), N-Methyl-2-pyrrolidone (NMP), toluene, xylenes and the like and combinations thereof. In various embodiments, the solvent is water. In various embodiments, the polymer is substantially/completely soluble in water without being substantially hydrolyzed (e.g. hydrolytically stable or resistant to being hydrolyzed back to its starting materials). In various
5 embodiments, the thermophotochromic polymer is a water-soluble polymer under ambient conditions (e.g., room temperature at about 20°C to 40°C, or about 25°C and pressure at about 1 atm).

In various embodiments, the thermophotochromic polymer is stable and/or
15 possess good stability. In various embodiments, the thermophotochromic polymer is stable and/or possess good stability in aqueous medium (e.g., water or aqueous solutions). In various embodiments, the thermophotochromic polymer can be stably stored under ambient conditions (e.g., room temperature at about 25°C and pressure at about 1 atm) over a time period of at least about 12 hours,
20 at least about 24 hours, at least about 2 days, at least about 3 days, at least about 4 days, at least about 5 days, at least about 6 days, at least about 7 days, at least about 8 days, at least about 9 days, at least about 10 days, at least about 11 days, at least about 12 days, at least about 13 days, at least about 2 weeks, at least about 3 weeks, at least about 4 weeks, at least about 2 months, at least
25 about 3 months, at least about 4 months, at least about 5 months, or at least about 6 months. For example, embodiments of the polymer retain their absorbance characteristics after at least about 1 week, at least about 2 weeks, at least about 3 weeks, at least about 4 weeks, at least about 5 weeks, at least about 6 weeks, at least about 7 weeks, at least about 8 weeks, at least about 9
30 weeks, at least about 10 weeks, at least 11 weeks, at least about 12 weeks, at least 13 weeks, or at least about 14 weeks of storage under ambient conditions. Accordingly, in various embodiments, the number of cycles in which the polymer

undergoes reversible transformation is not limited for e.g., by degradation processes.

In various embodiments, the polymer possesses lower critical solution temperature behavior. In various embodiments, the polymer has a lower critical solution temperature in the range of from about 40°C to about 100°C, from about 45°C to about 95°C, from about 50°C to about 90°C, from about 55°C to about 85°C, from about 60°C to about 80°C, from about 65°C to about 75°C, or about 70°C. In various embodiments, the lower critical solution temperature (LCST) varies according to the structure of the polymer. For example, the range of LCST observed for different polymers is from about 48°C to about 77°C.

In various embodiments, the thermophotochromic polymer possesses good adhesive nature or adhesive strength which allows embodiments of the polymer to be coated onto a substrate. The substrate may be any supporting structure such as glass (e.g., glass slide).

In various embodiments, the spiropyran units/groups or derivatives thereof is/are present as monomeric unit(s) in the polymer.

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In various embodiments, the thermophotochromic polymer comprises at least one of a polyester polymer, polyurethane polymer and combinations thereof. In various embodiments, the spiropyran units or derivatives thereof are coupled to at least one of carbamate/urethane linkage(s), ester linkage(s) and combinations thereof. The spiropyran units or derivatives thereof may be linked together or to another structural unit (which may be the same or a different structural unit) via at least one of carbamate/urethane linkage(s), ester linkage(s) and combinations thereof. For example, in various embodiments where the thermophotochromic polymer comprises a polyurethane, the spiropyran monomeric units may be joined/linked together or to another structural unit (which may be the same or a different structural unit) via carbamate/urethane linkages. For example, in various embodiments where the thermophotochromic polymer

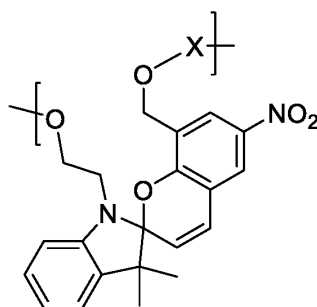
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comprises a polyester, the spiropyran monomeric units are joined/linked together or to another structural unit (which may be the same or a different structural unit) via ester linkages.

- 5 In various embodiments, the thermophotochromic polymer comprises one or more spiropyran unit(s)/group(s) or derivative(s) thereof per structural/repeating unit of the polymer. In some embodiments, the number of spiropyran units per structural/repeating unit of the polymer chain is one only. In some embodiments, the polymer comprises more than one spiropyran
10 units/groups or derivatives thereof per structural/repeating unit of the polymer. For example, there may be 2, 3, 4, 5, 6, 7, 8, 9 or 10 spiropyran units per structural/repeating unit of the polymer chain.

- In various embodiments, the thermophotochromic polymer comprises one
15 or more (or a plurality, or at least two) structural unit/repeating unit represented by Formula I:



Formula I

wherein

- 20 X comprises linear aliphatic, branched aliphatic, cyclic, aromatic hydrocarbons and combinations thereof that is/are linked to the adjacent O of Formula I via at least one of carbamate/urethane linkage(s), ester linkage(s) and combinations thereof;
one or more of the C atoms in the linear aliphatic, branched aliphatic, cyclic,
25 aromatic hydrocarbons and combinations thereof is/are optionally replaced by $-O-$, $-C(=O)-$, $-C(=O)-O-$, $-O-C(=O)-$, $-NR^b-C(=O)-$ and/or $-C(=O)-NR^b-$;

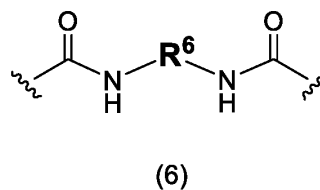
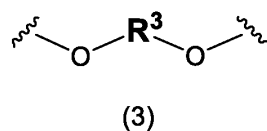
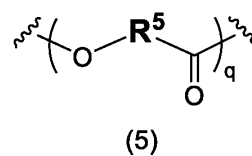
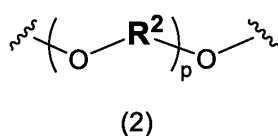
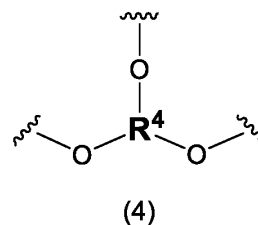
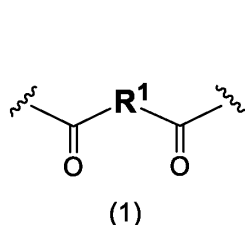
R^a and R^b are each independently selected from H, optionally substituted alkyl, optionally substituted alkenyl or optionally substituted alkynyl.

In various embodiments, X comprises or is part of the carbamate/urethane
5 linkage(s), ester linkage(s) and combinations thereof.

In various embodiments, R^a and R^b are each independently selected from the group consisting of H, optionally substituted C₁-C₂₀ alkyl, optionally substituted C₁-C₂₀ alkenyl and optionally substituted C₁-C₂₀ alkynyl. In various
10 embodiments, R^a and R^b are each independently selected from the group consisting of H and C₁-C₂₀ alkyl substituents. The C₁-C₂₀ alkyl substituents may be straight or branched substituents selected from methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl,
15 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl,
20 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl and the like and combinations thereof.

In various embodiments, when two or more of the the structural/repeating units represented by Formula I are present in the polymer, each of these
25 structural/repeating units may have the same or different types of X.

In various embodiments, X comprises one or more of the following general formula (1), (2), (3), (4), (5) and (6):



wherein

- 5 R¹, R², R³, R⁴, R⁵ and R⁶ are each independently selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkylcycloalkyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted aryl, optionally substituted alkylaryl, optionally substituted heteroaryl, optionally substituted alkylheteroaryl
 10 and combinations thereof;
 p ≥ 1; and q ≥ 1.

In various embodiments, X comprises at least 1, at least 2, at least 3, at least 4, at least 5, at least 6, at least 7, at least 8, at least 9, at least 10, at least 15, at least 20, at least 25, at least 30, at least 35, at least 40, at least 45 or at
 15 least 50 of the general formula (1), (2), (3), (4), (5) and/or (6). In various embodiments, each general formula (1), (2), (3), (4), (5) and/or (6) is linked to another general formula (1), (2), (3), (4), (5) and/or (6) *via* at least one of

carbamate/urethane linkage(s), ester linkage(s) and combinations thereof. For example, general formula (1) may be linked to general formula (2), (3) and/or (4) via ester linkage(s). General formula (5) may be linked to general formula (2), (3) and/or (4) via ester linkage(s). General formula (6) may be linked to general
5 formula (2), (3), (4) and/or (5) via carbamate/urethane linkage(s).

In various embodiments, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently selected from optionally substituted C_1 - C_{20} alkyl, optionally substituted C_1 - C_{20} alkenyl, optionally substituted C_1 - C_{20} alkynyl, optionally substituted C_1 - C_{20}
10 alkylcycloalkyl, optionally substituted C_1 - C_{20} cycloalkyl, optionally substituted C_1 - C_{20} cycloalkenyl, optionally substituted C_1 - C_{20} aryl, optionally substituted C_1 - C_{20} alkylaryl, optionally substituted C_1 - C_{20} heteroaryl, optionally substituted C_1 - C_{20} alkylheteroaryl and combinations thereof.

In various embodiments, R^1 , R^2 , R^3 , R^4 and R^5 are each independently selected from optionally substituted C_1 - C_{20} alkyl. The C_1 - C_{20} alkyl substituents may be straight or branched substituents selected from methyl, ethyl, n-propyl, 2-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, hexyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-
20 methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl,
25 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl and the like and combinations thereof. For example, R^1 , R^2 , R^3 , R^4 and R^5 may be each independently selected from the group consisting of $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$ and $CH_3CH_2C(CH_2)_3-$.

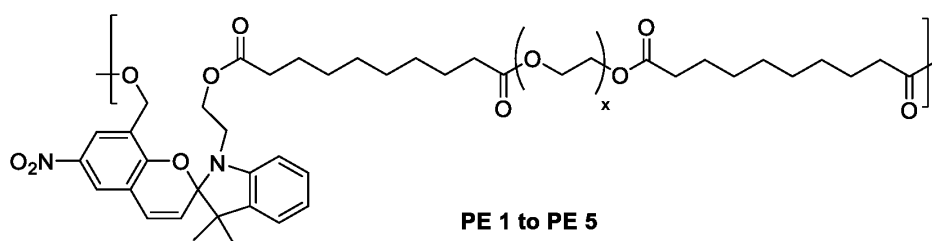
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In various embodiments, R^6 comprises an optionally substituted cycloalkyl ring. R^6 may comprise an optionally substituted cyclopentane, optionally

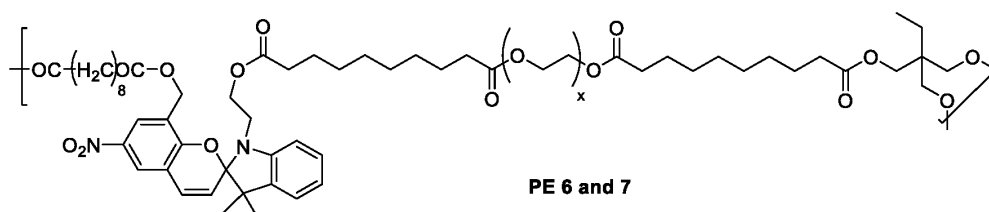
substituted cyclopentene or optionally substituted cyclohexane. In various embodiments, R^6 comprises an optionally substituted C_1 - C_{20} alkylcycloalkyl. For example, R^6 may be $-CH_2-C_6H_7-(CH_3)_3-$.

5 In various embodiments, $p \geq 1$. For example, p may be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, or 50. In various embodiments, $q \geq 1$. For example, q is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, or 50.

