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(54) Title: AROMATIC POLYMERS OBTAINABLE BY CYCLOADDITION REACTION

(57) Abstract: Polymers obtainable by cycloaddition reaction of non-polymeric compounds are herein disclosed. Said polymers are useful for a variety of industrial uses, such as the manufacture of films, coatings or shaped articles.



Description**Aromatic polymers obtainable by cycloaddition reaction****Related application**

[0001] This application claims priority to U.S. provisional application No. 62/524,667, filed on June 26, 2017, and to European application No. 17181642.4, filed on July 17, 2017, the whole content of each of these applications being incorporated herein by reference for all purposes.

Technical Field

[0001] The present invention relates to polymers obtainable by cycloaddition reactions of non-polymeric compounds, said polymer being useful for a variety of industrial uses, such as the manufacture of films, coatings or shaped articles.

Background Art

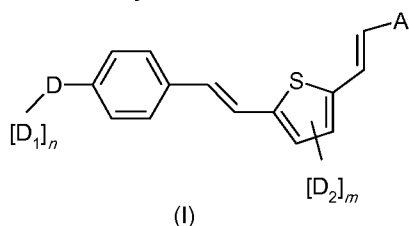
[0002] In organic chemistry, cyclization reactions are known to promote the formation of rings starting from one or two compounds (the latter being commonly referred to as cyclodimerization or cycloaddition reactions). Cyclizations can be promoted by heating (thermal cyclizations) or by UV light (photocyclizations).

[0003] A widely known example of a cyclization reaction is the Diels-Alder (DA) reaction, i.e. is a [4+2] cycloaddition reaction between a conjugated diene and a substituted alkene (referred to as "dienophile"), to provide a cyclohexene system. The synthetic value of this reaction lies mainly in the fact that, through appropriate selection of the diene and dienophile, it allows control of the regio-/stereochemistry of the final product. DA reactions involving at least one heteroatom of either the diene or the dienophile (referred to as "hetero DA") are a useful synthesis tool to obtain heterocycles.

- [0004] In addition, under certain conditions, the DA reaction is reversible; this reaction is called "retro DA".
- [0005] For the above reasons, the DA reaction has been exploited for the synthesis of different categories of products, including polymers.
- [0006] Another well-known example of cyclization reaction is the [4+4] photodimerization of anthracene, whereby two molecules of anthracene connect via four atoms of each molecule to create an eight-membered ring. This reaction is attractive mainly in view of the fact that in one single step an eight membered ring with complex stereocenters can be created. The reaction is induced by UV light and is reversible under different UV light frequencies or under heating.
- [0007] **US 2009/0148717** (Washington University, OF), published on June 11, 2009, relates to a cross-linkable polymer useful for making cross-linked films having electro-optic activity and to cross-linked polymers and films obtained therefrom. The cross-linkable polymer consists essentially of:
- (a) one or more chromophore groups attached as pendants to a polymer backbone; and
 - (b) one or more of either diene or dienophile groups attached as pendants to the polymer backbone, wherein the diene or dienophile groups are reactive to form 4+2 cycloaddition products (par. [0025] and claim 22).
- [0008] Preferably, the cross-linkable polymer comprises two or more anthracene moieties.
- [0009] The cross-linked polymer consists essentially of:
- (a) one or more chromophore groups attached as pendants to a crosslinked polymer; and (b) one or more crosslinks formed by the 4+2 cycloaddition reaction of a diene and a dienophile, wherein the cycloaddition moieties are formed by the reaction of one or more diene or dienophile moieties of a crosslinkable polymer and one or more diene or dienophile moieties of a crosslinking agent. Representative crosslinking agents include bismaleimides and trismaleimides.

[0010] **US 2009/0299021** (Washington University, OF), published on December 3, 2009, relates to DA crosslinkable dendritic nonlinear optical (NLO) chromophore compounds, films and crosslinked polymer composites formed from the DA crosslinkable dendritic chromophores, methods for making and using the DA crosslinkable dendritic chromophores, films, and crosslinked polymer composites, and electro-optic devices that include films and crosslinked polymer composites formed from the DA crosslinkable dendritic chromophores (par. [0008]). It is stated that such films and crosslinked polymer composites are endowed with satisfactory electro-optical properties and thermal stability.

[0011] Preferably, the crosslinkable **compounds** comply with formula (I):



wherein D is a π -electron donor group; A is a π -electron acceptor group; D_1 is a dendron moiety functionalized with one or more crosslinkable groups; D_2 is a dendron moiety functionalized with one or more crosslinkable groups; n is 0, 1, or 2; m is 0, 1, or 2; and $m+n \geq 1$; wherein the crosslinkable groups are independently selected from the group consisting of an anthracenyl group and an acrylate group.

[0012] Preferably, D_1 and D_2 are selected from dendritic groups comprising at least two anthracene or acrylate moieties (par. [0013] and [0014]). It also stems from par. [0015] to [0018], [0021] and [0097] that the cross-linked polymer (and films or composites) can be obtained by Diels-Alder reaction of a compound (I) wherein both D_1 and D_2 comprise anthracene moieties with another compound (I) wherein both D_1 and D_2 comprise acrylate moieties or by reaction of a compound (I) wherein either D_1 or D_2 is anthracene and the other one is acrylate.

- [0013] Therefore, the sole cross-linkable groups disclosed in this document that react together through DA reaction are anthracenyl and acrylate groups.
- [0014] **US 2010/0108996 A1** (Electronics and Communications Research Institute, Gwangju Institute of Science and Technology), published on May 6, 2016, relates to a composition for organic thin film transistor and film formed from the composition. The composition comprises a polymer (for example a polymethylmethacrylate polymer) having pendant groups comprising anthracenyl moieties [formulae (I) and (II) on page 1] and a cross-linker comprising two or three maleimide groups [see formulae (III) - (VI) on page 1]. The film can be manufactured by means of a process which comprises heat treatment (par. [0017]); in some embodiments, the heat treatment makes a DA reaction occur between the polymer and cross-linker.
- [0015] **JP 2010185049 A2** (NK RES KK), published on August 26, 2010, relates to a method for obtaining a biodegradable poly-L-lactic acid (PLLA) block copolymer by reaction of anthracenyl-terminated PLLA and maleimide-terminated PLLA.
- [0016] **JP 2011236325 A2** (MUSASHINO CHEMICAL LABORATORY LTD; MUTUAL CORP; KYOTO INST OF TECHNOLOGY), published on November 24, 2011, relates to a multiblock polylactic acid block copolymer obtained by DA reaction of:
- a poly-D-lactic acid having a maleimide group at the end of at least one end of the polymer chain and
 - a poly-L-lactic acid having an anthracenyl group or a furanyl group at both ends of the polymer chain.
- [0017] Thomas, Iain, P., et al, *Chem. Commun.*, 1999, 1507-1508 discloses the DA reaction of polystyrene resin beads carrying respectively maleimide and anthracene groups attached to extended side-chains.
- [0018] Kriegel, Robert M. et al, *Macromolecular Chemistry and Physics*, 2005, 206, 1479-1487 discloses the heat-promoted DA reaction between low molecular weight anthracene-terminated polyester macromers with bismaleimides to provide polymeric materials with high molecular weights. It is stated that the

resulting materials have lower crystallinity than PET homopolymers and display enhanced strength and elongation.

- [0019] On the other hand, it is known in the art that the step-growth reactions used to prepare aromatic polymers such as aromatic polyethers (namely polyaryl ether sulfones and polyaryl ether ketones) produce byproducts such as inorganic salts that must be removed from the final product. In addition, these reactions are normally carried out in polar, high-boiling organic solvents capable of promoting the polymerization and keeping the viscosity low. Because of these requirements, these types of reactions are poorly suited to additive manufacturing, where it would be impossible to remove salts or high-boiling solvents from a manufactured article without destroying the manufactured article, or without inducing undesirable changes to the same.
- [0020] Additive manufacturing may also make use of molten aromatic polymers, but the high viscosity of molten aromatic polymers and their high T_g in general present difficulties for conventional three-dimensional (3D) printers.
- [0021] Thermoplastic composites are usually prepared by impregnation of carbon fibers or glass fiber fabrics with high performance thermoplastics like aromatic polymers; however, due to the high polymer viscosity in the molten state, the fabrics or fibers are not sufficiently impregnated and holes form in the composite that negatively affect mechanical properties. Viscosity in the molten state can be reduced by reducing the molecular weight of the thermoplastic polymer; this solves the impregnation issue, but leads to poor mechanical properties of the resulting thermoplastic composite. There is an outstanding need to recycle thermoplastic composites in order to recover the carbon of glass fibers.

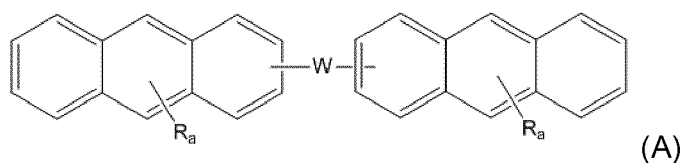
Summary of invention

- [0022] The Applicant has now found out that cycloaddition reactions, in particular the [4+2] cycloaddition reaction [Diels-Alder (DA) reaction] between certain non-polymeric dienes and certain non-polymeric dienophiles and the photodimerization of certain non-polymeric anthracene-containing monomers

can be conveniently exploited to obtain aromatic polymers, without obtaining undesirable inorganic byproducts. Therefore, due to their purity and low viscosity, the resulting aromatic polymers obtained thereby can be easily processed, optionally together with additives, to obtain films, coatings or shaped articles, in particular shaped articles by 3D printing and composites. In addition, thanks to the reversibility of such reactions, the polymers can be easily degraded and recycled without the use of chemicals, but by appropriately selecting the conditions that induce a retro-cycloaddition reaction.

[0023] Accordingly, in one embodiment, the present invention relates to a polymer (P) comprising recurring units obtainable by cycloaddition reaction of:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:
 - (i) a bond;
 - (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 - (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 18, preferably 0;
- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A).

[0024] For the avoidance of doubts, polymers obtainable by cycloaddition reaction of the compounds of formula (I) of the above-cited US 2009/0299021 are excluded from the scope of the present application.

[0025] Further, for the purpose of clarity, the optionally substituted anthracenyl rings of monomer (A) can be equal to or different from each other.

