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(71) Applicant: SOLVAY SPECIALTY POLYMERS USA, LLC [US/US]; 4500 McGinnis Ferry Road, ALPHARETTA, Georgia 30005-3914 (US).

(72) Inventors: MONDSCHN, Ryan; 6505 Bradford Pl, Cumming, Georgia 30040 (US). POLLINO, Joel; 10513 New Cove Rd, John Creeks, Georgia 30022 (US). KWAN, Kermit S.; 1035 Ballington Drive, Cumming, Georgia GA 30041 (US). KERCHER, David; 2740 Brook Valley Dr., Cumming, Georgia 30041 (US). KAPELYUSHKO, Valeriy; 63 Corso Giuseppe Romita, 15121 Alessandria (IT).

(74) Agent: BANFI, Gaia; Viale Lombardia, 20, 20021 Bollate MI (IT).

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(54) Title: AROMATIC OLIGOMERS AND POLYMERS MADE THEREFROM

(57) Abstract: The present disclosure relates to new and inventive aromatic oligomers, including the use of such oligomers in the production of useful polymers. Such oligomers contain an aromatic core, flexible spacers, and reactive functionalities. The new and inventive oligomers enable the synthesis of useful polymers in various forms and by multiple processing techniques.

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AROMATIC OLIGOMERS AND POLYMERS MADE THEREFROM

Cross-reference to related applications

- 5 This application claims priority to US provisional application 63/284222 filed on 30 November 2021, the whole content of this application being incorporated herein by reference for all purposes.

Field of the Disclosure

10

The present disclosure relates to new aromatic oligomers suitable for use in the production of useful polymers. Such oligomers comprise versatile functionality that enable the synthesis of useful polymers in various forms and by multiple processing techniques. The reaction of these new molecules with various difunctional
15 comonomers can produce thermoplastic-like linear or branched polymers while homopolymerization or polymerization with multifunctional comonomers can produced crosslinked thermoset structures.

Background of the Disclosure

20

Polymeric materials, such as thermoplastic and thermoset materials, find applications in many industries, including the aviation, automotive, and marine industries. Such materials also find applications in the areas of health, medicine, and biotechnology, which is a rapidly developing domain based largely on known
25 materials but moving to designed and engineered polymers, as well as information and communications, which is an emerging field for polymers significantly based on their electronic properties.

30

Articles and parts comprising polymeric materials are made by a variety of manufacturing processes, including, for example, extrusion, injection molding, thermoforming, liquid resin casting, additive manufacturing, such as 3D printing, and the like. However, there remains many challenges in the manufacturing of polymeric articles and parts. For example, one such challenge is that the nature of the polymeric material and the process used to manufacture articles and parts from it

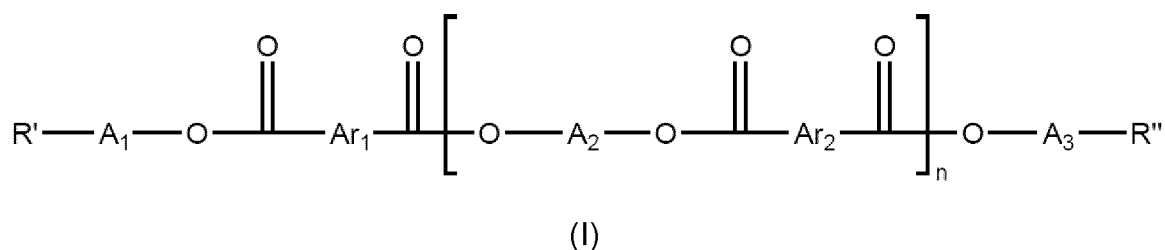
must be considered, as heating causes expansion, and the following cooling process can cause shrinkage and warping. These phenomena can affect the strength and integrity of the final product. Such features must also be balanced with the properties required for the product being made, such as mechanical and electrical properties, to name a few.

Thus, there is an ongoing need for new and improved compounds that can enable the production of useful polymeric materials, such as thermoplastics and thermosets, using a multitude of processing methods, such as, for example, extrusion, injection molding, thermoforming, liquid resin casting, additive manufacturing, such as 3D printing, etc. Herein, new and inventive oligomers, including the use of such oligomers in the production of useful polymers, are described.

Summary of the Invention

This objective, and others which will become apparent from the following detailed description, are met, in whole or in part, by the compounds, methods and/or processes of the present disclosure.