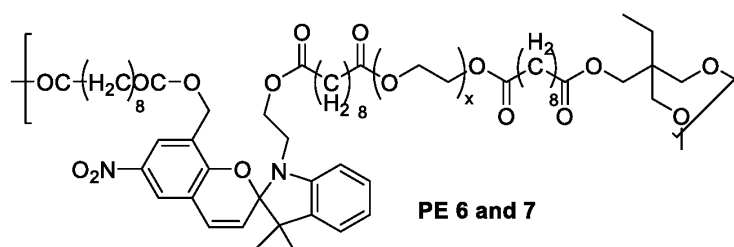
10 In various embodiments, the polymer comprises one or more (or a plurality, or at least two) structural unit/repeating unit selected from the following:



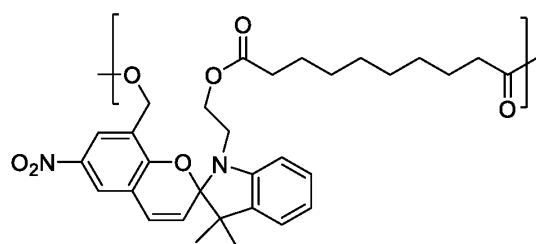
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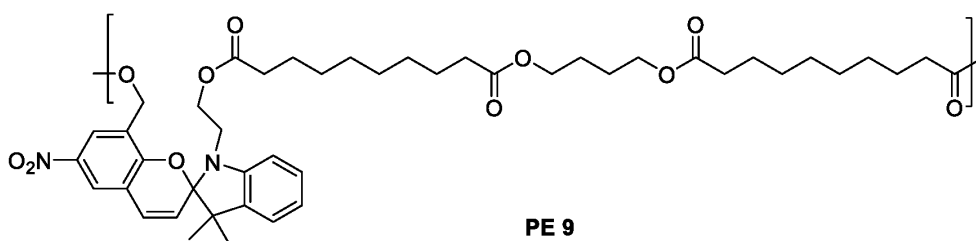
Or



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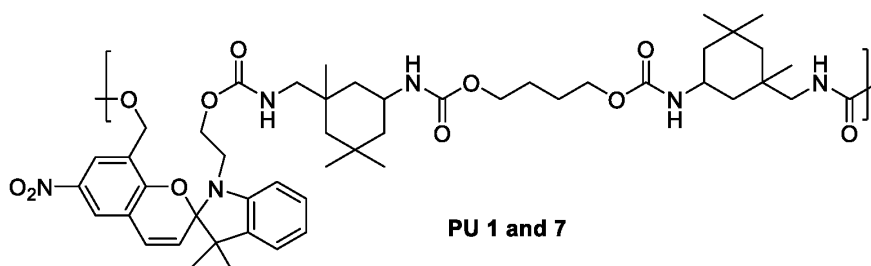


PE 8

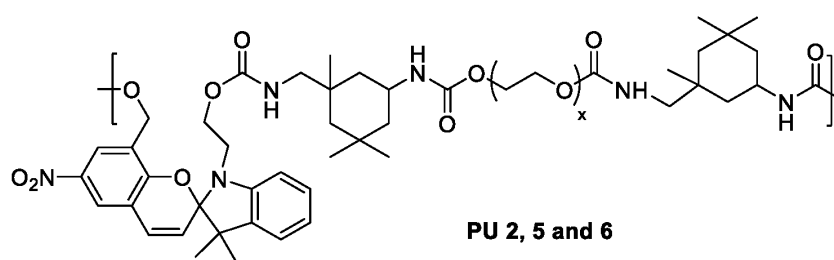


PE 9

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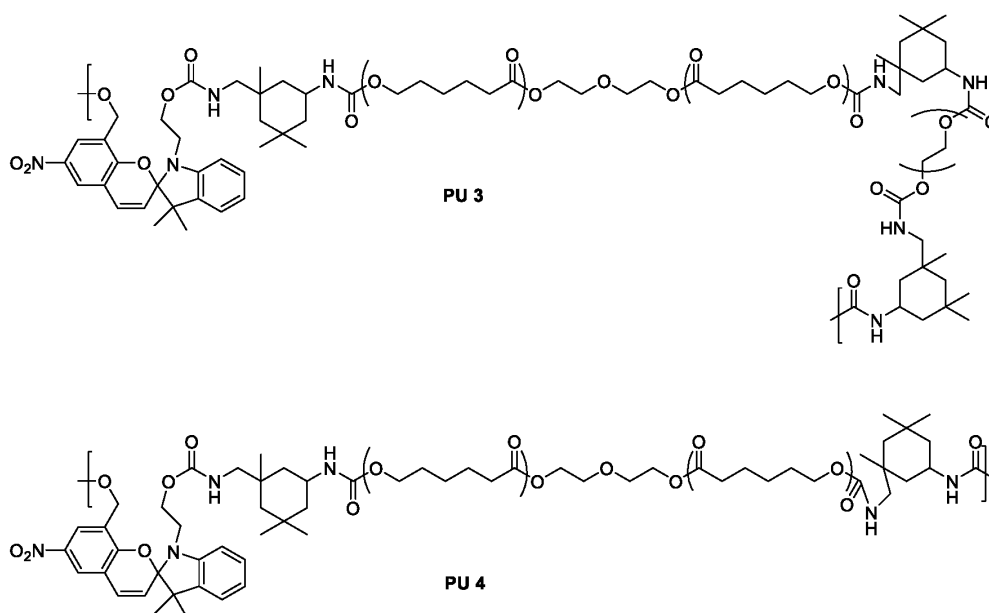


PU 1 and 7



PU 2, 5 and 6

39



5 In various embodiments, x is from 2 to 50. For example, x may be 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45 or 50. In various embodiments, x represents the repeating unit of polyethylene glycol. In various embodiments, x is 32 for PEG 2000. In various embodiments, x is from 2 (for diethylene glycol having MW 106) to 50.

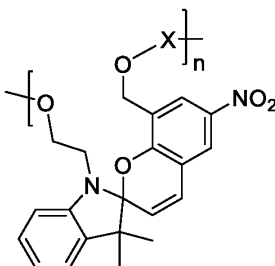
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In various embodiments, the structural unit/repeating unit comprises at least one electron donating group (e.g. an electron donating group such as a oxymethylene unit attached to an aromatic ring) and at least one electron withdrawing group (e.g. an electron withdrawing group such as nitro group attached to the same aromatic ring).

15

20

In various embodiments, wherein the polymer comprises two or more repeating units represented by Formula IA:



Formula IA

5

In various embodiments, $n \geq 2$. For example, n may be 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 2,000, 5,000, 10,000 or 20,000.

10 In various embodiments, the absorbance of the polymer is indicative of the content of spiropyran in the polymer. In various embodiments, the absorbance of the polymer increases with increasing content of spiropyran.

15 In various embodiments, the Z-average size of thermophotochromic polymer particles in the aqueous solution is in the range of from about 10 nm to about 10,000 nm, from about 20 nm to about 9,000 nm, from about 30 nm to about 8,000 nm, from about 40 nm to about 7,000 nm, from about 50 nm to about 6,000 nm, from about 60 nm to about 5,000 nm, from about 70 nm to about 4,000 nm, from about 80 nm to about 3,000 nm, from about 90 nm to about 2,000 nm, 20 from about 100 nm to about 1,000 nm, from about 200 nm to about 900 nm, from about 300 nm to about 800 nm, from about 400 nm to about 700 nm, or from about 500 nm to about 600 nm.

25 In various embodiments, the thermophotochromic polymer has a number average molecular weight (M_n) from about 500 to about 100,000, from about 1,000 to about 90,000, from about 1,500 to about 80,000, from about 2,000 to

about 70,000, from about 2,500 to about 60,000, from about 3,000 to about 50,000, from about 3,500 to about 40,000, from about 4,000 to about 30,000, from about 4,500 to about 20,000, from about 5,000 to about 10,000, from about 5,500 to about 9,500, from about 6,000 to about 9,000, from about 6,500 to about 8,500, from about 7,000 to about 8,000, or about 7,500.

In various embodiments, the thermophotochromic polymer has a weight average molecular weight (M_w) from about 500 to about 100,000, from about 1,000 to about 90,000, from about 1,500 to about 80,000, from about 2,000 to about 70,000, from about 2,500 to about 60,000, from about 3,000 to about 50,000, from about 3,500 to about 40,000, from about 4,000 to about 30,000, from about 4,500 to about 20,000, from about 5,000 to about 10,000, from about 5,500 to about 9,500, from about 6,000 to about 9,000, from about 6,500 to about 8,500, from about 7,000 to about 8,000, or about 7,500.

15

In various embodiments, the thermophotochromic polymer has a polydispersity index (PDI) of from about 1.0 to about 10.0, from about 1.05 to about 9.0, from about 1.10 to about 8.0, from about 1.15 to about 7.0, from about 1.20 to about 6.0, from about 1.25 to about 5.5, from about 1.30 to about 5.0, from about 1.35 to about 4.5, from about 1.40 to about 4.0, from about 1.45 to about 3.5, from about 1.50 to about 3.0, from about 1.55 to about 2.95, from about 1.60 to about 2.90, from about 1.65 to about 2.85, from about 1.70 to about 2.80, from about 1.75 to about 2.75, from about 1.80 to about 2.70, from about 1.85 to about 2.65, from about 1.90 to about 2.60, from about 1.95 to about 2.55, from about 2.00 to about 2.50, from about 2.05 to about 2.45, from about 2.10 to about 2.40, 2.15 to about 2.35, from about 2.20 to about 2.30, or about 2.25. As may be appreciated, although theoretically, step growth polymers show a PDI of 2, the actual PDI of the polymer could be higher or lower than 2 in practice due to various experimental reasons/factors.

30

In various embodiments, the thermophotochromic polymer is a reaction product between one or more spiropyran diol and one or more compounds selected from the group consisting of dicarboxylic acids, dicarboxylic acid derivatives (for e.g., diacid chlorides), diisocyanates, diisocyanate derivatives, isocyanate derivatives, multifunctional carboxylic acids such as trifunctional carboxylic acids, polyfunctional carboxylic acids, monofunctional and multifunctional carboxylic acid derivatives such as difunctional carboxylic acid derivatives (for e.g., difunctional acid chlorides), trifunctional carboxylic acid derivatives (for e.g., trifunctional acid chlorides), polyfunctional carboxylic acid derivatives (for e.g., polyfunctional acid chlorides), multifunctional isocyanates and multifunctional isocyanate derivatives, and optionally with one or more alcohols selected from dihydroxy (or diols), trihydroxy (or triols) and polyhydroxy (or polyols).

There is also provided a method of preparing the thermophotochromic polymer, the method comprising: mixing/reacting one or more spiropyran diol with one or more compounds selected from the group consisting of dicarboxylic acids, dicarboxylic acid derivatives (for e.g., diacid chlorides), diisocyanates, diisocyanate derivatives, isocyanate derivatives, multifunctional carboxylic acids such as trifunctional carboxylic acids, polyfunctional carboxylic acids, monofunctional and multifunctional carboxylic acid derivatives such as difunctional carboxylic acid derivatives (for e.g., difunctional acid chlorides), trifunctional carboxylic acid derivatives (for e.g., trifunctional acid chlorides), polyfunctional carboxylic acid derivatives (for e.g., polyfunctional acid chlorides), multifunctional isocyanates and multifunctional isocyanate derivatives, and optionally with one or more alcohols selected from dihydroxy (or diols), trihydroxy (or triols) and polyhydroxy (or polyols).

In various embodiments, the multifunctional compounds have functionality greater than two, for e.g., containing two or more different types of functional groups. The multifunctional compounds may contain two or more, three or more,

four or more, five or more, six or more, seven or more, eight or more, nine or more, or ten or more different types of functional groups.

In various embodiments, the method uses spiropyran diol as a monomer/comonomer. Advantageously, the method is a straightforward reaction and does not require tedious multi-step synthesis procedures in order to prepare a starting monomer. Even more advantageously, the presently disclosed method of preparing the thermophotochromic polymer presents more versatility and advantages than conventional methods (e.g., methods that use spiropyran diol as an initiator). By using spiropyran diol as a monomer/comonomer in the method disclosed herein, the number of spiropyran units present in the backbone of the polymer chain can be designed/alterd as desired.