[0026] In another embodiment, the present invention relates to a formulation comprising polymer (P) in admixture with additional components, for example for use for 3D printing.

[0027] In another embodiment, the present invention relates to methods for the manufacture of films, coatings or shaped articles from polymer (P) or from composition (C).

[0028] In another embodiment, the present invention relates to a method of recycling said films, coatings or shaped articles by submitting said films, coatings or shaped articles to retro-cycloaddition reaction.

General definitions, symbols and abbreviations

[0029] For the purposes of the present description:

- a cycloaddition reaction is a reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic adduct in which there is a net reduction of the bond multiplicity, as defined in International Union of Pure and Applied Chemistry, Compendium of Chemical Terminology, Gold Book, Version 2.3.3 February 24, 2014, page 367);
- a Diels-Alder (DA) reaction is a [4+2] cycloaddition reaction between a

conjugated diene and a substituted alkene (referred to as “dienophile”), to provide a cyclohexene system. For the purpose of the present application, the expression “DA reaction” includes also hetero DA reactions, i.e. those DA reactions involving at least one heteroatom of either the diene or the dienophile;

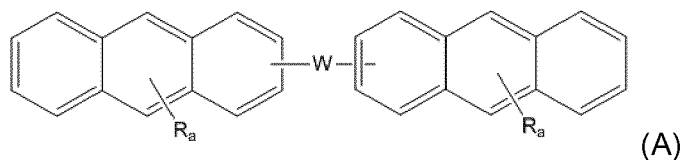
- a [4+4] photocycloaddition reaction is a reaction in which two unsaturated molecules connect via four atoms from each molecule to form an eight membered ring;
- the term “halogen” includes fluorine, chlorine, bromine and iodine, unless indicated otherwise;
- the term “method” is used as synonym of process and *vice-versa*;
- the use of parentheses “()” before and after names of compounds, symbols or letters identifying formulae, e.g. “polymer (P)”, “monomer (A)”, “monomer (B)”, “film (F)”, etc..., has the mere purpose of better distinguishing that name, symbol or letter from the rest of the text; thus, said parentheses could also be omitted;
- when numerical ranges are indicated, range ends are included;
- “aromatic” denotes any mono- or polynuclear cyclic group (or moiety) having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer; an aromatic group can be an aryl or an arylene group (or moiety); an aromatic group may also include in any of its cyclic group one or more heteroatoms, preferably selected from N, O or S and may also be substituted with optionally halogenated straight or branched alkyl groups, optionally comprising one or more heteroatoms selected from N, O or S or functional groups comprising such heteroatoms;
- an “aryl group” is a hydrocarbon monovalent group consisting of one core composed of one benzenic ring or of a plurality of benzenic rings either linked together via a C-C bond between one carbon atom of one ring and one carbon atom of an adjacent ring or fused together by sharing two or more neighboring ring carbon atoms, and of one end. The end of an aryl group is a free electron of a carbon atom contained in a (or the) benzenic ring of the aryl

group, wherein a hydrogen atom linked to said carbon atom has been removed. The end of an aryl group is capable of forming a linkage with another chemical group;

- an "arylene group" is a hydrocarbon divalent group consisting of one core composed of one benzenic ring or of a plurality of benzenic rings either linked together via a C-C bond between one carbon atom of one ring and one carbon atom of an adjacent ring or fused together by sharing two or more neighboring ring carbon atoms, and of two ends. An end of an arylene group is a free electron of a carbon atom contained in a (or the) benzenic ring of the arylene group, wherein an hydrogen atom linked to said carbon atom has been removed. Each end of an arylene group is capable of forming a linkage with another chemical group.

[0030] Monomer (A)

[0031] According to the present invention, monomer (A) comprises at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:

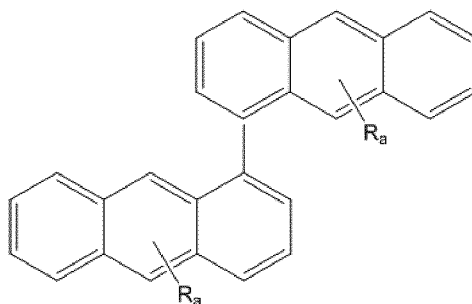
- (i) a bond;
- (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
- (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- (preferably

at least one divalent –O– or at least one divalent –S–) and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

- a is 0 or an integer from 1 to 18, preferably 0;

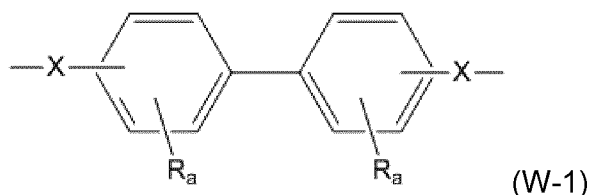
[0032] According to an embodiment, monomer (A) is according to formula (A-1):

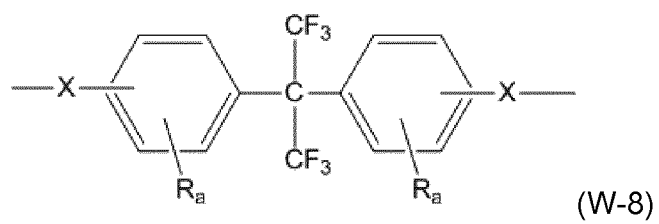
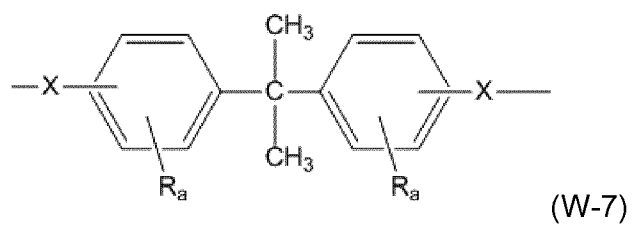
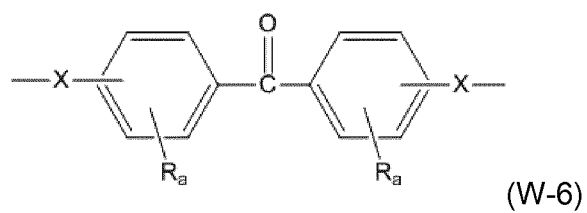
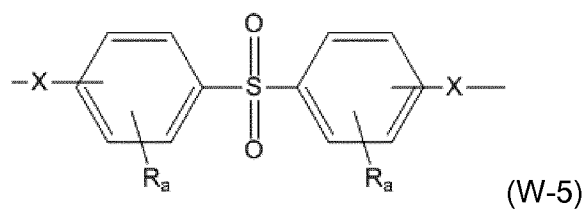
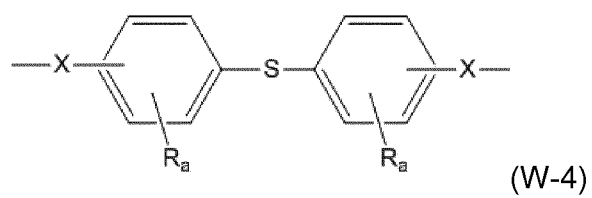
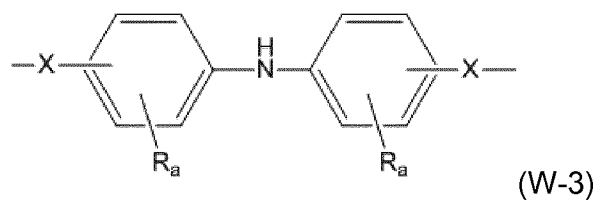
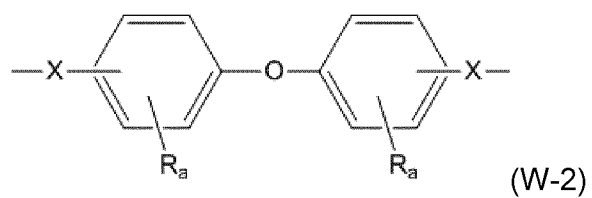


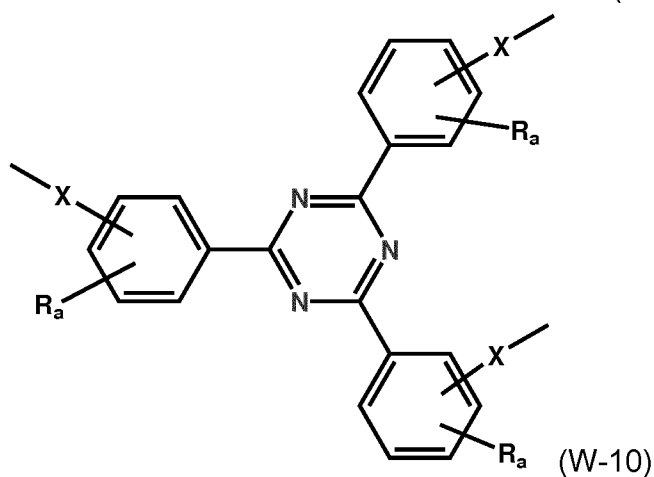
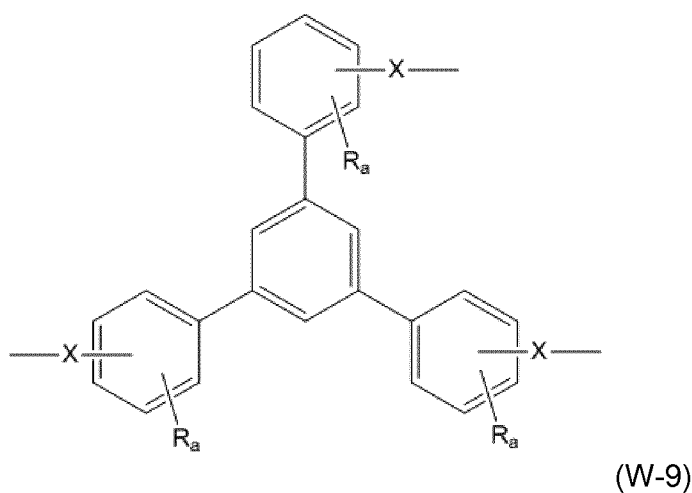
(A-1).