Advantageously, the method disclosed herein also allow customization of the thermophotochromic polymer with the desired functionality, property and/or characteristics. For example, diisocyanates may be added to the reaction mixture for inducing/introducing urethane/carbamate functionality. Diacid chlorides may be added to the reaction mixture for inducing/introducing ester functionality. Alcohols may be added for inducing/introducing new characteristics to the polymer.

In various embodiments, the spiropyran diol is mixed/reacted with compounds selected from the group consisting of dicarboxylic acids, dicarboxylic acid derivatives (for e.g., diacid chlorides), diisocyanates, diisocyanate derivatives, isocyanate derivatives, multifunctional carboxylic acids such as trifunctional carboxylic acids, polyfunctional carboxylic acids, monofunctional and multifunctional carboxylic acid derivatives such as difunctional carboxylic acid derivatives (for e.g., difunctional acid chlorides), trifunctional carboxylic acid derivatives (for e.g., trifunctional acid chlorides), polyfunctional carboxylic acid derivatives (for e.g., polyfunctional acid chlorides), multifunctional isocyanates and multifunctional isocyanate derivatives in a molar ratio of from about 1:1 to

about 1:30, from about 1:2 to about 1:29, from about 1:3 to about 1:28, from about 1:4 to about 1:27, from about 1:5 to about 1:26, from about 1:6 to about 1:25, from about 1:7 to about 1:24, from about 1:8 to about 1:23, from about 1:9 to about 1:22, from about 1:10 to about 1:21, from about 1:11 to about 1:20, from about 1:12 to about 1:19, from about 1:13 to about 1:18, from about 1:14 to about 1:17, or from about 1:15 to about 1:16.

In various embodiments, the spiropyran diol may be mixed/reacted with alcohols in a molar ratio of from about 1:0 to about 1:30, from about 1:1 to about 1:30, from about 1:2 to about 1:29, from about 1:3 to about 1:28, from about 1:4 to about 1:27, from about 1:5 to about 1:26, from about 1:6 to about 1:25, from about 1:7 to about 1:24, from about 1:8 to about 1:23, from about 1:9 to about 1:22, from about 1:10 to about 1:21, from about 1:11 to about 1:20, from about 1:12 to about 1:19, from about 1:13 to about 1:18, from about 1:14 to about 1:17, or from about 1:15 to about 1:16.

In various embodiments where the polymer comprises a polyurethane polymer, the method comprises mixing/reacting one or more spiropyran diol with (i) one or more diisocyanates and (ii) optionally one or more alcohols selected from dihydroxy (or diols), trihydroxy (or triols) and polyhydroxy (or polyols).

In various embodiments where the polymer comprises a polyester polymer, the method comprises mixing/reacting one or more spiropyran diol with (i) one or more dicarboxylic acids or dicarboxylic acid derivatives (for e.g., diacid chlorides) and (ii) optionally with one or more alcohols selected from dihydroxy (or diols), trihydroxy (or triols) and polyhydroxy (or polyols).

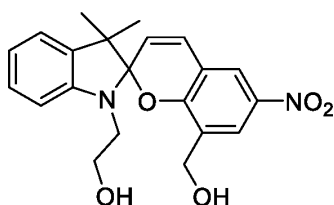
In various embodiments, the addition of alcohols (e.g., diols) impart characteristics such as water solubility, lighten colour of polymer and increase molecular weight of the polymer. The addition of diols may impart water solubility to the polymer PEG. The addition of diols may also help to make the polymer

lighter in colour. Otherwise, the polymer formed by using spiropyran diol alone may be darker in colour. The molecular weight of the polymer may also be higher in the presence of additional diol. It will be appreciated that in various embodiments, the addition of alcohols (e.g., diols) may be optional and not
5 necessary for the preparation of the polyester or polyurethane as the polymerization may proceed with spiropyran diol and diacid chloride or diisocyanate.

In various embodiments where the polymer comprises a polyester polymer
10 and a polyurethane polymer, the method comprises mixing/reacting one or more spiropyran diol with (i) one or more dicarboxylic acids or dicarboxylic acid derivatives (for e.g., diacid chlorides), (ii) one or more diisocyanates and (iii) optionally with one or more alcohols selected from dihydroxy (or diols), trihydroxy (or triols) and polyhydroxy (or polyols).

15

In various embodiments, the spiropyran diol is represented by Formula II:



Formula II

In various embodiments, the one or more alcohols is/are selected from the
20 group consisting of C₂ to C₁₀ diols, oligomeric and polymeric ethylene and propylene glycols of molecular weight of from about 100 to about 10,000, from about 100 to about 5,000 or from about 100 to about 2,000. In various embodiments, C₂ to C₁₀ diols are compounds having two hydroxyl groups such
25 as ethylene glycol, propanediol, butanediol, pentanediol, hexanediol, heptanediol, octanediol, nonanediol and decanediol.

In various embodiments, the one or more diisocyanates is/are selected from the group consisting of hexamethylene diisocyanate, tetramethylene diisocyanate, cyclohexane diisocyanate, tetramethylxylene diisocyanate, dodecylene diisocyanate, tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, 5 isophorone diisocyanate, their derivatives thereof and the like and combinations thereof.

In various embodiments, the one or more diacid chlorides is/are selected from the group consisting of ethanedioyl dichloride (or oxalyl chloride), 10 propanedioyl dichloride (or malonyl chloride), butanedioyl dichloride (or succinyl chloride), pentanedioyl dichloride (or glutaryl chloride), hexanedioyl dichloride (or adipoyl chloride), heptanedioyl dichloride (or pimeloyl chloride), octanedioyl dichloride (or suberoyl chloride), nonanedioyl dichloride (azalaoyl chloride), decanedioyl dichloride (or sebacoyl chloride), undecanedioyl chloride, 15 dodecanedioyl acid, isophthaloyl chloride, terephthaloyl chloride, trimesyl chloride, the like, derivatives thereof and combinations thereof. In various embodiments, the diacid chloride further comprises one or more chemical moiety or a functional group selected from the group consisting of alcohol, alkoxy, alkanoyloxy, alkoxycarbonyl, alkenyl, alkyl (e.g., methyl, ethyl, propyl, t-butyl), 20 alkynyl, alkylcarbonyloxy ($-\text{OC}(\text{O})\text{alkyl}$), amide ($-\text{C}(\text{O})\text{NH-alkyl-}$ or $-\text{alkylNHC}(\text{O})\text{alkyl}$), tertiary amine (such as alkylamino, arylamino, arylalkylamino), aryl, aryloxy, azo, carbamoyl ($-\text{NHC}(\text{O})\text{O-alkyl-}$ or $-\text{OC}(\text{O})\text{NH-alkyl}$), carbamyl (e.g., CONH_2 , as well as CONH-alkyl , CONH-aryl , and CONH-arylalkyl), carboxyl, carboxylic acid, carboxylic acid salt (e.g., $-\text{COO}^-\text{Na}^+$), cyano, 25 ester, ether (e.g., methoxy, ethoxy), halo, haloalkyl (e.g., $-\text{CCl}_3$, $-\text{CF}_3$, $-\text{C}(\text{CF}_3)_3$), heteroalkyl, isocyanate, isothiocyanate, nitrile, nitro, phosphodiester, sulfide, sulfonamido (e.g., SO_2NH_2), sulfone, sulfonyl (including alkylsulfonyl, arylsulfonyl and arylalkylsulfonyl), sulfoxide, thiol (e.g., sulfhydryl, thioether) and urea ($-\text{NHCONH-alkyl-}$). In various embodiments, one or more hydrogen and/or 30 carbon atoms in the diacid chlorides are optionally substituted with a chemical moiety or functional group. For example, one or more hydrogen atoms attached

to a ring (e.g., benzene or aromatic ring) in the diacid chloride may be substituted with functional group such as nitro or azo. In various embodiments, the diacid chloride comprise nitro and/or azo groups. The diacid chlorides may be substituted isophthaloyl chlorides (e.g., isophthaloyl chlorides comprising nitro
5 substituent(s)), terephthaloyl chlorides (e.g., isophthaloyl chlorides comprising nitro substituent(s)) or aromatic diacid chlorides possessing azo group(s).

In various embodiments, the acid chloride is monofunctional, difunctional, trifunctional or polyfunctional. Monofunctional acid chlorides may be used for the
10 purpose of terminating the polymer chain.

In various embodiments, the one or more dicarboxylic acids is/are selected from the group consisting of ethanedioic acid (or oxalic acid), propanedioic acid (or malonic acid), butanedioic acid (or succinic acid), pentanedioic acid (or
15 glutaric acid), hexanedioic acid (or adipic acid), heptanedioic acid (or pimelic acid), octanedioic acid (or suberic acid), nonanedioic acid (azelaic acid), decanedioic acid (or sebacic acid), undecanedioic acid, dodecanedioic acid, aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, 2-(2-carboxyphenyl)benzoic acid, and 2,6-naphthalenedicarboxylic acid
20 and the like and combinations thereof.

In various embodiments, the one or more trifunctional carboxylic acids or tricarboxylic acids is/are selected from the group consisting of citric acid, isocitric acid, aconitic acid, propane-1,2,3,-tricarboxylic acid, agaric acid, trimesic acid
25 (benzene-1,3,5-tricarboxylic acid), trimellitic acid (benzene-1,2,4-tricarboxylic acid), hemimellitic acid (benzene-1,2,3-tricarboxylic acid) and the like and combinations thereof.

In various embodiments, the mixing/reacting step is optionally carried out
30 in the presence of a catalyst such as a base and/or a metal catalyst. The base

may be an inorganic base (e.g., potassium carbonate) or an organic base (e.g., base comprising amines). In various embodiments, the catalyst is a base comprising tertiary amines and/or a metal catalyst comprising a tin catalyst selected from the group consisting of alkyltin compounds, aryltin compounds and
5 dialkyltin diesters such as dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dioctanoate and dibutyltin distearate.

In various embodiments, the mixing/reacting step is optionally carried out in the presence of a base such as tertiary amines that are free of labile hydrogen
10 atoms as represented in the form of hydroxyl group and R_2NH (for e.g. trimethylamine, triethylamine, tripropylamine, tributylamine, pyridine, 4-N,N-dimethylaminopyridine, N-substituted piperidine and the like and combinations thereof). A base may be added to neutralise the reaction mixture. In various embodiments, the role of the base is to activate the diol (e.g., spiropyran diol)
15 and/or quench the acidic byproduct that is formed.

In various embodiments, the mixing/reacting step is carried out in the presence of an organic solvent that is free of labile protons such as tetrahydrofuran (THF), dichloromethane (DCM), chloroform, dimethylformamide
20 (DMF), acetone, acetonitrile (ACN), dimethyl sulfoxide (DMSO), propylene carbonate (PC), dimethylcarbonate (DMC), dioxane, dioxolane, diglyme, methyl ethyl ketone (MEK), dimethylacetamide (DMAc), N-Methyl-2-pyrrolidone (NMP) and the like and combinations thereof.

25 In various embodiments, the mixing/reacting step is carried out or undertaken at a temperature of from about 0°C to about 100°C, from about 5°C to about 95°C, from about 10°C to about 90°C, from about 15°C to about 85°C, from about 20°C to about 80°C, from about 25°C to about 75°C, from about 30°C to about 70°C, from about 35°C to about 65°C, from about 40°C to about 60°C,
30 from about 45°C to about 55°C, or about 50°C.

In various embodiments, the mixing/reacting step is carried out or undertaken for a time period of from about 30 mins to about 5 days. The mixing step may be carried out for about 30 mins, about 35 mins, about 40 mins, about 45 mins, about 50 mins, about 55 mins, about 60 mins, about 65 mins, about 70 mins, about 75 mins, about 80 mins, about 85 mins, about 90 mins, about 100 mins, about 120 mins, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 20 hours, about 24 hours, about 48 hours, about 72 hours, about 96 hours, or about 120 hours.

10

In various embodiments, the polymer is a polymer produced via condensation polymerization, that is, the reacting moieties condense to remove some moieties during polymerization. Advantageously, the method is designed such that embodiments of the method are substantially devoid of ring opening metathesis polymerisation (ROMP) which would otherwise yield dark colored polymers that may impair with the colored to colorless transitions accompanying the exposure to UV and visible lights. In various embodiments therefore, the thermophotochromic polymer disclosed herein is different/distinguished from conventional mechanochromic/ photochromic materials (e.g., conventional mechanochromic/photochromic polymers comprising polycaprolactone that is formed by polymerising caprolactone and using spiropyrandiol as initiator) at least in their polymerisation method and/or polymerisation reaction mechanism. For example, the thermophotochromic polymer disclosed herein is not a polymer produced via ring opening polymerization. In various embodiments therefore, the thermophotochromic polymer is a step-growth polymer or a polymer produced *via* step-growth polymerization or condensation polymerization. In various embodiments, the polymer is not a chain-growth polymer or a polymer produced *via* chain-growth polymerization.

30

In various embodiments, the method of preparing the thermophotochromic polymer disclosed herein is substantially devoid of a ring opening reaction (e.g.,

ring opening polymerisation) while the method of preparing conventional mechanochromic/photochromic materials (e.g., conventional mechanochromic/photochromic polymers comprising polycaprolactone) is substantially devoid of a condensation polymerisation. In some embodiments, although, technically, polycaprolactone may also be thought of as a condensation polymer since
5 theoretically it may be formed by the reaction of hydroxy acid through the elimination of water, it will be appreciated that ring opening polymerization is the method employed exclusively for making polycaprolactone.

10 In various embodiments, the method is substantially devoid of a step containing the use of Grubb's catalyst (which is required in ring opening metathesis polymerisation (ROMP)). In various embodiments, the method of preparing the polymer is carried out in the absence of a Grubb's catalyst.

15 In various embodiments, the method of preparing the polymer is substantially devoid of cyclization reaction which would otherwise require highly dilute conditions and therefore, large quantities of solvents. It will be appreciated that in methods that use cyclization reaction, chromatographic separations are required to purify the starting cyclic compound which further adds to the
20 complication.

In various embodiments, the method of preparing the polymer is substantially devoid of the use of cyclic unsaturated compounds that contain multiple ether linkages. It will be appreciated that presence of multiple ether
25 linkages in cyclic unsaturated compound may interfere with the catalyst, thus reducing its activity.

In various embodiments, the polymer is not or does not comprise an acidic phase change material. In various embodiments, the spiropyran moiety
30 exists either as a backbone or pendant group of the polymer. In various embodiments, the spiropyran moiety is not or does not exist separately as part of

a heterogenous mixture. In various embodiments, the thermal effect of the polymer is direct and not indirect e.g. does not require melting of an acid phase change material to release the photochromic compound/moiety.

5 BRIEF DESCRIPTION OF FIGURES

FIG. 1 is a schematic diagram 100 showing polymers designed in accordance with various embodiments disclosed herein exhibiting thermophotochromism. The figure shows images of aqueous solution (0.1 wt%) of spiropyran polymer PE 2, which exhibits a reversible transition between a light coloured state and a dark coloured state. The colour change was most pronounced at steps 104 and 106. At step 104, irradiating a red-violet solution 112 with visible light/sunlight changed the colour of the aqueous solution from red-violet 112 to brick beige 114. At step 106, exposing the brick beige solution 114 to heat (e.g., to a temperature of about 50°C) caused the brick beige solution 114 to revert to red-violet solution 112. Cooling the red-violet solution 112 to ambient temperature at step 108 changed the colour from red-violet to orange pink 110, while heating the orange pink solution 110 caused the orange pink solution 110 to revert to red-violet solution 112.

20

FIG. 2 shows UV-visible (UV-Vis) absorption spectra of 0.1 wt% aqueous solution of spiropyran polymer PE 5 after irradiated with UV light and white light. The arrow on the right points to UV-Vis spectra obtained after exposing the 0.1 wt% of aqueous solution of spiropyran polymer PE 5 to UV light. The image on the right of the spectra shown as a purple solution belongs to 0.1 wt% aqueous solution of spiropyran polymer PE 5 after irradiated with UV light. The arrow on the left points to UV-Vis spectra obtained after exposing the 0.1 wt% of aqueous solution of spiropyran polymer PE 5 to visible light. The image on the left of the spectra shown as a colourless solution belongs to 0.1 wt% aqueous solution of spiropyran polymer PE 5 after irradiated with white light.

30

FIG. 3 are images of 0.1 wt% aqueous solution of spiropyran polymer PE 5 showing thermophotochromic response under ambient conditions, upon heating and exposure to sunlight. The images are captured under ambient conditions, upon heating to 50°C for 10 minutes, upon heating to 50°C for 20 minutes, upon heating to 50°C for 30 minutes and upon exposure to sunlight. The colour of the initial solution at ambient temperature is pale pink. Upon heating to 50°C, the solution turned dark purple and maintained at the same colour intensity after heating for 10, 20 and 30 minutes. Upon exposure to sunlight, the dark purple solution rapidly turned colourless within a minute of exposure.

10

FIG. 4 is an absorbance (Abs) versus time graph showing the stability of thermophotochromic response of 0.1 wt% aqueous solutions of spiropyran polymer PE 5 over time, i.e. respectively after 1 week (●), after 2 weeks (■) and after 3 weeks (▲) (Note: Absorbance was recorded at various time intervals upon heating the sample at 50°C. The drop in absorbance at extreme right is upon exposure to sunlight).

15

FIG. 5 is a graph showing the changes in absorbance of 0.1 wt% aqueous solutions of spiropyran polymer PE 5 over time, i.e. respectively after 1 week, after 2 weeks, after 4 weeks and after 14 weeks.

20

FIG. 6 is a graph showing the changes in absorbance of 0.2 wt% aqueous solution of thermophotochromic polymer PU 2 upon exposure to UV and Vis radiations. The figure shows images of aqueous solution of PU 2, which exhibits reversible transitions between a light coloured state and a dark coloured state. The colour of the initial solution (i.e. as prepared) is very light orange. Upon exposure to UV radiation (with a wavelength of about 365 nm), there is a change in the colour from light orange to reddish brown. Exposing the reddish brown solution to visible light turned the reddish brown solution into a light orange solution.

25

30

FIG. 7 shows UV-visible (UV-Vis) absorption spectra of 0.2 wt% aqueous solution of thermophotochromic polymer PU 2 after irradiating with UV light/radiation (top) and visible light/radiation (bottom).

5 FIG. 8 shows images of glass slides coated with thermophotochromic polymer PE 9 (i.e. in solid state) that were induced by (i) light emitting diode based visible light and (ii) sunlight passing through the window. The colour changes were compared and as shown, the extent of color change is marginally greater when light emitting diode based visible light was used. The initial glass slides
10 were purple-brown in colour. After 2 hours of exposure to sunlight, the colour of the glass slide turned from purple-brown to pale brownish yellow. However, after 2 hours of exposure to light emitting diode based visible light, the colour of the glass slide turned from purple-brown to light yellow.

15 FIG. 9 shows images of glass slides coated with thermophotochromic polymer PU 4 (i.e. in solid state) that were exposed to (i) UV radiation having a wavelength of about 365 nm and then followed by (ii) white light/visible light radiation. The initial glass slides were pale brownish yellow in colour. After 15 minutes of exposure to 365 nm UV radiation, the colour of the glass slide turned
20 from pale brownish yellow to deep purple-brown. Exposing the deep purple-brown glass slide to 15 minutes of white light/visible light radiation converted the colour of the glass slide from deep purple-brown back to pale brownish yellow.

 FIG. 10 shows images of hydrogels of thermophotochromic polymer PE 7
25 (i.e. in gel form). The hydrogels were placed in direct sunlight passing through the window (step 1002). It was observed that the hydrogels repeatedly changed colour between reddish brown and pale yellow following day (1002) and night (1004) cycles, thereby showing reversible thermophotochromism.

EXAMPLES

Example embodiments of the disclosure will be better understood and readily apparent to one of ordinary skill in the art from the following examples, tables and if applicable, in conjunction with the figures. It should be appreciated that other modifications related to structural, and chemical changes may be made without deviating from the scope of the invention. Example embodiments are not necessarily mutually exclusive as some may be combined with one or more embodiments to form new example embodiments. The example embodiments should not be construed as limiting the scope of the disclosure.

Example 1: Thermophotochromism of Polymers in Aqueous Solutions

FIG. 1 is a schematic diagram 100 showing polymers designed in accordance with various embodiments disclosed herein exhibiting thermophotochromism.

In this example, thermophotochromism was observed in 0.1 wt % of aqueous solution of spiropyran polymer PE 2 as shown in FIG. 1. As can be noticed in FIG. 1, even at room/ambient temperature, the polymer retained some of the ring opened merocyanine form (shown as orange pink solution 110 in FIG. 1). The effect of sunlight was more pronounced to cause ring closure of the polymer (shown as a brick beige solution 114 in FIG. 1).

The UV-Vis absorption spectra of 0.1 wt% aqueous solution of spiropyran polymers PE 5 after irradiating with UV light and white light is shown in FIG. 2. After irradiating with UV light, a coloured solution (i.e. purple solution) was obtained. After irradiating with white light, a colourless solution was obtained.

FIG. 3 shows the change in color occurring in 0.1 wt% aqueous solutions of spiropyran polymers PE 5 upon heating to 50°C due to merocyanine formation and the reversion to ring closed spiropyran form upon exposure to sunlight. The

change in color upon exposure to sunlight was rapid and happened within a minute of exposure.

Table 1. Absorbance of spiropyran polymers PE 1, PE 2 and PE 3

Polymer	Spiropyran content (molar ratio between BHSP and PEG 2000) %	Concentration of aqueous solution, wt%	Absorbance (as obtained from x-axis of UV-Vis spectra) (arbitrary units)
PE 1	11.5	0.4	0.326
PE 2	25	0.4	0.839
PE 3	35	0.2	1.781

5

As shown in Table 1, the absorbance of the polymer is indicative of the content of spiropyran in the polymer. In various embodiments, the absorbance of the polymer increases with increasing content of spiropyran. The absorbance may also increase with increasing concentration of the solution. However, it will be appreciated that with increased spiropyran content, it is possible to achieve higher absorbance at lower concentration of solutions.

10

Example 2: Stability of Polymers in Aqueous Solutions

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FIG. 4 shows the storage stability of 0.1 wt% aqueous solution of spiropyran polymer PE 5. The absorbance characteristics were retained even after 3 weeks of storing under ambient conditions, unlike aqueous solutions of conventional spiropyran polymers reported in the art where the loss of absorbance due to hydrolysis was nearly instantaneous. Without being bound by theory, it is believed that the increased absorbance after the first week noticed in FIG. 4 is most likely due to the aggregation of chromophore in water.

20

FIG. 5 is a graph showing the changes in the absorbance of 0.1 wt% aqueous solution of spiropyran polymer PE 5 with time, i.e. respectively after 1

week, after 2 weeks, after 4 weeks and after 14 weeks. The aqueous solution of thermophotochromic polymers designed in accordance with various embodiments disclosed herein (FIG. 5) retained 50% of absorbance even after 14 weeks. Advantageously, embodiments of the thermophotochromic polymers display higher stability than comparative photochromic compounds such as aqueous bile salt solutions which are noted to decompose slowly due to hydrolysis. Decomposition of such bile salt solutions may be observed by appearance of a shoulder around 400 nm in their absorption spectra. In some comparative bile salt aggregate examples (e.g., reference is made to Figure S9 of R. Li, et al., *Chem. Commun.*, 2010, 46, 1941–1943), a complete loss of absorbance can even be observed in merely about 8 days. Advantageously, embodiments of the polymer disclosed herein possess (i) flexibility in terms of adjusting the concentration of chromophore in the polymer; and (ii) water solubility induced by copolymer vs. the host-guest system.