[0033] According to another embodiment, the polymer (P) is such that W in formula is an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one a divalent oxygen or sulphur, preferably two divalent oxygens or sulphurs, more preferably two divalent oxygens. According to this embodiment, W may for example be composed of at least one benzene moiety, for example two, three or four benzene moieties. According to this embodiment the at least two optionally substituted anthracenyl rings (AnR) are preferably linked to the benzene moiety(ies) by one(several) divalent oxygen(s) or sulphur(s).

[0034] According to another embodiment, the polymer (P) is such that W in formula (A) is selected from the group consisting of:







wherein:

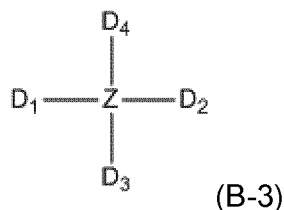
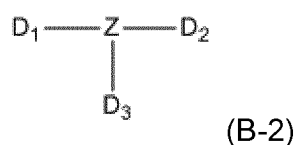
- X is a divalent oxygen or sulphur, preferably divalent oxygen;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 8, preferably 0.

[0035] Preferred monomers (A) are 2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene (BANDS), 2,4,6-tris(4-(anthracen-2-yloxy)phenyl)-1,3,5-triazine (TANTA), or oxybis(4,1-phenylene))bis((2-(anthracen-1-yloxy)-6-(anthracen-2-yloxy)phenyl)methanone (BDABPE).

[0036] Optional monomer (B)

[0037] According to the present invention, monomer (B) comprises at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A).

[0038] According to an embodiment of the present invention, monomer (B) is selected from the group consisting of:



wherein:

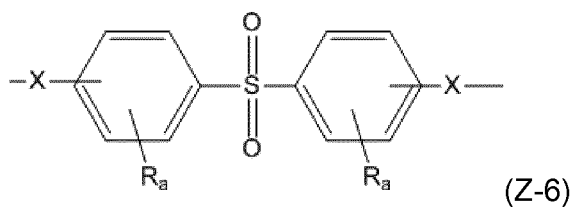
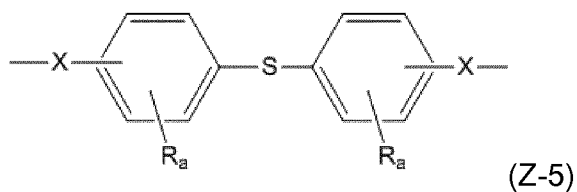
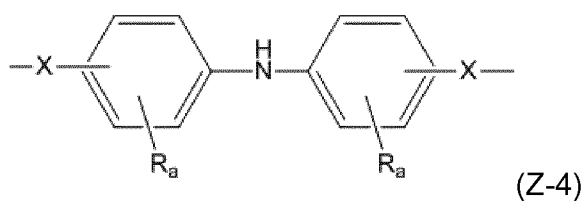
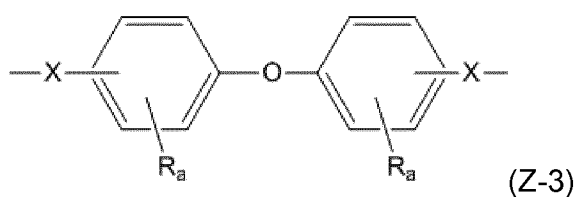
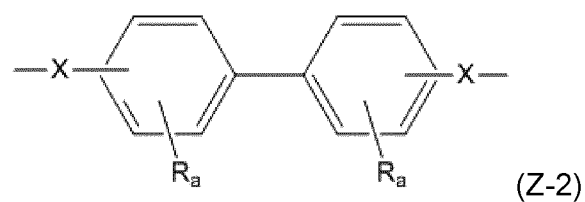
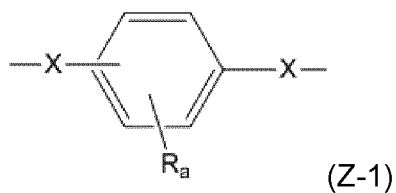
- Z is selected from the group consisting of:

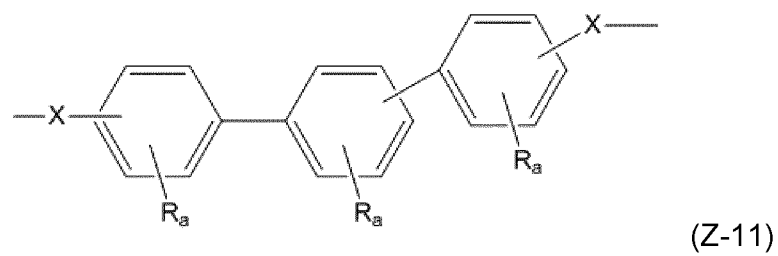
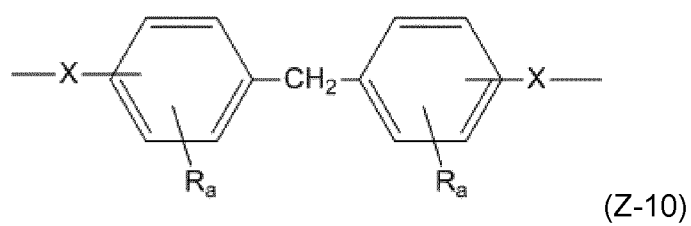
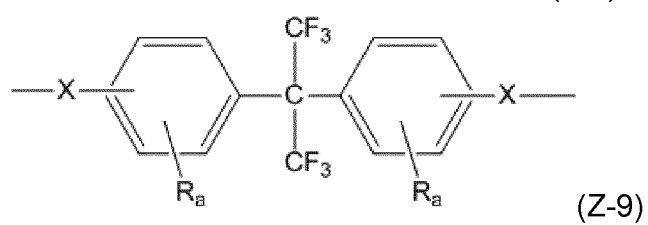
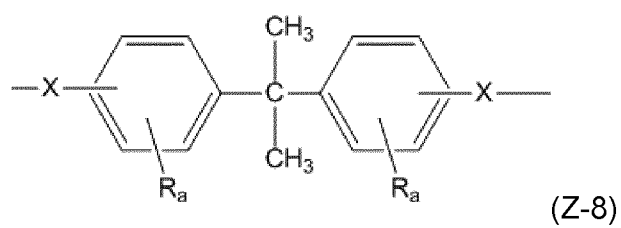
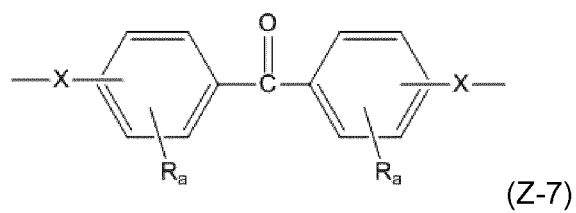
- (i) a bond;
- (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
- (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

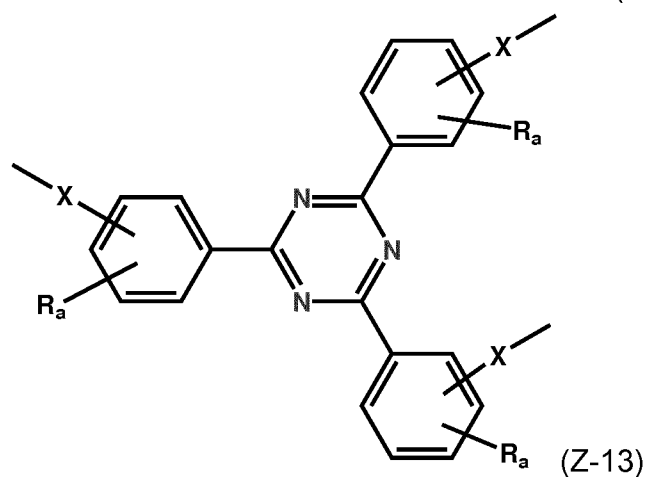
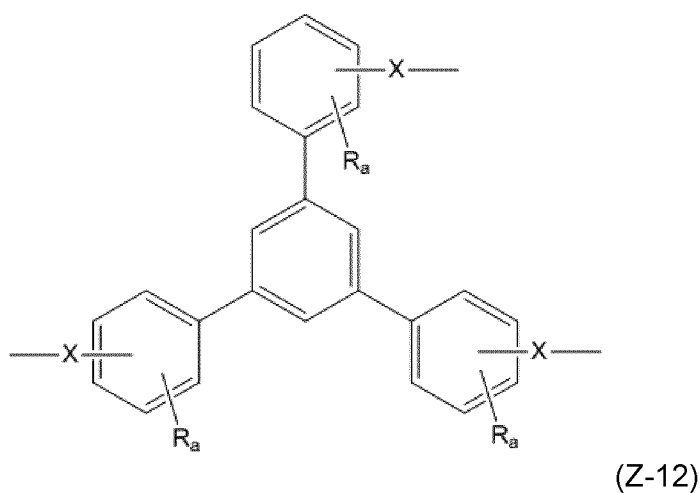
- R is a halogen atom or an alkyl group, optionally branched, preferably an C₁-C₁₈ alkyl group optionally substituted with one or several halogen atoms, and

- D₁, D₂, D₃, D₄, independently from each other, is a moiety able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A).

[0039] According to this embodiment, Z in formula (B-1), (B-2) or (B-3) above is selected from the group consisting of:







wherein:

- X is a bond, a divalent oxygen or a divalent sulphur;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 8, preferably 0.

[0040] Preferred monomer (B) is 4,4'-bismaleimido-diphenylmethane (BMI).

[0041] Polymers (P) and methods of preparation

[0042] As explained above, polymers (P) according to the present invention can be obtained by cycloaddition reaction of at least one monomer (A) and, optionally, at least one monomer (B) as defined above. In one embodiment, the cycloaddition reaction is a [4+2] cycloaddition reaction (DA reaction); in

another embodiment the cycloaddition reaction is a [4+4] photocycloaddition reaction.