15

Example 3: Photochromism of Polymers in Aqueous Solutions

The thermophotochromic polymers designed in accordance with various embodiments disclosed herein responded to UV and visible light exposures in the same way as conventional photochromic materials. For example, FIG. 6 shows the normal photochromic behavior of 0.2 wt% aqueous solution of thermophotochromic polymer PU 2. The corresponding UV-Vis spectra is shown in FIG. 7.

Example 4: Thermophotochromism of Polymers in Solid State

FIG. 8 and FIG. 9 show changes taking place in the solid state.

Glass slides were coated with thermophotochromic polymer PE 9 and exposed to (i) light emitting diode based visible light and (ii) sunlight passing through the window. As shown in FIG. 8, visible changes in color could be noticed in both cases although the extent of color change is marginally greater in light

30

emitting diode based visible light. However, considering the fact that the duration of daytime with effective sunlight can be longer and vary according to the season, appreciable changes to coated substrates can be expected under natural circumstances.

5

Complete recovery to the original state within the short exposed time can be noticed by the similarity of appearance of coated slides shown as “initial” and “15 min white light” in FIG. 9.

10 **Example 5: Surface Wettability Characteristics of Polymers in Solid State**

Additionally, static water contact angle measurements showed that changes in appearance also accompany change in water contact angle (as shown in Table 2), thereby indicating the dynamic nature of surface in the solid state. Advantageously, it is shown that surface characteristics of the thermophotochromic polymer designed in accordance with various embodiments disclosed herein can be tuned with alternating exposure between UV light and visible light.

20 Table 2. Change in contact angle of glass slides coated with PU 4

Light source	30 sec average contact angle	60 sec average contact angle
Initial (before exposure)	65.5	61.6
15 min 365 nm UV	92.9	88.1
15 min white light	82.5	77.7

Example 6: Thermophotochromism of Polymers in Gel Form (i.e. Hydrogel)

Hydrogels with swelling ratio of 200 repeatedly changed colour following the day night cycles 1002 and 1004 as shown in FIG. 10. Even after three weeks of exposure, reversibility was retained. As prepared gels were reddish brown in colour that transformed to pale yellow within minutes of exposure to direct sunlight passing through the window (step 1002). The colour intensified back to its original level after sunset, during overnight or upon removing away from sunlight and placing in a darker, poorly lit location (step 1004).

Example 7: Critical Solution Temperature (CST) Behavior

In addition to thermophotochromism, these polymers also showed critical solution temperature (CST) behavior. The observed lower critical solution temperature (LCST) varied with the polymer composition. Depending on polymer composition, polymers with LCST of 48, 61.5, 74.5, 75, 75.5 and 77°C were obtained. The change in size of 0.1 wt% aqueous solution of thermophotochromic polymer PE 4 upon heating at a rate of 0.5°C/min as studied by dynamic light scattering (DLS) technique is given in Table 3.

Table 3. Lower critical solution temperature (LCST) behavior of 0.1 wt% aqueous solution of thermophotochromic polyester PE 4

Temperature (°C)	Particle Size Z-average (nm)	PDI
70	30.74	0.362
70.5	31.39	0.373
71	31.14	0.345
71.5	31.14	0.305
72	23.5	0.3041
72.5	32.02	0.33
73	32.16	0.31
73.5	32.74	0.313
74	33.11	0.282
74.5	33.98	0.338

75	34.72	0.345
75.5	34.49	0.331
76	34.87	0.287
76.5	36.2	0.323
77	561.7	0.846
77.5	3933	0.773
78	6237	1

Example 8: Materials and Methods

9,9,9a-Trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole

5 A solution of 2,3,3-trimethyl-3*H*-indole (18.0445 g, 0.1133 mol) and 2-bromoethanol (17.6648 g, 0.1414 mol) in acetonitrile (135 mL) was heated under reflux for 48 h. After the mixture was cooled to ambient temperature, the solvent was removed in a rotavapor. The purple coloured solid was soaked in DI water. Potassium hydroxide solution (8 g, in 100 mL DI water) was added. It was stirred
10 under ambient conditions for 20 min. Then, it was extracted with diethyl ether (3x50 mL). The organic phase was dried over anhydrous MgSO₄, filtered and concentrated in a rotavapor (20 g, 87%) as a dark coloured oil: ¹H NMR (CDCl₃) δ, ppm: 7.16-7.08 (m, 2H), 6.94-6.92 (m, 1H), 6.79-6.77 (d, 1H), 3.9-3.81 (m, 1H), 3.76-3.72 (m, 1H), 3.63-3.50 (m, 2H), 1.45 (s, 3H), 1.41 (s, 3H), 1.21 (s, 3H).

15

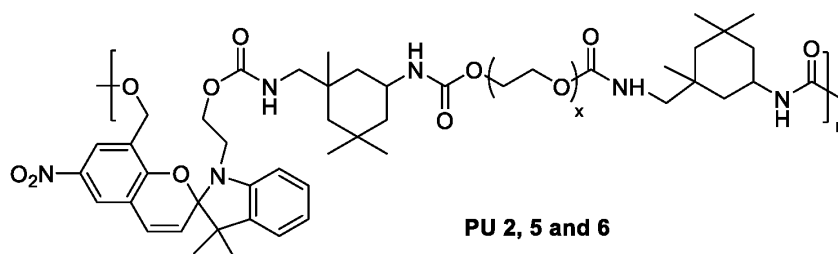
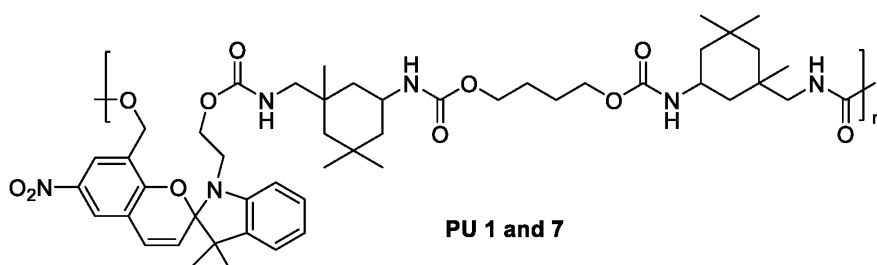
3-Hydroxymethyl-5-nitrosalicylaldehyde

3-Chloromethyl-5-nitrosalicylaldehyde (8.9777 g, 0.04164 mol) was dissolved in 48 mL of acetone in a single neck 150 mL round bottom flask. DI water (16.2 mL) was added with stirring. The solution was heated to reflux with
20 stirring for 20 min. Sodium hydroxide solution (2.4271 g dissolved in 10 mL of DI water) was added drop wise. The reaction mixture was stirred and refluxed for 3 h. Then it was cooled to room temperature. The volatiles from the resulting solution were removed in a rotavapor. The bright yellow solid was washed thoroughly with chloroform followed by DI water. Dried under ambient conditions
25 to obtain 7 g (85 % yield) of bright yellow solid. ¹H NMR (d₆-Acetone) δ, ppm: 10.07 (s, 1 H, -CHO), 8.56 (s, 1 H, ArH), 8.47 (s, 1 H, Ar-H), 4.65 (s, 2 H, -CH₂OH).

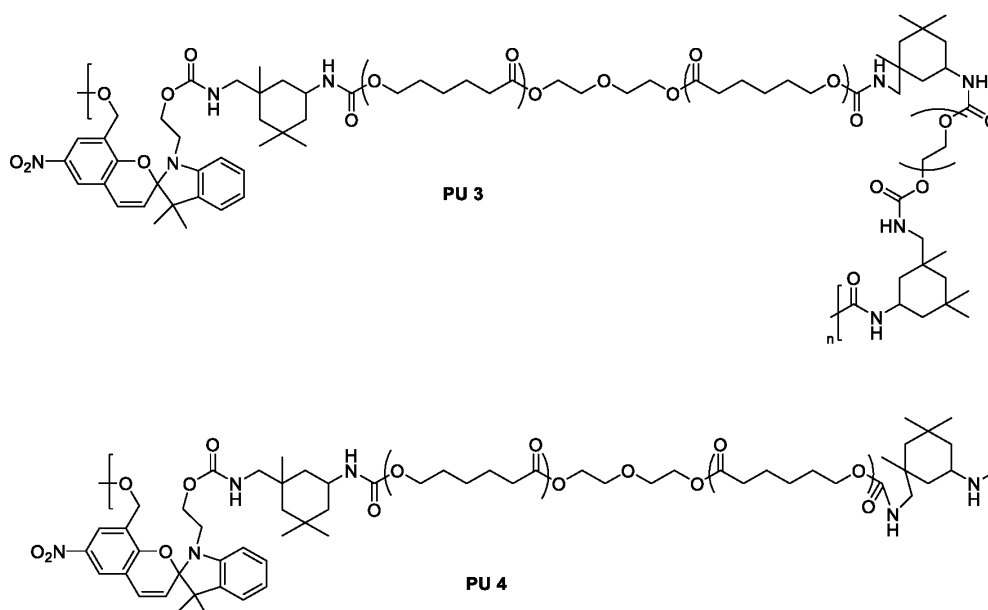
2-(8-(Hydroxymethyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (BHNSP)

3-Hydroxymethyl-5-nitrosalicylaldehyde (2.0786 g, 0.01054 mol) was dispersed in 30 mL of ethanol in a 100 mL round bottom flask. 9,9,9a-Trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole (2.1433 g, 0.01054 mol) dissolved in 20 mL ethanol was added. The reaction mixture was heated to reflux for 24 h. The dark solution was filtered and then concentrated in a rotavapor. The concentrated solution was added dropwise to sodium chloride solution, stirred well and allowed to settle overnight. The dark coloured solid was then filtered, washed with DI water and filtered. Dark coloured solid (3g, 74%). ¹H NMR (CDCl₃) δ , ppm: 8.01 and 7.88 (s, 2x1H, Ar-H o, o'-NO₂), 7.11-7.0 (m, 2 H, ArH), 6.86-6.78 (m, 2 H, ArH), 6.57-6.54 (d, 1H, =CH), 5.81-5.78 (d, 1 H, =CH), 4.49-4.45 (d, 1H, Ar-CH₂-OH), 4.32-4.29 (d, 1H, ArCH₂OH), 3.66-3.63 (t, 2H, -NCH₂CH₂OH), 3.45-3.36 (m, 1H, -NCH₂CH₂OH), 3.26-3.21 (m, 1H, -NCH₂CH₂OH), 1.21 and 1.12 (s, 2x3H, C(CH₃)₂).

Preparation of Polyurethanes, PU



61



5 Polyurethane, PU 1

BHNSP (0.2275g, 0.0006 mol) and 1,4-butanediol (0.2184, 0.0024 mol) were dissolved in tetrahydrofuran (THF) (15 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.6714g, 0.003 mol). The reaction mixture was then refluxed for 48 hours. After cooling, the viscous solution was slowly added to excess of methanol, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 1g (90%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 1 using THF as eluent: av. M_n = 5,433 av. M_w = 18,023 PD = 3.32. PU 1 formed free standing film when cast from 10 wt/vol% solution in chloroform.

Water soluble polyurethane, PU 2

BHNSP (0.2579g, 0.0007 mol) and polyethylene glycol (av MW 2000) (2.0041, 0.001 mol) were dissolved in tetrahydrofuran (THF) (25 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.3776g, 0.0017 mol). The reaction mixture was then

refluxed for 48 hours. After cooling, the viscous solution was slowly added to excess of diethyl ether, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 2.2g (83%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 2 using THF as eluent: av. M_n = 7,936 av. M_w = 16,982 PD = 2.14. PU 2 was also soluble in deionized water.