- [0043] “At least one” means that each of monomer (A) and, optionally, monomer (B) can be equal to or different from one another.
- [0044] In one embodiment, polymers (P) can be obtained by cycloaddition reaction of at least one monomer (A) comprising only optionally substituted anthracenyl rings [herein after “polymers (P1)”], without the use of any monomer (B).
- [0045] In another embodiment, polymers (P) can be obtained by cycloaddition reaction of at least one monomer (A) comprising at least one substituted anthracenyl ring and at least another moiety able to react in a cycloaddition reaction with said optionally substituted anthracenyl ring, without the use of any monomer (B). In one embodiment, the at least one monomer (A) comprises at least one substituted anthracenyl ring and at least another moiety able to react as dienophile in a [4+2] cycloaddition reaction with said at least one optionally substituted anthracenyl.
- [0046] In another embodiment, polymers (P) can be obtained by cycloaddition reaction of at least one monomer (A) comprising only optionally substituted anthracenyl rings, and at least one monomer (B).
- [0047] Preferred polymers (P) are those that can be obtained by DA reaction of monomers (A) and monomers (B) substituted with maleimide moiety. Even more preferred are polymers obtained by DA reaction of 2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene (BANDS), 2,4,6-tris(4-(anthracen-2-yloxy)phenyl)-1,3,5-triazine (TANTA) or oxybis(4,1-phenylene))bis((2-(anthracen-1-yloxy)-6-(anthracen-2-yloxy)phenyl)methanone (BDABPE) with 4,4'-bismaleimido-diphenylmethane (BMI).
- [0048] For polymers (P) obtainable by [4+4] photocycloaddition, the reaction of monomers (A), optionally monomers (B), is advantageously carried out by exposure to light of wavelength from 300 to 600 nm, preferably from 340 to 450 nm or from 350 to 400 nm, more preferably at a wavelength of 365 nm. The reaction can be carried out in a solvent or in the melt.

- [0049] For polymers (P) obtainable by DA reaction, the reaction of monomers (A) and monomers (B) is advantageously carried out by heating at temperatures ranging from 50 to 300°C, preferably from 60 to 250 °C, more preferably from 50 to 200 °C. The reaction can be carried out in a solvent or in the melt.
- [0050] The way of conveying UV radiation to the composition (C) is not specifically restrained, and UV radiation sources of different type may be used. Further, a source emitting a monochromatic radiation or a source emitting a wider range of wavelength may be used.
- [0051] Due to the structure of monomers (A) and monomers (B), the polymerization reaction proceeds via a cycloaddition reaction between monomers (A) and, optionally monomers (B).
- [0052] The polymer (P) of the present invention may have a number average molecular weight M_n of less than 15,000 g/mol, as determined by Gel Permeation Chromatography (GPC) in methylene chloride, preferably less than 10,000 g/mol or less than 7,500 g/mol.
- [0053] In the case of polymers (P) obtained from difunctional monomers, the number average molecular weight M_n (e.g. obtained by multiplying the number average degree of polymerization by the molecular weight of the monomer unit) can be controlled by choosing the number/concentration of reactive groups, so-called optionally substituted anthracenyl rings (AnR), and it will depend on the extent of the reaction that is controlled mainly by choosing the time and intensity of exposure to heat and/or UV light, or by a stoichiometric imbalance of A and B monomers. The desired number average degree of polymerization can be calculated according to Carothers' equation. The progress of the reaction can be monitored by means known to those skilled in the art, such as the viscosity of the reaction mixture or GPC of reaction aliquots. When a solvent is used, polymers (P) can then be isolated from the reaction mixture by known methods, preferably by precipitation with a polar protic organic solvent, typically methanol, and drying.
- [0054] The cycloaddition reaction does not involve the formation of by-products that would need to be removed from the polymer and can also be directly carried

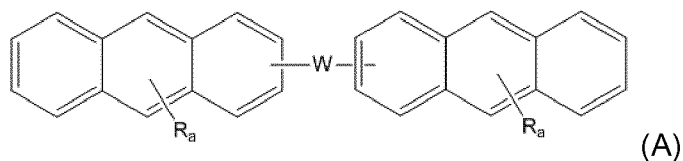
out in an extruder, in a compression mold or in a 3D printer, while conventional reactions for producing aromatic polymers are not amenable to being carried out in this type of equipment. An additional advantage is the possibility of conducting the polymerization in the melt phase with very low amounts of solvent or no solvent at all; this eliminates the cost and environmental consequences of using a solvent, and further improves the compatibility of the reaction with equipment normally used for extrusion, compression molding or 3D printing.

[0055] Method of using the blend of monomer (A), optionally monomers (B)

[0056] The present invention relates to a method for coating a surface, comprising:

a) applying to the surface:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:

(i) a bond;

(ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and

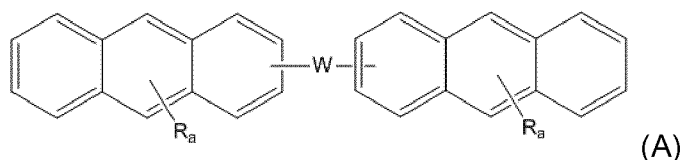
(iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 18, preferably 0;
- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A), optionally in combination with one or more solvents and/or additives, and
- b) irradiating the surface at a wavelength ranging from 300 nm to 600 nm, preferably from 350 nm to 400 nm, more preferably at a wavelength of 365nm.

[0057] The present invention also relates to a method for coating a surface, comprising:

a) applying to the surface:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:
 - (i) a bond;
 - (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 - (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at

least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

- a is 0 or an integer from 1 to 18, preferably 0;

- at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A),

optionally in combination with one or more solvents and/or additives,

b) heating the surface at a temperature ranging from 60 °C to 250 °C, preferably from 65 °C to 200 °C.

[0058] Monomers (A) and optionally monomers (B) in these methods may be in the form of a powder or a solution in a solvent.

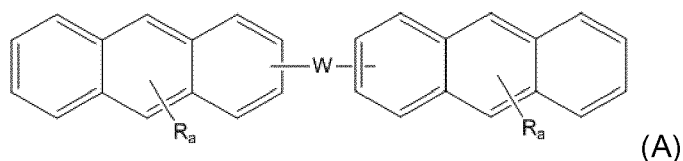
[0059] The methods described above may also comprise at least one step consisting of:

- applying the monomers in the form of liquid coatings, and
- drying the coating before curing in order to allow the solvent to evaporate.

[0060] Polymer formulation (F) and uses

[0061] The present invention also relates to a polymer formulation (F) comprising:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:

(i) a bond;

(ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
(iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

- a is 0 or an integer from 1 to 18, preferably 0;

- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A),

- at least one solvent,

- optionally at least one additive selected from the group consisting of excitation transfer reagents, upconverters, complex formers and Lewis acids.

[0062] Excitation transfer reagents are molecules that absorb photons to reach an excited state, that then transfer the excited state to anthracene moieties. The excited anthracene moiety can then react to form dimers without ever having absorbed a photon.

[0063] Upconverters are excitation transfer reagents that can absorb photons at wavelengths ineffective for anthracene dimerization, but are still able to transfer the excited state to anthracene moieties.

[0064] Complex formers are molecules, such as gamma-cyclodextrin, that can form complexes with two anthracene moieties to geometrically constrain them into close proximity that favors dimerization.

- [0065] Diels Alder reactions with electron poor dienophiles (e.g. maleimide) can be promoted by adding Lewis acids that can complex the ketone oxygens, making the double bond even more electron poor.
- [0066] The present invention also relates to a method for manufacturing a three-dimensional (3D) article, comprising:
- a) preparing a polymer formulation (F) as above-described,
 - b) printing layers of the 3D article from the polymer formulation (F).
- [0067] According to an embodiment, the polymer formulation (F) is heated to a temperature of at least 200°C , at least 250°C or at least 280°C before printing.
- [0068] According to an embodiment, the step of printing comprises irradiating the polymer formulation (F), for example a layer of such formulation (F) deposited onto the printing surface, with UV light. The layer preferably presents a size in the range of 10 µm to 300 µm, for example 50 µm to 150 µm.
- [0069] The UV light can for example be laser light. The irradiation is preferably of sufficient intensity to cause substantial curing of the polymer formulation (F), for example the layer of such formulation (F). Also, the irradiation is preferably of sufficient intensity to cause adhesion of the layers of polymer formulation (F).
- [0070] Recycling
- [0071] The present invention also relates to a method for recycling a coating or a formed article, comprising the polymer (P) of claim 7, wherein the method comprises submitting the coating or formed article to UV irradiation at a wavelengths lower than 300 nm.
- [0072] The present invention also relates to a method for recycling a coating or a formed article, comprising the polymer (P) of claim 8, wherein the method comprises submitting the coating or formed article to heating at a temperature ranging from 100°C to 500°C.
- [0073] The present invention also relates to a recycled material obtainable by these recycling methods.

[0074] The present invention also relates to films, coatings or shaped articles obtained from the polymer (P) as above-described.

[0075] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

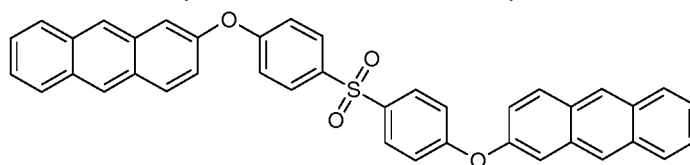
[0076] The invention will be now described in more detail with reference to the following examples whose purpose is merely illustrative and not limitative of the scope of the invention.

[0077] **Examples**

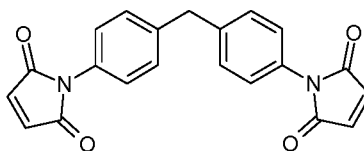
[0078] In the examples below, molecular weight was determined using gel permeation chromatography (GPC) analysis with *N,N*-dimethylformamide (DMF) as the eluent and referenced to polystyrene standards of known molecular weight. GPC analysis was performed with a Waters 2695 separations module with a Waters 2487 Dual Wavelength UV detector (Milford, MA, USA).