Polyurethane, PU 3

10 BHNSP (0.2663g, 0.0007 mol), polycaprolactonediol (av. MW 2000) (1.0105g, 0.0005 mol) and polyethylene glycol (av MW 2000) (1.0556, 0.0005 mol) were dissolved in tetrahydrofuran (THF) (25 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.3776g, 0.0017 mol). The reaction mixture was then refluxed for 66 hours. After
15 cooling, the viscous solution was slowly added to excess of diethyl ether, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 2.5g (92%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 3 using THF as eluent: av. M_n = 5,433 av. M_w = 18,023 PD = 3.32.
20

Polyurethane, PU 4

BHNSP (0.2684g, 0.0007 mol), and polycaprolactonediol (av. MW 2000) (2.0051g, 0.001 mol) were dissolved in tetrahydrofuran (THF) (25 mL).
25 Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.3776g, 0.0017 mol). The reaction mixture was then refluxed for 66 hours. After cooling, the viscous solution was slowly added to excess of diethyl ether, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions.
30 Yield: 2.2g (83%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 4 using THF as eluent: av. M_n = 11,412 av. M_w = 28,995 PD = 2.54.

Water soluble polyurethane, PU 5

BHNSP (0.2075g, 0.0005 mol) and polyethylene glycol (av MW 2000) (2.0956, 0.0011 mol) were dissolved in tetrahydrofuran (THF) (25 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.3462g, 0.0016 mol). The reaction mixture was then refluxed for 24 hours. After cooling, the viscous solution was slowly added to excess of diethyl ether, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 2.3g (87%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the higher molecular weight fraction of polymer, PU 5 using THF as eluent: av. M_n = 11,785 av. M_w = 16,541 PD = 1.40. PU 5 was also soluble in deionized water.

Water soluble polyurethane, PU 6

BHNSP (0.2075g, 0.0005 mol) and polyethylene glycol (av MW 2000) (1.085g, 0.0005 mol) were dissolved in tetrahydrofuran (THF) (20 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (0.3462g, 0.001 mol). The reaction mixture was then refluxed for 24 hours. After cooling, the viscous solution was slowly added to excess of diethyl ether, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 1.3g (85%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 6 using THF as eluent: av. M_n = 6,632 av. M_w = 11,442 PD = 1.73. PU 6 was also soluble in deionized water.

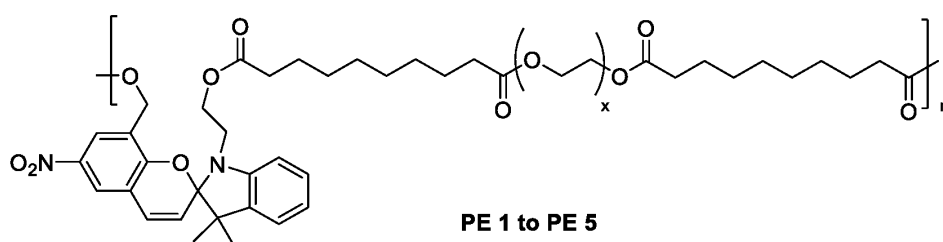
Polyurethane, PU 7

BHNSP (0.5090g, 0.001 mol) and 1,4-butanediol (0.6142, 0.007 mol) were dissolved in tetrahydrofuran (THF) (25 mL). Dibutyltindilaurate (about 3 drops) was added to this solution followed by isophorone diisocyanate (1.7833g, 0.008 mol). The reaction mixture was then refluxed for 30 hours. After cooling, the viscous solution was slowly added to excess of 3:1 mixture of diethyl ether:

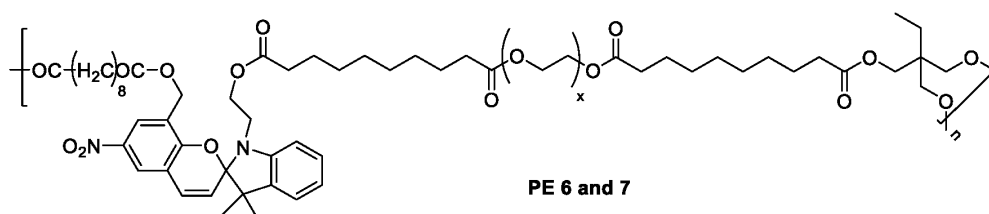
hexane, stirred well and allowed to settle. After settling of the solids, the liquid layer was decanted off and then dried under ambient conditions. Yield: 2.5g (86%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PU 7 using THF as eluent: av.

5 $M_n = 3,557$ av. $M_w = 7,246$ PD = 2.04.

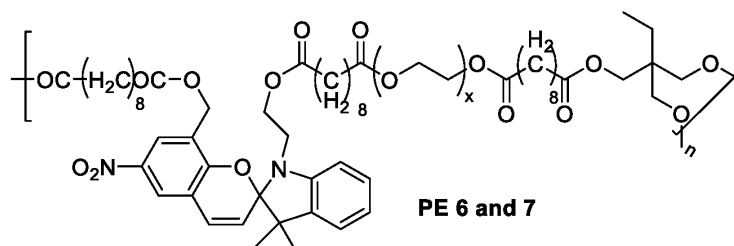
Preparation of polyesters, PE



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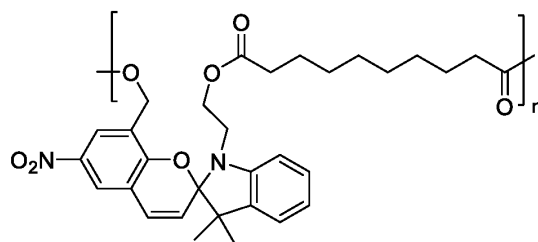
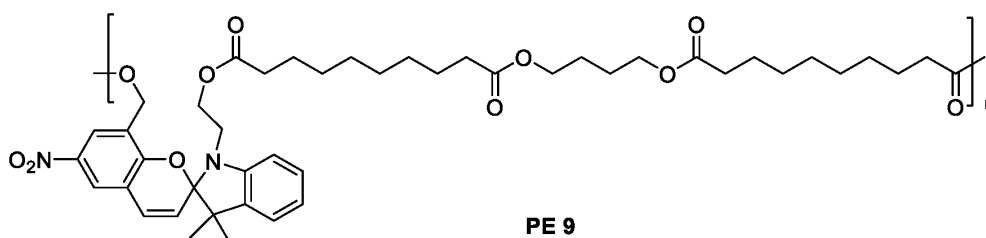


Or



15

65

**PE 8****PE 9**

5 Water soluble polyester, **PE 1**

BHNSP (0.0896g, 0.00023 mol) and polyethylene glycol (av MW 2000) (4.2203g, 0.002 mol) were dissolved in dichloromethane (DCM) (40 mL). Sebacoyl chloride (diacid chloride of sebacic acid) (0.5605g, 0.0023 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.5082g, 0.005 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of hexane. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 4 g (85%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PE 1 using THF as eluent: av. M_n = 7,856 av. M_w = 15,499 PD = 1.97. PE 1 was also soluble in deionized water.

20 Water soluble polyester, **PE 2**

BHNSP (0.1807g, 0.0005 mol) and polyethylene glycol (av MW 2000) (3.7619g, 0.002 mol) were dissolved in dichloromethane (DCM) (40 mL).

Sebacoyl chloride (0.5605g, 0.0023 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.5082g, 0.005 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 3.5g (81%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the polymer, PE 2 using THF as eluent: av. M_n = 11,700
av. M_w = 15,984 PD = 1.37. PE 2 was also soluble in deionized water.

Water soluble polyester, PE 3

BHNSP (0.2702g, 0.0007 mol) and polyethylene glycol (av MW 2000) (3.3861g, 0.002 mol) were dissolved in dichloromethane (DCM) (40 mL). Sebacoyl chloride (0.5717g, 0.0024 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.5082g, 0.005 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 3.2g (79%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the high molecular weight fraction of polymer, PE 3 using THF as eluent: av. M_n = 13,331 av. M_w = 18,372 PD = 1.38. PE 3 was also soluble in deionized water.

Water soluble polyester, PE 4

BHNSP (0.104g, 0.0003 mol) and polyethylene glycol (av MW 2000) (1.088g, 0.0005 mol) were dissolved in dichloromethane (DCM) (20 mL). Sebacoyl chloride (0.18g, 0.0008 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.2178g, 0.002 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was

removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 1.1g (84%).

- 5 The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the high molecular weight fraction of polymer, PE 4 using THF as eluent: av. M_n = 9,868 av. M_w = 11,861 PD = 1.20. PE 4 was also soluble in deionized water.

10 Water soluble polyester, PE 5

- BHNSP (0.2011g, 0.0005 mol) and polyethylene glycol (av MW 2000) (1.1276g, 0.0006 mol) were dissolved in dichloromethane (DCM) (25 mL). Sebacoyl chloride (0.2466g, 0.001 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.2178g, 0.002 mol). The reaction mixture
- 15 was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 1.3g (87%).
- 20 The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the high molecular weight fraction of polymer, PE 5 using THF as eluent: av. M_n = 10,794 av. M_w = 13,261 PD = 1.23. PE 5 was also soluble in deionized water.

25 Water soluble polyester, PE 6

- BHNSP (0.1831g, 0.0005 mol), polyethylene glycol (av MW 2000) (3.7869g, 0.002 mol) and 1,1,1-trihydroxymethyl propane (0.4556g, 0.003 mol) were dissolved in dichloromethane (DCM) (50 mL). Sebacoyl chloride (1.7936g, 0.008 mol) was added to this solution followed by the dropwise addition of triethyl
- 30 amine (1.5246g, 0.02 mol). Immediately after adding triethyl amine the reaction mixture swelled. The swollen reaction mixture was stirred under ambient conditions for 24 hours. Then the reaction mixture was diluted by adding

methanol and the solvents were removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 5g (88%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics of the high molecular weight fraction of polymer, PE 6 using THF as eluent: av. M_n = 8,803 av. M_w = 22,297 PD = 2.53. PE 6 was also soluble in deionized water.

10 Water swelling polyester, PE 7

BHNSP (0.1067g, 0.0003 mol) and polyethylene glycol (av MW 2000) (1.0662g, 0.0005 mol) were dissolved in dichloromethane (DCM) (30 mL). Sebacoyl chloride (1.01g, 0.004 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.8712g, 0.01 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then, 1,1,1-trihydroxymethyl propane (0.1504g, 0.001 mol) was added and stirred for another 24h. DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 1.8g (89%). The solid was insoluble in common organic solvents like chloroform and THF after drying. It swelled in deionized water with a swelling ratio of about 200 (average of three tests).

25 Polyester, PE 8

BHNSP (1.0468g, 0.003 mol) was dissolved in DCM (20 mL). Sebacoyl chloride (0.6726g, 0.003 mol) was added to this solution followed by the dropwise addition of triethyl amine (0.5808g, 0.06 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of hexane. After stirring well the solids were allowed to settle and then the supernatant liquid layer

was decanted off. Dried under ambient conditions. Yield: 1.2g (79%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics PE 8 using THF as eluent: av. M_n = 1,140 av. M_w = 2,354 PD = 2.06.

5

Polyester, PE 9

BHNSP (0.6047g, 0.0016 mol) and 1,4-butanediol (0.6166g, 0.0068 mol) were dissolved in DCM (25 mL). Sebacoyl chloride (1.9057g, 0.008 mol) was added to this solution followed by the dropwise addition of triethyl amine (1.5972g, 0.016 mol). The reaction mixture was stirred under ambient conditions for 24 hours. Then the solvent, DCM was removed in a rotavapor. The residue was dissolved in THF and filtered. The filtrate was concentrated in a rotavapor and then precipitated in excess of diethyl ether. After stirring well the solids were allowed to settle and then the supernatant liquid layer was decanted off. Dried under ambient conditions. Yield: 2.2g (86%). The solid was soluble in common organic solvents like chloroform. The molecular weight characteristics PE 9 using THF as eluent: av. M_n = 3,174 av. M_w = 6,415 PD = 2.02.