[0079] **Example 1 – Synthesis of a polymer of the invention by heating of :**

- monomer A: 2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene
(abbreviated as BANDS):



- monomer B: 4,4'-bismaleimido-diphenylmethane (abbreviated as BMI):



[0080] Step 1 – Synthesis of BANDS

[0081] Synthesis of 2-anthrol

[0082] In a 2000 mL 2-neck round bottom flask (equipped with a nitrogen gas inlet/outlet) potassium carbonate (Armand Products Company, 30.912 g) was dissolved in 1000 mL of deionized water. After complete dissolution of base, 2-hydroxyanthraquinone (TCI Chemicals, 20.070 g) was added portion wise turning the colorless solution briefly to yellow and quickly to dark red. After the addition of 2-hydroxyanthraquinone, 10 mL of isopropyl alcohol (Fisher Scientific) was added to the reaction mixture and allowed to stir for 10 minutes under nitrogen flow. Sodium borohydride (Alfa Aesar, 27.113 g) was added in 5 portions over a period of 4 hours. The mixture was allowed to stir at room temperature for 24 hours resulting in a light brown solution. The mixture was acidified by the drop wise addition of concentrated hydrochloric acid (Fisher Scientific) until the pH was about 5. The resulting precipitate was collected by vacuum filtration, washed with deionized water, and dried in a vacuum oven (80 °C @ 30 mmHg) overnight to obtain a greenish brown solid (17.949 g).

[0083] The product was sublimed by heating under vacuum (200 °C @ 2-5 mmHg) and condensed on a glass finger cooled with ice water. The apparatus was taken apart and rinsed with acetone (Acros) to wash the collected yellow solid off of the cold finger. The collected acetone solution was evaporated to yield a yellow solid (3.563 g).

[0084] Synthesis of BANDS (2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene)

[0085] In a 2-neck 250-mL round bottomed flask (equipped with N₂ inlet/outlet, distillation head with condenser, and thermocouple), 2-anthrol (2.630 g, 13.55 mmol), 4,4'-dichlorodiphenyl sulfone (Solvay, 1.938 g, 6.749 mmol), and potassium carbonate (Armand Products Company, 2.002 g, 14.49 mmol) were suspended in 60 mL of anhydrous *N*-methylpyrrolidone (NMP, Alfa Aesar). The reaction mixture was allowed to heat to 185 °C, the reaction progress was monitored by TLC, and the reaction was determined to be complete after 3 hours. The reaction mixture was allowed to cool down to room temperature and then the product was precipitated by pouring reaction

solution into 400 mL of deionized water. The crude product was collected by vacuum filtration and was again washed by suspending in 400 mL of deionized water. The crude product was again collected by vacuum filtration and placed in vacuum oven (60 °C @ 30 mmHg) for 18 hours to dry. After drying, 4.189 g of crude solid was obtained (102.9% yield). The final product was obtained by recrystallization from *n*-butoxyethanol (Alfa Aesar) to provide 1.782 g (43.8% yield) of black solid.

[0001] NMR spectra were consistent with the expected structure of the title product. ¹H NMR (500 MHz, DMF-*d*₇) δ 8.69 (s, 1H), 8.58 (s, 1H), 8.27 (d, *J* = 9.2 Hz, 1H), 8.12 (dd, *J* = 25.1, 7.2 Hz, 4H), 8.11 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.60 – 7.52 (m, 4H), 7.39 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (126 MHz, DMF) δ 161.9, 152.6, 136.5, 132.5, 132.3, 131.7, 131.5, 130.4, 129.7, 128.6, 128.1, 126.9, 126.4, 125.9, 125.8, 121.2, 118.8, 115.7.

[0002] The average molecular weight data from the GPC curve is shown in Table 1 below.

[0003] Table 1 - GPC data for BANDS dissolved in DMF

		BANDS
M _n	g/mol	631
M _w	g/mol	659
M _w /M _n	g/mol	1.17
M _z	g/mol	798
M _z +1	g/mol	978

[0004] Step 2 – Polymer synthesis

[0005] In a 50 mL 3-neck round bottomed flask equipped with a mechanical stirrer and blanketed under nitrogen, 0.100 g (0.166 mmol) of BANDS and 0.059 g (0.166 mmol) of 4,4'-bismaleimido-diphenylmethane were dissolved in 0.372 g of *N,N*-dimethylformamide (DMF). The reaction mixture was subsequently heated to 120 °C, allowed to stir at this temperature for 10 h, cooled to room

temperature, and a sample was collected for GPC analysis. The final polymer was obtained by adding methanol to precipitate the product, collecting the solid by vacuum filtration, and drying for 6 hours under high vacuum (0.2 torr) to give a beige solid.

GPC data was used to confirm polymerization occurred as shown in Table 2 below.

Table 2 - GPC Data Showing Increased Molecular Weight of Maleimide Anthracene Diels – Alder adduct compared to starting monomers.

		BANDS	4,4'-Bismaleimido-diphenylmethane	1:1 mixture after heating in DMF at 120 °C for 10 h
M_n	g/mol	631	561	1,982
M_w	g/mol	659	572	12,025
M_w/M_n	g/mol	1.17	1.02	6.07
M_z	g/mol	798	582	39,055
M_z+1	g/mol	978	591	90,103

[0006] **Example 2 - Synthesis of a polymer of the invention by photopolymerization of BANDS (monomer A)**

Example 2A - A 20mL scintillation vial was charged with 60 mg of 2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene (abbreviated as BANDS), magnetic stir bar, and 10 mL of N-Methyl-2-pyrrolidone (NMP). The suspension was capped and the sample was irradiated under 100W, 365nm light for 48h with agitation while heated at 55°C. After the 48h, the vial was removed from the light source and allowed to stand to cool to room temperature.

[0007] Example 2B- A 20mL scintillation vial was charged with 60 mg of 2,2'-((sulfonylbis(4,1-phenylene))bis(oxy))dianthracene (BANDS), magnetic stir bar, and 10 mL of 1,4-Dioxane. The suspension was capped and the sample was under 100W, 365nm light source for 48h with agitation while heated at 55°C. After the 48h, the vial was removed from the light source and allowed to stand to cool to room temperature.

[0008] Table 3. GPC Data Showing Changes in Molecular Weight of BANDS dissolved in NMP or 1,4-dioxane after exposure to 365 nm UV light.

		BANDS	Poly-BANDS after irradiation at 366 nm in NMP	Poly-BANDS after irradiation at 365 nm in 1,4-Dioxane
Mn	g/mol	127	2113	2858
Mw	g/mol	197	3209	3659
Mw/Mn	g/mol	1.55	1.52	1.28
Mz	g/mol	6.29	4694	4703
Mz+1	g/mol	1651	6372	5877

[0009] **Example 3 - Light-induced dissociation of Poly-BANDS**

[0010] 2 mL of the each pf the reaction matrixes from Example 2 was placed in a well plate and irradiated using a 14W, 254 nm light source for 4h at room temperature.

[0011] Table 4. GPC Data Showing Changes in Molecular Weight of poly-BANDS dissolved in NMP or 1,4-dioxane after exposure to 254 nm UV light.

		Dissociation poly-BANDS in NMP	Dissociation poly-BANDS in 1,4-Dioxane
Mn	g/mol	1283	1438

Mw	g/mol	1987	2432
Mw/Mn	g/mol	1.55	1.69
Mz	g/mol	2952	3766
Mz+1	g/mol	4126	5260

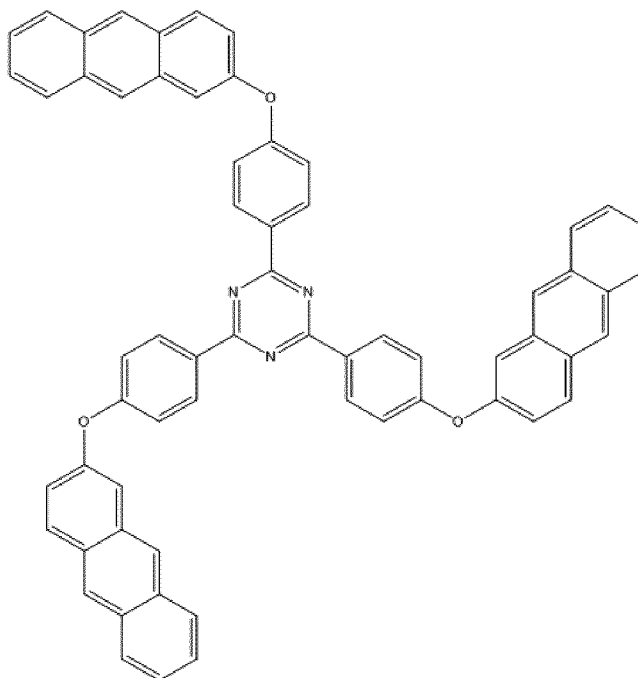
[0012] **Example 4 - Thermal-induced dissociation of Poly-BANDS**

[0013] 2 mL of each of the reaction matrixes of Example 2 was placed in a three-neck round bottom flask. The flask was then equipped with a magnetic stirbar, reflux condenser, and a gas inlet/out and charged with 5g of diphenyl ether. The reaction flask was then heated on an oil bath with agitation at 210°C for 14h under a flow of nitrogen. After heating, the reaction was allowed to stand to reach room temperature.

[0014] Table 5. GPC Data Showing Changes in Molecular Weight of poly-BANDS dissolved in NMP or 1,4-dioxane after heating at 210 °C.

		Thermal dissociation poly-BANDS in NMP	Thermal dissociation poly-BANDS in 1,4-Dioxane
Mn	g/mol	285	462
Mw	g/mol	1120	960
Mw/Mn	g/mol	3.43	2.09
Mz	g/mol	2535	1622
Mz+1	g/mol	3917	2315

[0015] **Example 5 - Synthesis of a polymer of the invention by photopolymerization of monomer A = 2,4,6-tris(4-anthracen-2-yloxy)phenyl)-1,3,5-triazine (TANTA)**



[0016] Step 1 – Synthesis of TANTA

[0017] In a 100 mL 2-neck round bottomed flask equipped with a Dean-Stark trap, a condenser, a thermocouple, and a gas inlet/outlet, 2-hydroxyanthracene (0.4509 g) and anhydrous potassium carbonate (0.3298 g) were combined with 10.00 mL of anhydrous *N*-methyl pyrrolidone. The mixture was heated to 110 °C under a flow of nitrogen and allowed to stir for 1 hour. After an hour, the mixture was cooled down to 60 °C and 2,4,6-tris(4-fluorophenyl)-1,3,5-triazine (0.2777 g) was added to reaction mixture. The mixture was heated to 165 °C and allowed to stir for 2 hours under a flow of nitrogen. The crude product was precipitated by the addition of 20 mL of hexane and 30 mL of diethyl ether and collected by vacuum filtration. The crude product was washed with three 100 mL portions of deionized water and three 100 mL portions of methanol. The resulting product was collected by vacuum filtration and placed under vacuum at 30 mmHg and 80 °C for 24 hours to obtain 0.5266 g of product 2,4,6-tris(4-anthracen-2-yloxy)phenyl-1,3,5-triazine (TANTA).

[0018] ^1H NMR (400 MHz, DMSO- d_6): δ 8.80 (d, 6H), 8.64 (s, 3H), 8.52 (s, 3H), 8.23 (d, 3H), 8.06 (dd, 6H), 7.73 (s, 3H), 7.52 (m, 6H), 7.42 (dd, 3H), 7.37 (d, 3H) ppm.

[0019] Step 2 – Polymer synthesis

[0020] In a 20mL scintillation vial, 0.090 g of TANTA from step 1 and 10.0 mL of *N*-methyl-2-pyrrolidone (NMP) were combined. The vial was capped and the sample was irradiated under 100W, 365 nm light for 72h with magnetic stirring while heated at 55°C. After the 72 hours, the vial was removed from the light source, allowed to stand and cool to room temperature.

[0021] Table 6 - GPC data for TANTA dissolved in DMF

		TANTA	Poly-TANTA
M_n	g/mol	261	4758
M_w	g/mol	520	66932
M_w/M_n	g/mol	1.99	14.07
M_z	g/mol	897	168212
M_z+1	g/mol	1233	211248

[0022] Example 6 - Light-induced dissociation of Poly-TANTA

[0023] A 2mL sample from Example 5 was placed in a well plate and irradiated using a 14W, 254 nm light source for 4h at room temperature.

[0024] Table 7. GPC Data Showing Changes in Molecular Weight of poly-TANTA after exposure to UV-Light

		Dissociation poly-TANTA
M_n	g/mol	1436
M_w	g/mol	29674

Mw/Mn	g/mol	20.67
Mz	g/mol	122121
Mz+1	g/mol	166268

[0025] **Example 7 - Thermal dissociation of Poly-TANTA**

[0026] A 2mL sample from Example 5 was placed in a three-neck round bottomed flask. The flask was then equipped with a magnetic stir bar, dean-stark trap with condenser above, and a gas inlet/outlet and charged with 3.5g of diphenyl ether. The reaction flask was then heated in an oil bath at 215°C, to remove via distillation, 2+ mL of N-methyl-2-pyrrolidone, distilled over 2 mL of *N*-methyl-2-pyrrolidone, and the resulting mixture allowed to stir for 4 hours under a flow of nitrogen. After 4 hours of reacting at 215 °C, the mixture was allowed to cool to room temperature.

[0027] Table 8. GPC Data Showing ReducedMolecular Weight of poly-TANTA after exposure to heat

		Dissociated poly-TANTA
Mn	g/mol	415
Mw	g/mol	1075
Mw/Mn	g/mol	2.59
Mz	g/mol	2416
Mz+1	g/mol	3918

[0028] **Example 8 – Synthesis of a polymer of the invention by heating of :**

- monomer A: TANTA

- monomer B: BMI

[0029] In a 100 mL 3-neck round bottomed flask equipped with a condenser, mechanical stirrer, and inert gas inlet/outlet, was charged with 0.506 g of

2,4,6-tris(4-(anthracen-2-yloxy)phenyl)-1,3,5-triazine (TANTA), 0.327 g of bismaleimido diphenyl methane (BMI), and 0.660 g of butylated hydroxy toluene were combined with 15.00 mL of degassed chlorobenzene. The mixture was heated to 130 °C under a flow of nitrogen and allowed to stir overnight. The reaction was determined to be complete in 20 hours by TLC. The product was precipitated by the addition of 20 mL of methanol and collected by vacuum filtration. The crude product was washed with three 100 mL portions of methanol. The resulting product was collected by vacuum filtration and placed under vacuum at 30 mmHg and 50 °C for 24 hours to obtain 1.1806 g of a white solid. A sample of 0.062 g of TANTA-co-BMI was washed with three 50 mL portions of dichloromethane and the insoluble fraction was collected by vacuum filtration, indicative of the formation of a crosslinked polymer. polymer.

[0030] **Example 9 - Thermally-Induced de-polymerization of TANTA-co-BMI**

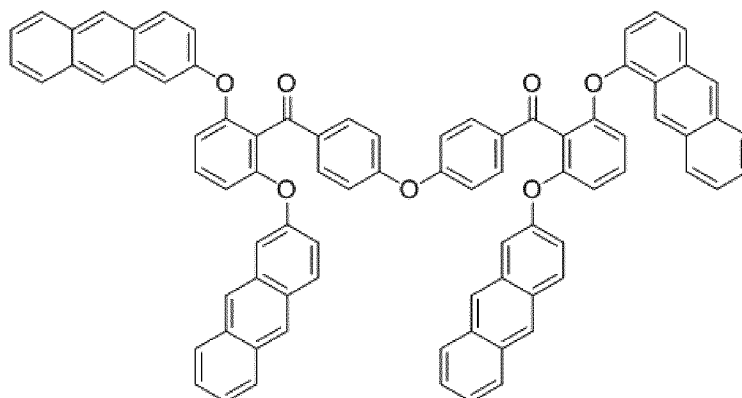
[0031] A 100 mL three-neck amber round bottomed flask equipped with a reflux condenser, gas inlet/outlet and magnetic stir-bar was charged with 0.0623 g of TANTA-co-BMI, 0.1243 g of butylated hydroxyl toluene and 3.06 g of diphenyl ether. The mixture was then placed on an oil bath and heated under a flow of inert gas (nitrogen) at 225°C for 4 hours. After 4 hours, an aliquot of the reaction mixture was quenched and sent for GPC analysis. The product was precipitated with methanol and was collected by vacuum filtration. The crude product was washed with three 25 mL portions of methanol. The resulting product was collected by vacuum filtration and placed under vacuum at 30 mmHg and 50 °C for 24 hours to obtain 0.054 g of material. The product was completely soluble in dichloromethane, which proves the depolymerisation (in comparison to the polymer which was insoluble in dichloromethane).

[0032] Table 9. GPC Data Showing Changes in Molecular Weight of TANTA-co-BMI

		TANTA-co-BMI	Dissociation TANTA-co-BMI
Mn	g/mol	4622	3445
Mw	g/mol	7553	10243
Mw/Mn	g/mol	1.63	2.97
Mz	g/mol	11729	23279
Mz+1	g/mol	15803	38114

[0033] **Example 10** – Synthesis of a polymer of the invention by heating of :

- monomer A: oxybis(4,1-phenylene))bis((2-(anthracen-1-yloxy)-6-(anthracen-2-yloxy)phenyl)methanone (abbreviated as BDABPE)



- monomer B: BMI

[0034] **Step 1 – Synthesis of BDABPE**

A 250 ml amber two neck round-bottomed flask equipped with a Dean-Stark trap was charged with 45mL of anhydrous toluene, 50mL anhydrous NMP, and a magnetic stir bar, and the mixture was agitated under a flow of N₂. The flask was then charged with 4.85 g of 2-anthrol, 1.2 g of potassium hydroxide, and 0.7 g of potassium carbonate and then heated to 140°C for 2h to azeotrope all water out of the flask. The mixture was then heated to 160 °C to remove the toluene via distillation. After the removal of toluene, the reaction mixture was then allowed to cool to 60°C. A separate solution composed of 2.25g (oxybis(4,1-phenylene))bis((2,6-difluorophenyl)methanone in 15mL of anhydrous NMP was made and

injected into the amber flask. After the addition, the resulting mixture was then heated at 200 °C for 120h and then cooled to room temperature by standing. After cooling, 100 mL of DI water was added to the flask and the resulting mixture was collected by vacuum filtration. The collected solid was then washed with three 250 mL portions of hot DI water and vacuum dried at 30°C and 25 in Hg for 48h yielding 3.33 g of an off white solid. The solid was recrystallized from DMF twice before further use.

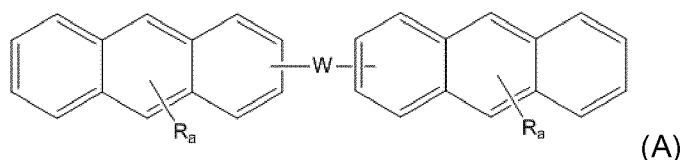
[0035] Step 2 – Polymer synthesis

[0036] A 100mL three-neck RBF equipped with a thermocouple, a reflux condenser, a gas inlet/outlet, and a mechanical stirrer was charged with 580 mg of BDABPE, 159 mg of BMI, 125 mg of butylated hydroxyl toluene (BHT), and 10 mL of chlorobenzene. The suspension was then placed on an oil bath and heated under a flow of inert gas (nitrogen) at 130°C for 20h. After heating, the reaction was allowed to stand for 1h to cool to room temperature. The reaction mixture was then poured into 100mL of methanol, and the precipitate was collected by vacuum filtration and washed with 200 mL methanol. The resulting powder, BDABPE-co-BMI, was then dried under vacuum at 50°C, and 30inHg for 72h.