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APPLICATIONS

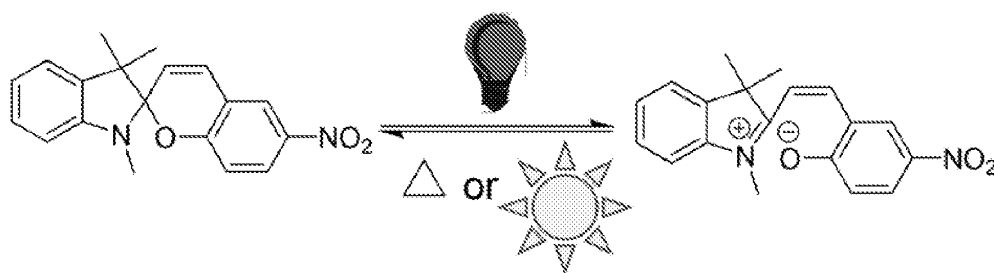
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Thermophotochromic polymers comprising two or more spiropyran units or derivatives thereof have been developed. Advantageously, the spiropyran polymers designed in accordance with various embodiments disclosed herein are soluble in water (i.e. water soluble) and/or exhibit thermophotochromism with good stability in the aqueous medium (i.e. hydrolytically stable). In various other embodiments, the spiropyran polymers may alternatively be designed to be water insoluble and can be used for preparing coated substrates. Embodiments of the spiropyran polymers are also capable of responding to lower/lesser energy sources. For example, the spiropyran polymers designed in accordance with various embodiments disclosed herein can work with a low power UV source and/or thermal energy available from ambient conditions, and do not require a high energy radiation source or external infrastructure.

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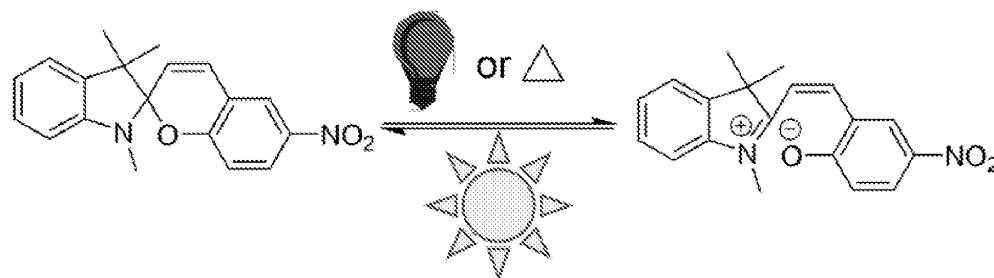
Embodiments of the polymers respond to heat and UV light synonymously unlike conventional photochromic materials where exposure to UV light and heat produce opposite results. A mechanism of a conventional photochromism (using spiro

5 spiropyran as an example) is shown in Scheme 3 below.



Scheme 3. Conventional photochromism (using spiropyran as an example)

10



Scheme 4. Thermophotochromism (using spiropyran as an example)

In conventional photochromism as shown in Scheme 3, UV irradiation causes colour formation via/through ring opening of spiropyran (i.e. a colourless ring closed form) to merocyanine dye (i.e. a coloured ring opened form). The reverse reaction leading to ring closure is induced by visible light or heat provided by ambient conditions. In a conventional photochromic mechanism, thermal energy and sunlight cause the same effect viz. ring closure to the spiropyran form.

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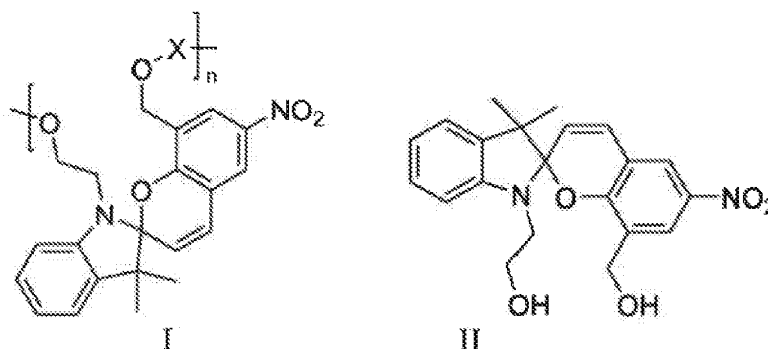
In the thermophotochromic system designed in accordance with various embodiments disclosed herein (as shown in Scheme 4), UV radiation and heat induce the same ring opening reaction. The merocyanine form is obtained upon heating or when exposed to UV light, which reverts to the colorless form upon exposure to sunlight. Particularly, sunlight is used to induce ring closure, and ring opening back to merocyanine form is achieved by thermal energy (e.g., that is available under ambient conditions).

Advantageously, embodiments of the method disclosed herein have successfully developed a thermophotochromic/ photochromic system that makes use of sunlight, particularly the day-night cycles so that no external infrastructure is required to induce photochromic behavior and to fully make use of the changes accompanying the photochromic behavior. Sunlight has been the energy source for earth for billions of years. Sunlight is readily available in abundance and is of a lower energy as compared to UV radiation. By using sunlight as an energy source to induce photochromism, the energy efficiency and sustainability of the presently disclosed photochromic/thermophotochromic process is improved and better than conventional photochromic systems which require UV radiation in order to induce photochromism. Even more advantageously, this thermophotochromism behaviour/property enables the formation of surfaces that show dynamic characteristics synchronized with day night cycles (that is, during daytime under direct sunlight it forms the colorless form and during night the ambient temperature induces the ring opened colored form). Such dynamism shown inherently also demonstrates the potential of the thermophotochromic polymer disclosed herein to maintain cleaner surfaces because adherence of foreign objects would be weakened by the surface that is in perpetual motion at the molecular level. In summary, advantages of the presently disclosed thermophotochromic polymer/system include: change in properties synchronized with day-night cycles, reduced power of energy source would help to prolong the life of chromophore, energy efficiency, sustainable nature and no necessity for additional infrastructure as would be required for UV source in conventional photochromism.

Advantageously, the spiropyran polymers designed in accordance with various embodiments disclosed herein also possess good adhesive nature which enable the polymers to be coated with/onto various substrates. As will be shown
5 in the following examples, the developed thermophotochromic polyesters and polyurethanes are capable of exhibiting/showing transformations in the form of gels, in the solid state and in solutions.

In various embodiments, the present technology comprises one or more
10 of the following features:

(A1) Polymers with thermophotochromic properties of structure I, wherein X may be derived from an ester or urethane linkage obtained by reacting spiropyran diol of structure II to obtain a thermophotochromic polymer having
15 more than two spiropyran units per polymer chain:



(A2) The thermophotochromic polymer may be obtained by reacting the spiropyran diol with dicarboxylic acids or preferably with its derivatives like diacid
20 chlorides or with diisocyanates or its derivatives, either alone or with other dihydroxy compounds.

(A3) The dihydroxy compounds are preferably C2 to C10 diol, oligomeric and polymeric ethylene and propylene glycols of molecular weight 100 to 10,000,
25 preferably 100 to 5000 and most preferably 100 to 2000.

(A4) The thermophotochromic polymer may be used in the solid form, as aqueous or organic solution and aqueous gels.

5 In various embodiments, the polymers of the present technology possess thermophotochromic properties that are not commonly found in other polymers of similar make-up. Without being bound by theory, it is believed that the thermophotochromism shown by embodiments of these polymers is likely due to one or more of the following reasons:

10

(i) The presence of substituent adjacent to the ring opening site; and

(ii) The electronic effect caused by the oxymethylene unit. It will be appreciated that in conventional photochromes, the substituent is at the 4 or para position of the chromone oxygen (Note: Going by substitution it is position 5. The 4-position is with respect to Oxygen which is in position 2). Also, conventional photochromic compounds by and large have electron withdrawing nitro group in the aromatic ring attached to the chromone unit. On the contrary, the presence of electron donating oxymethylene unit helps to increase the electron density. This change
15 in electron density helps to influence the electronic properties. In the absence of oxymethylene unit, the chromone ring is highly electron deficient because of the presence of electron withdrawing nitro group at the 5th position. The electron donating ability of oxymethylene unit helps to compensate this. Because of this, the hydrolytic stability of the spiropyran moiety is enhanced unlike electron
20 deficient compounds which are prone to attack by nucleophiles. Additionally, the substitution *ortho* to the chromone oxygen also plays a part in ring opening and ring closing mechanism. Because of its flexible nature, it does not adversely affect this process.

30

In various embodiments, the thermochromic polymer disclosed herein may be used in one or more of the following applications:

(a) Dynamic surfaces (e.g., dynamic coating)

- 5 The change in wettability characteristics as determined by contact angle changes accompanying day and night cycles on surfaces coated with thermophotochromic polymer may be used as proof for the surface being dynamic. Surfaces coated with poly(methyl methacrylate) may be used as reference. Along with this natural exposure, the changes may also be studied under simulated conditions using low
10 intensity UV and visible lights.

- Advantageously, thermophotochromic polymer designed in accordance with various embodiments disclosed herein may be applied as dynamic surfaces for
(i) loosening the adherence of dirt particles for long term preservation of functions
15 and pristine appearance; (ii) refreshing the surface to lessen accumulation of microorganisms; and (iii) modifying wettability characteristics for minimising resource utilization.

(b) Thermogelling and or viscosity modifier for aqueous formulations

- 20 Rheology studies may be conducted to monitor the change in viscosity with temperature.

(c) Sensors/Biosensors

- The change in absorption of aqueous solution of thermophotochromic polymers
25 upon adding metal salts and water soluble organic compounds may be determined.

(d) 3D printed materials

- 3D printed polymeric articles incorporated with thermophotochromic materials.
30 Thermophotochromic polymer incorporated in 3D printed article may be used as a security tag.

(e) Applications in personal care industry, device screens, advertising surfaces, vehicles etc by utilizing/applying/exploiting/making use of changes in colour.

(f) Optical materials, optical information storage, cosmetics, authentication
5 systems, flow filed visualization by utilizing/applying/exploiting/making use of changes in absorption and/or emission spectra.

(g) Applications that utilize/apply/exploit/make use of changes in physico-chemical characteristics – refractive index, dielectric constant, electric
10 conductivity, phase transitions, solubility, viscosity and surface wettability.

(h) Applications that utilize/apply/exploit/make use of photomechanical effects

(i) Chiroptical molecular switches – random coil to α -helix transition of poly(α -aminoacids) accompanying photoisomerization.
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(j) Applications that utilize/apply/exploit/make use of sol-gel transition temperature/technology.

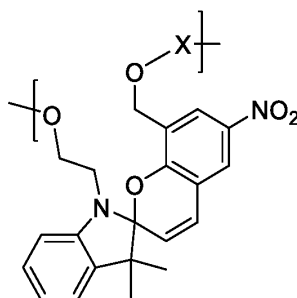
20 (k) Optobioelectronic devices.

It will be appreciated by a person skilled in the art that other variations and/or modifications may be made to the embodiments disclosed herein without departing from the spirit or scope of the disclosure as broadly described. For
25 example, in the description herein, features of different exemplary embodiments may be mixed, combined, interchanged, incorporated, adopted, modified, included etc. or the like across different exemplary embodiments. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. A thermophotochromic polymer comprising two or more spiropyran units or
5 derivatives thereof, wherein the polymer is configured to reversibly change its absorbance characteristics upon an application of thermal energy and/or ultraviolet light.
2. The thermophotochromic polymer of claim 1, wherein an application of
10 thermal energy facilitates a change in absorbance characteristics in a same direction as an application of ultraviolet light.
3. The thermophotochromic polymer of any one of the preceding claims,
15 wherein an application of visible light facilitates a change in absorbance characteristics in an opposite direction as an application of thermal energy and/or ultraviolet light.
4. The thermophotochromic polymer of any one of the preceding claims,
20 wherein the polymer changes from a lighter colour to a darker colour upon application of thermal energy and/or UV light.
5. The thermophotochromic polymer of any one of the preceding claims,
25 wherein the polymer is configured to further reversibly change its surface wettability characteristics upon an application of thermal energy and/or ultraviolet light.
6. The thermophotochromic polymer of any one of the preceding claims,
30 wherein an application of thermal energy and/or ultraviolet light result(s) in the ring opening of the spiropyran units or derivatives thereof in the polymer.

7. The thermophotochromic polymer of any one of the preceding claims, wherein an application of visible light facilitates ring closing of the spiropyran units or derivatives thereof in the polymer.
- 5 8. The thermophotochromic polymer of any one of the preceding claims, wherein the polymer is present at a concentration of from 0.01 wt% to 50.0 wt% in solution.
9. The thermophotochromic polymer of any one of the preceding claims,
10 wherein the polymer is soluble in a solvent.
10. The thermophotochromic polymer of any one of the preceding claims, wherein the polymer comprises at least one of a polyester polymer, polyurethane polymer and combinations thereof.
- 15 11. The thermophotochromic polymer of any one of the preceding claims, wherein the spiropyran units or derivatives thereof are coupled to at least one of carbamate/urethane linkage(s), ester linkage(s) and combinations thereof.
- 20 12. The thermophotochromic polymer of any one of the preceding claims, wherein the polymer comprises at least one structural unit represented by Formula I:



Formula I

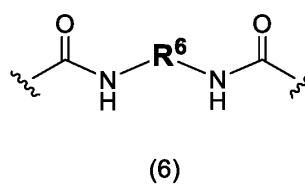
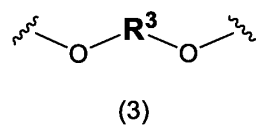
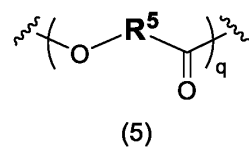
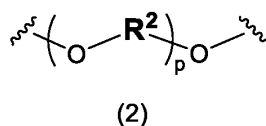
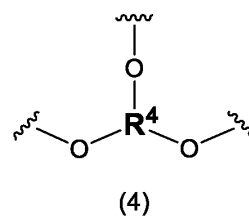
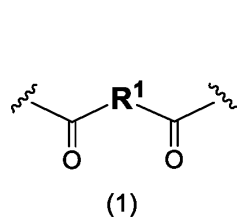
wherein

X comprises linear aliphatic, branched aliphatic, cyclic, aromatic hydrocarbons and combinations thereof;

one or more of the C atoms in the linear aliphatic, branched aliphatic, cyclic, aromatic hydrocarbons and combinations thereof is/are optionally replaced by $-O-$, $-C(=O)-$, $-C(=O)-O-$, $-O-C(=O)-$, $-NR^b-C(=O)-$ and/or $-C(=O)-NR^b-$; and

R^a and R^b are each independently selected from H, optionally substituted alkyl, optionally substituted alkenyl or optionally substituted alkynyl.

13. The thermophotochromic polymer of claim 12, wherein X comprises one or more of the following general formula (1), (2), (3), (4), (5) and (6):



wherein

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkylcycloalkyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally

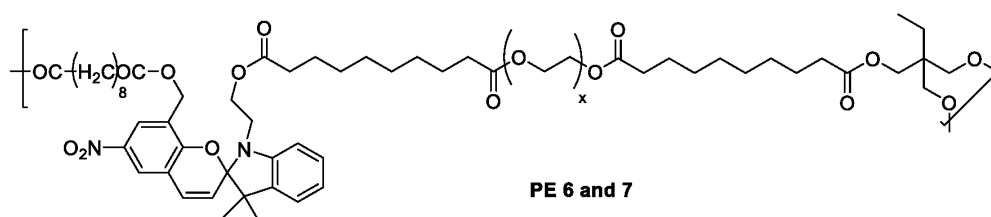
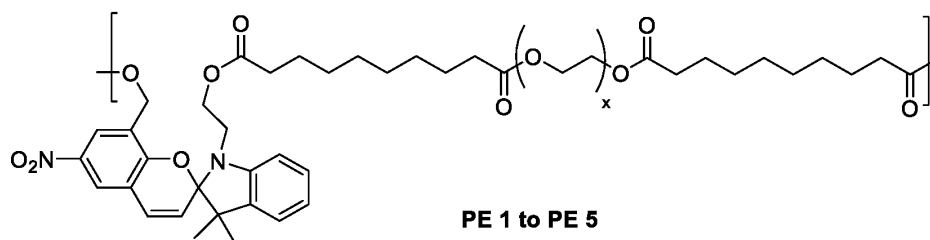
substituted aryl, optionally substituted alkylaryl, optionally substituted heteroaryl, optionally substituted alkylheteroaryl and combinations thereof;

$p \geq 1$; and

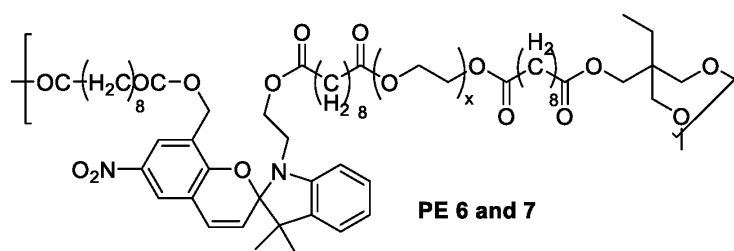
$q \geq 1$.

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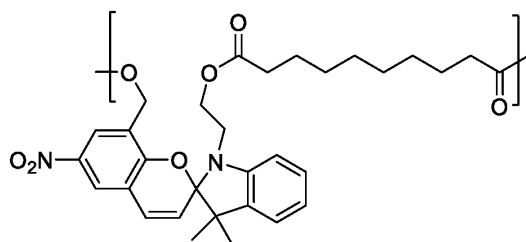
14. The thermophotochromic polymer of any one of the preceding claims, wherein the polymer comprises at least one structural unit selected from the following:



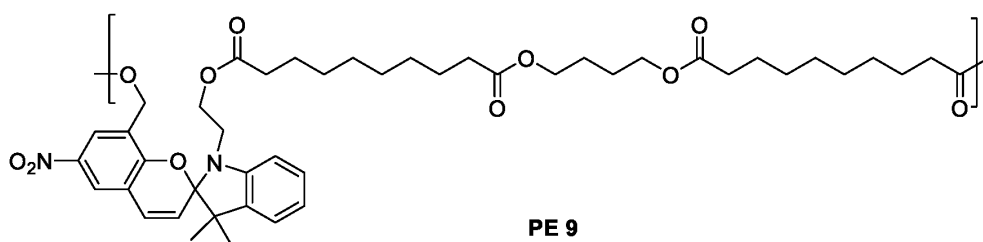
Or



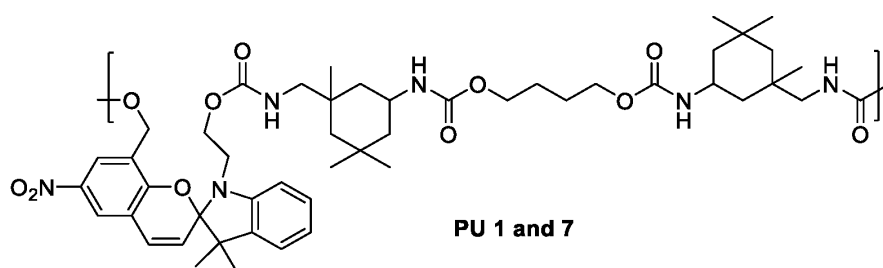
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PE 8

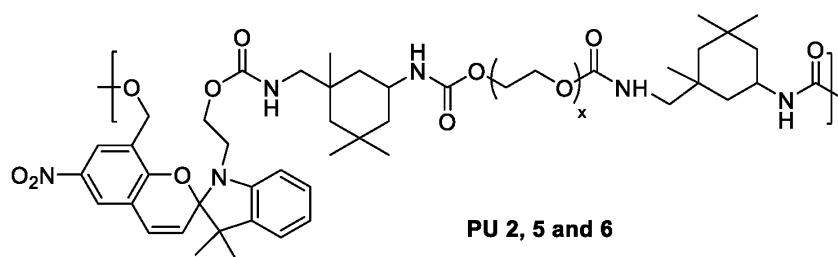


PE 9



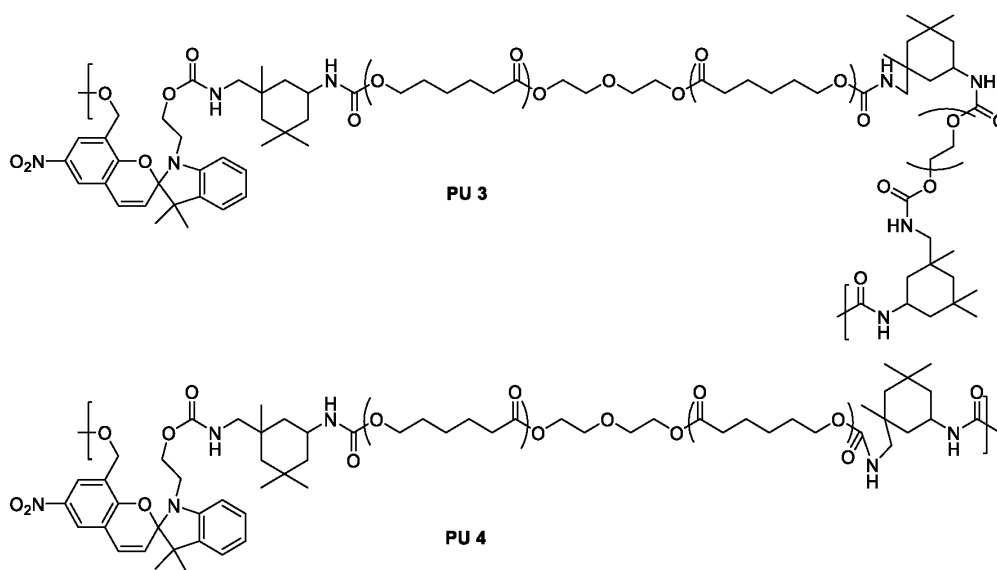
PU 1 and 7

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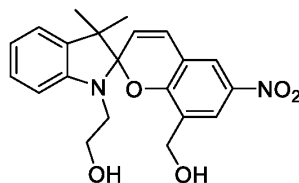
PU 2, 5 and 6

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15. A method of preparing the thermophotochromic polymer of any one of the preceding claims, the method comprising: reacting one or more spirocyclic diol with one or more compounds selected from the group consisting of dicarboxylic acids, dicarboxylic acid derivatives, diacid chlorides, diisocyanates, diisocyanate derivatives, isocyanate derivatives, multifunctional carboxylic acids such as trifunctional carboxylic acids, polyfunctional carboxylic acids, monofunctional and multifunctional carboxylic acid derivatives such as difunctional carboxylic acid derivatives, trifunctional carboxylic acid derivatives, polyfunctional carboxylic acid derivatives, multifunctional isocyanates and multifunctional isocyanate derivatives, and optionally with one or more alcohols selected from dihydroxy, trihydroxy and polyhydroxy.
16. The method of claim 15, wherein the spirocyclic diol is reacted with the compounds in a molar ratio of from 1:1 to 1:30, and optionally with the alcohols in a molar ratio of from 1:1 to 1:30.

17. The method of any one of claims 15 to 16, wherein the spiropyran diol is represented by Formula II:



Formula II

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18. The method of any one of claims 15 to 17, wherein the one or more alcohols is/are present and is/are selected from the group consisting of C₂ to C₁₀ diol, oligomeric and polymeric ethylene, propylene glycols and combinations thereof.

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19. The method according to any one of claims 15 to 18, wherein the method comprises reacting one or more spiropyran diol with one or more diisocyanates selected from the group consisting of hexamethylene diisocyanate, tetramethylene diisocyanate, cyclohexane diisocyanate, tetramethylxylene diisocyanate, dodecylene diisocyanate, tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, isophorone diisocyanate, their derivatives thereof and combinations thereof.

15

20. The method according to any one of claims 15 to 19, wherein the method comprises reacting one or more spiropyran diol with one or more diacid chlorides selected from the group consisting of adipoyl chloride, dodecanedioyl chloride, succinyl chloride, sebacoyl chloride, heptanedioyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesyl chloride and combinations thereof.

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