Claims

Claim 1. A polymer (P) comprising recurring units obtainable by cycloaddition reaction of:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):

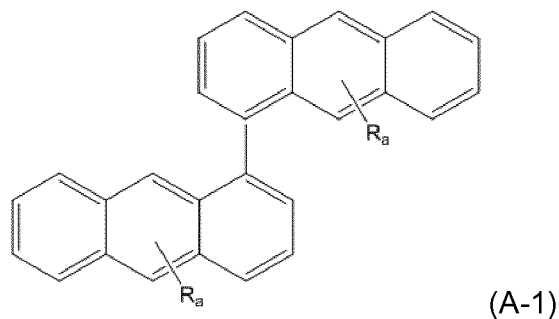


wherein

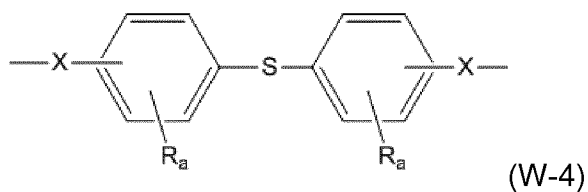
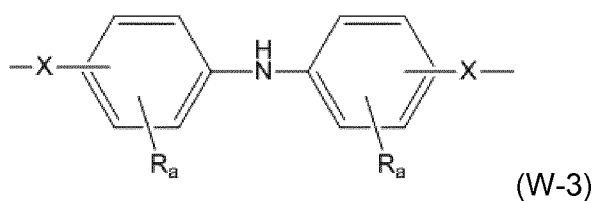
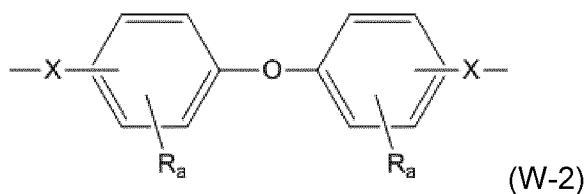
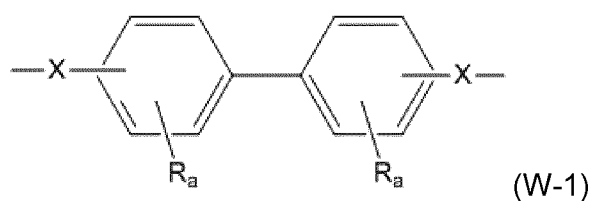
- W is selected from the group consisting of:
 - (i) a bond;
 - (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 - (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 18, preferably 0;
- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A).

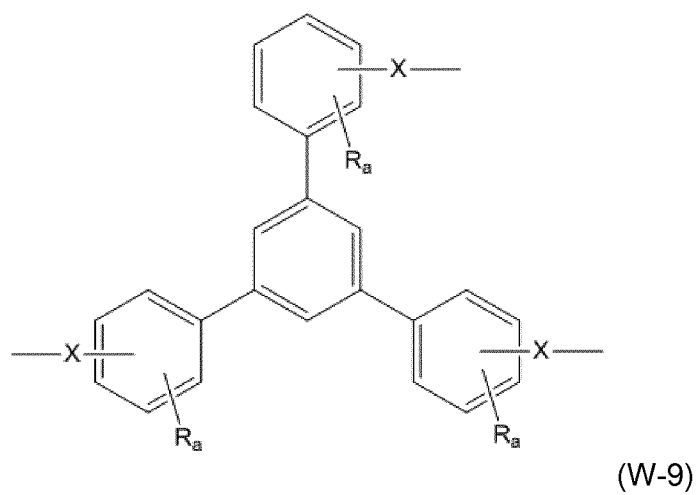
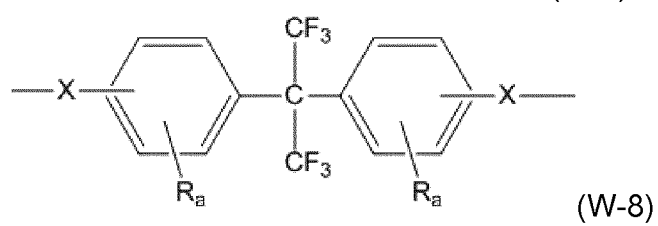
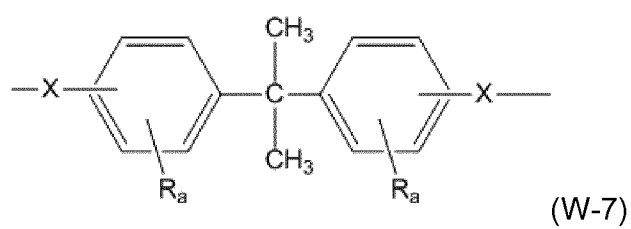
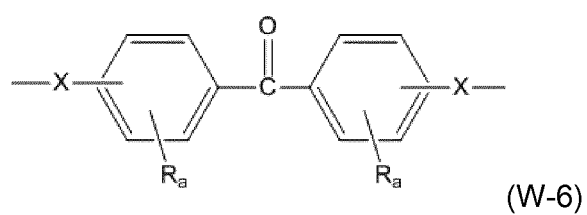
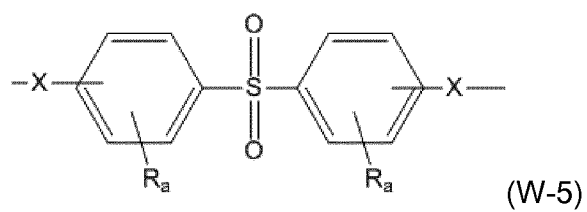
Claim 2. The polymer (P) of claim 1, having a Mn of less than 15,000 g/mol, as determined by Gel Permeation Chromatography (GPC) in methylene chloride, preferably less than 10,000 g/mol or less than 7,500 g/mol.

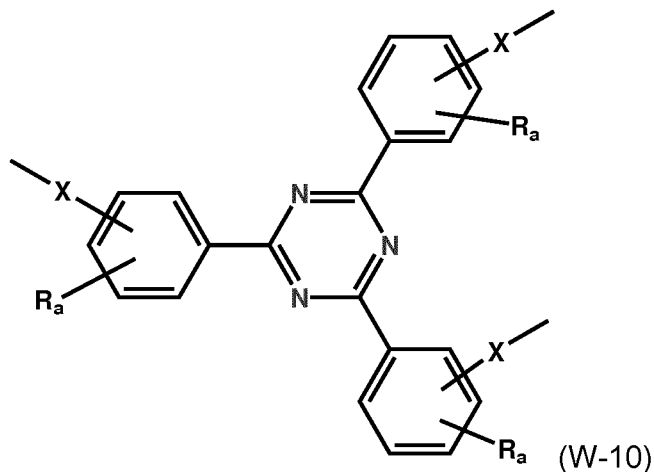
Claim 3. The polymer (P) of claim 1 or 2, wherein monomer (A) is according to formula (A-I):



Claim 4. The polymer (P) of claim 1 or 2, wherein W in formula (A) is selected from the group consisting of:



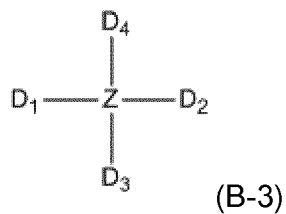
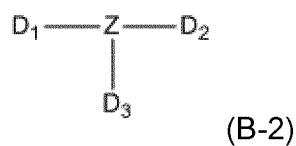




wherein:

- X is a divalent oxygen or sulphur, preferably divalent oxygen;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 8, preferably 0.

Claim 5. The polymer of any one of the preceding claims, wherein monomer (B) is selected from the group consisting of:



wherein:

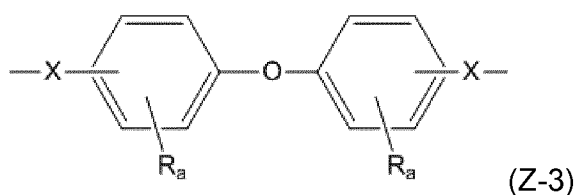
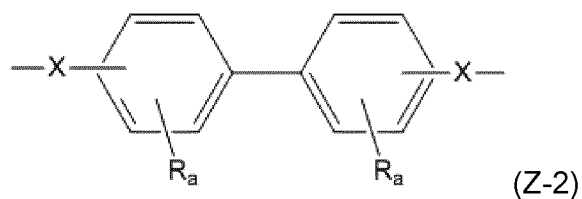
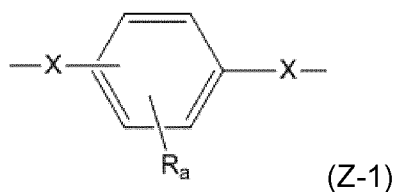
- Z is selected from the group consisting of:
 - (i) a bond;

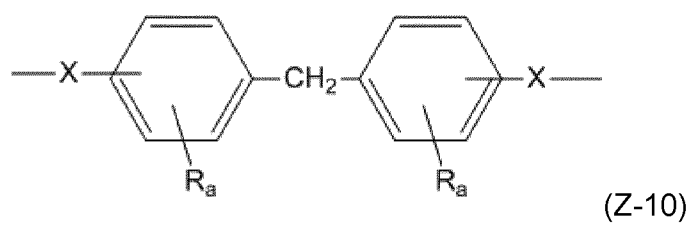
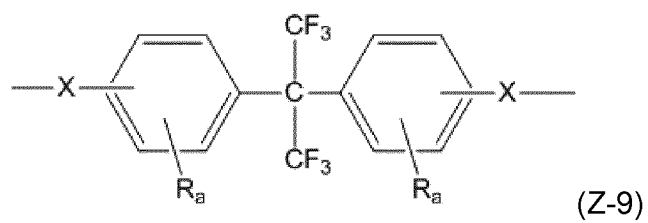
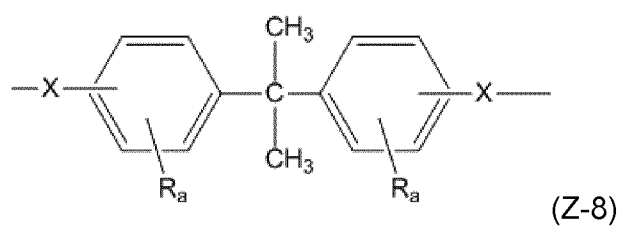
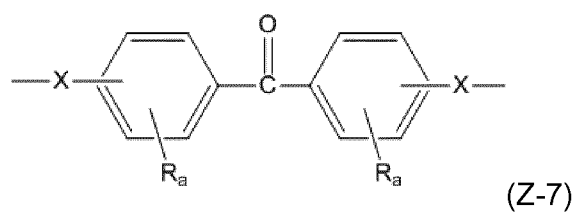
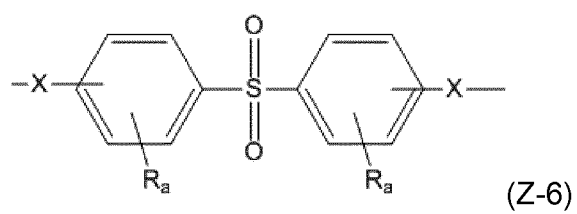
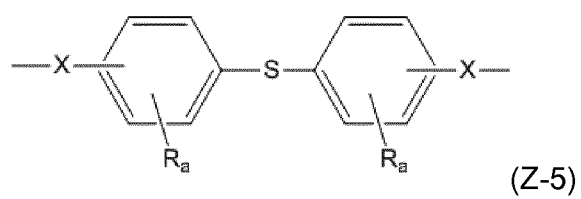
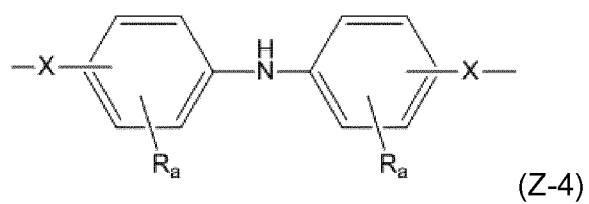
(ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

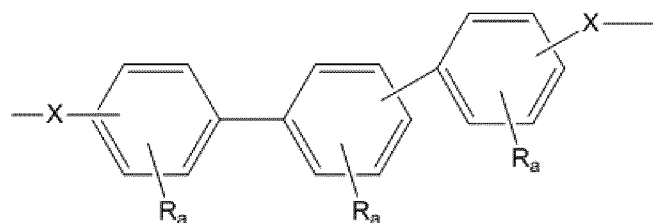
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

- D₁, D₂, D₃, D₄, independently from each other, is a moiety able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A).

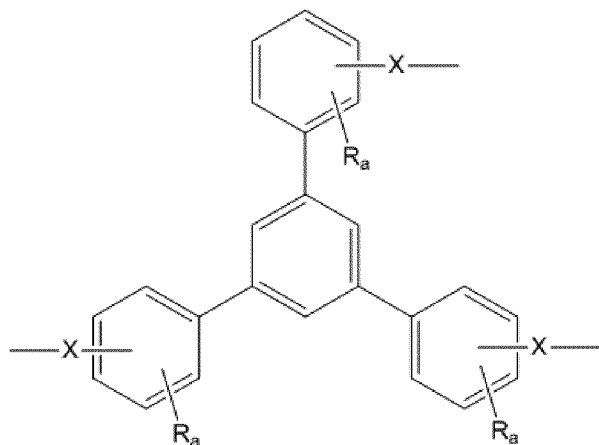
Claim 6. The polymer of claim 5, wherein wherein Z in formula (B-1), (B-2) or (B-3) is selected from the group consisting of:



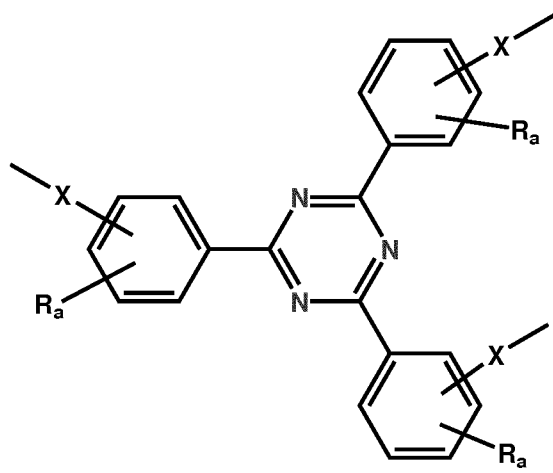




(Z-11)



(Z-12)



(Z-13)

wherein:

- X is a bond, a divalent oxygen or a divalent sulphur;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 8, preferably 0.

Claim 7. The polymer of any one of the preceding claims, obtained by exposing at least one monomer (A), optionally at least one monomer (B), to UV

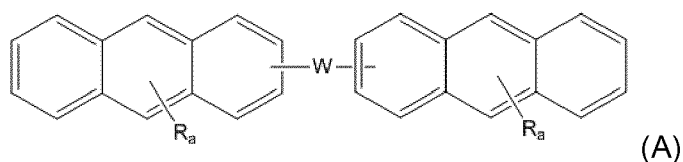
light at a wavelength ranging from 300 to 600nm, preferably from 350 nm to 400 nm.

Claim 8. The polymer of any one of claims 1-6, obtained by heating at least one monomer (A) and at least one monomer (B), to temperature ranging from 60 to 250°C, preferably from 65 °C to 200 °C.

Claim 9. A method for coating a surface, comprising:

a) applying to the surface:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:

(i) a bond;

(ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and

(iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;

- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

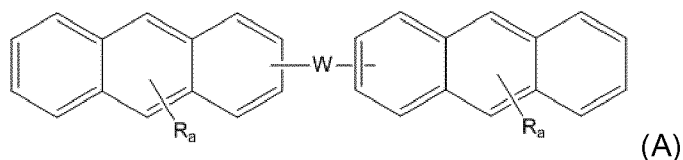
- a is 0 or an integer from 1 to 18, preferably 0;

- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A), optionally in combination with one or more solvents and/or additives, and
- b) irradiating the surface at a wavelength ranging from 300 nm to 600 nm, preferably from 350 nm to 400 nm.

Claim 10. A method for coating a surface, comprising:

a) applying to the surface:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

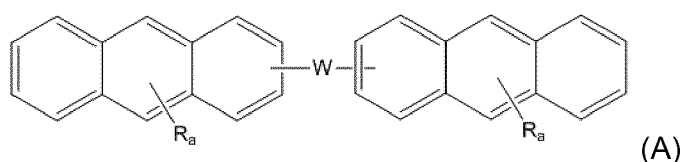
- W is selected from the group consisting of:
 - (i) a bond;
 - (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 - (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and
- a is 0 or an integer from 1 to 18, preferably 0;

- at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A), optionally in combination with one or more solvents and/or additives,
- b) heating the surface at a temperature ranging from 60 °C to 250 °C, preferably from 65 °C to 200 °C.

Claim 11. A method for manufacturing a three-dimensional (3D) article, comprising:

a) preparing a polymer formulation (F) comprising:

- at least one monomer (A) comprising at least two optionally substituted anthracenyl rings (AnR):



wherein

- W is selected from the group consisting of:
 - (i) a bond;
 - (ii) an atom or a moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂-, more preferably from the group consisting of -O-, -C(O)- and -SO₂-; and
 - (iii) an aromatic, aliphatic or cycloaliphatic moiety, said moiety optionally comprising one or several optionally substituted anthracenyl rings (AnR), said moiety optionally comprising at least one atom or moiety selected from the group consisting of -O-, -C(O)-, -NH-, -S-, -SO₂-, -C(CH₃)₂-, and -C(CF₃)₂- and said moiety optionally comprising one or several groups R;
- R is a halogen atom or an alkyl group, optionally branched, preferably an C1-C18 alkyl group optionally substituted with one or several halogen atoms, and

- a is 0 or an integer from 1 to 18, preferably 0;
- at least one solvent,
- optionally at least one monomer (B) comprising at least two moieties being able to react in a cycloaddition reaction with the optionally substituted anthracenyl ring (AnR) of monomer (A),
- optionally at least one additive,

b) printing layers of the 3D article from the polymer formulation (F).

Claim 12. A method for recycling a coating or a formed article, comprising the polymer (P) of claim 7, wherein the method comprises submitting the coating or formed article to UV irradiation at a wavelengths lower than 300 nm.

Claim 13. A method for recycling a coating or a formed article, comprising the polymer (P) of claim 8, wherein the method comprises submitting the coating or formed article to heating at a temperature ranging from 100°C to 500°C.

Claim 14. A recycled material obtainable by the method of claim 12 or 13.

Claim 15. Films, coatings or shaped articles obtained from the polymer of any one of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/067080

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08F32/08 C08J5/00	C08F2/60 C08J5/18
	C08F222/40 C08J11/06	C08F232/00 C09D165/00
	C08G61/12	
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C08G C08F C08J C09D C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YING-LING LIU ET AL: "Self-healing polymers based on thermally reversible Diels-Alder chemistry", POLYMER CHEMISTRY, vol. 4, no. 7, 1 January 2013 (2013-01-01), pages 2194-2205, XP055225692, GB ISSN: 1759-9954, DOI: 10.1039/c2py20957h abstract figures 9,12 text section "6 Extended practice of the DA reaction based self-healing polymers" on page 2201 ----- -/-	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 23 August 2018		Date of mailing of the international search report 07/09/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Meiners, Christian

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/067080

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MIRCEA GRIGORAS ET AL: "Copolymerization of a bisanthracene compound with bismaleimides by Diels-Alder cycloaddition", POLYMER INTERNATIONAL, vol. 50, no. 12, 1 December 2001 (2001-12-01), pages 1375-1378, XP055416959, GB ISSN: 0959-8103, DOI: 10.1002/pi.792 the whole document	1-15
X	MIYUKO OKADA ET AL: "Poly(polyrotaxane): Photoreactions of 9-Anthracene-Capped Polyrotaxane", MACROMOLECULES, vol. 36, no. 26, 1 December 2003 (2003-12-01), pages 9701-9703, XP055416983, US ISSN: 0024-9297, DOI: 10.1021/ma0304729 scheme 1	1,2,5, 7-10, 12-15
Y		11
A	M. GRIGORAS ET AL: "Synthesis and thermal behavior of some anthracene-based copolymers obtained by Diels-Alder cycloaddition reactions", JOURNAL OF APPLIED POLYMER SCIENCE, vol. 107, no. 2, 15 January 2008 (2008-01-15), pages 846-853, XP055416993, US ISSN: 0021-8995, DOI: 10.1002/app.26466 abstract schemes 1-5	1-15
A	CRISTOFOR I. SIMIONESCU ET AL: "Synthesis and polymerization of N-(1-anthryl) maleimide", JOURNAL OF POLYMER SCIENCE, POLYMER LETTERS EDITION, vol. 28, no. 2, 30 January 1990 (1990-01-30), pages 39-45, XP055417025, ISSN: 0360-6384, DOI: 10.1002/pol.1990.140280201 schemes 1,2	1-15
	----- -/-	

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AMUTHA N ET AL: "Synthesis and characterization of pyridine and anthracene containing bismaleimides, bisnadimides and polyaspartimides", JOURNAL OF POLYMER RESEARCH, KLUWER ACADEMIC PUBLISHERS-CONSULTANTS BUREAU, NL, vol. 15, no. 6, 29 April 2008 (2008-04-29), pages 487-499, XP019646004, ISSN: 1572-8935, DOI: 10.1007/S10965-008-9193-3 text section "Properties of BMI and BNI on pages 494/495; table 1	1-15
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