In a first aspect, the present disclosure relates to an oligomer represented by formula I:



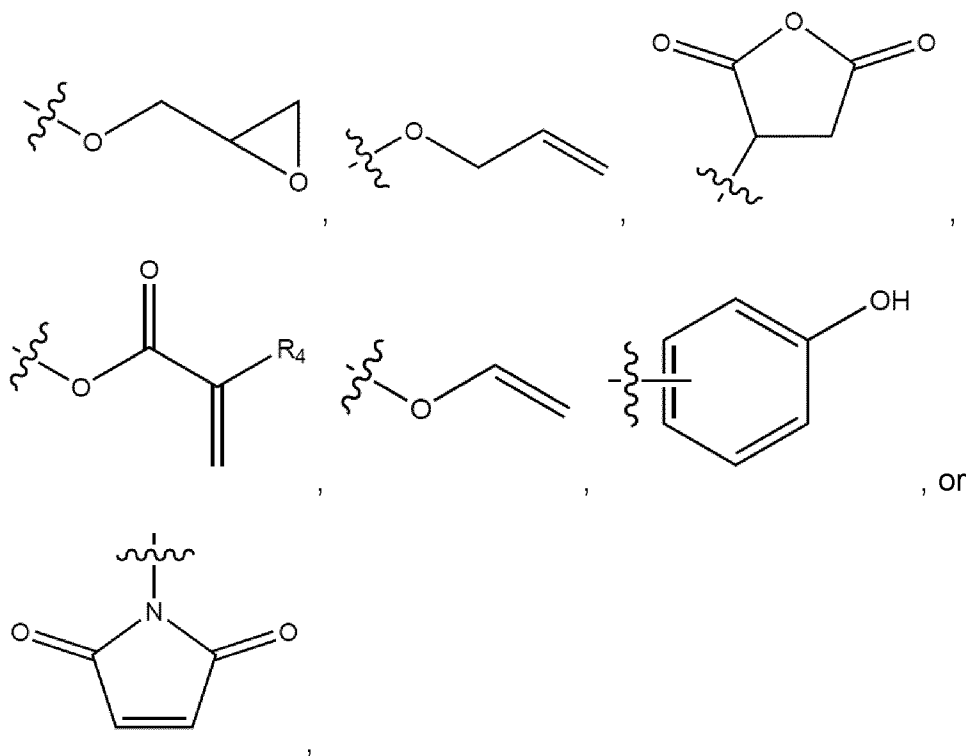
wherein

Ar_1 and Ar_2 are each, independently, a C_6 - C_{14} arylene group or $-\text{Ar}_a-\text{L}-\text{Ar}_b-$, wherein Ar_a and Ar_b are each a C_6 - C_{14} arylene group and L is $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{S})\text{O}-$, $-(\text{C}=\text{S})\text{S}-$, $-(\text{C}=\text{O})\text{NH}-$, $-\text{S}-$, $-\text{SO}-$, $-\text{SO}_2-$, $-\text{O}-$, or $-\text{NH}-$;

A_1 , A_2 , and A_3 are each, independently, $-(\text{CH}_2)_m-$, $-(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_2\text{CH}_2-$, or $-(\text{SiR}_1\text{R}_2\text{O})_q\text{SiR}_1\text{R}_2-$,

wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20;

5 R' and R'' are each, independently, $-NR_5R_6$, $-OR_7$, $-SR_8$, $-(C=O)OR_9$,

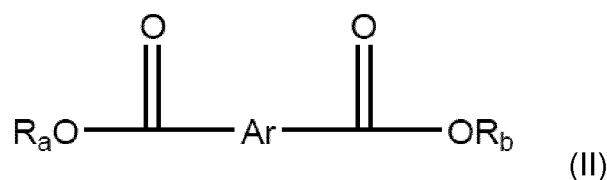


wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

R_7 , R_8 , and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation; and n is an integer from 1 to 30.

15 In a second aspect, the present disclosure relates to a process for producing the oligomer described herein, the process comprising:

a) reacting a compound represented by formula II:

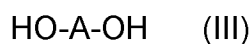


wherein

Ar is a C₆-C₁₄ arylene group or -Ar_a-L-Ar_b-, wherein Ar_a and Ar_b are each a C₆-C₁₄ arylene group and L is -(C=O)O-, -(C=S)O-, -(C=S)S-, -(C=O)NH-, -S-, -SO-, -SO₂-, -O-, or -NH-;

R_a and R_b are each, independently H, alkyl, typically C₁-C₆ alkyl, more typically methyl, or M⁺, wherein M⁺ is a monovalent cation;

with a compound represented by formula III:

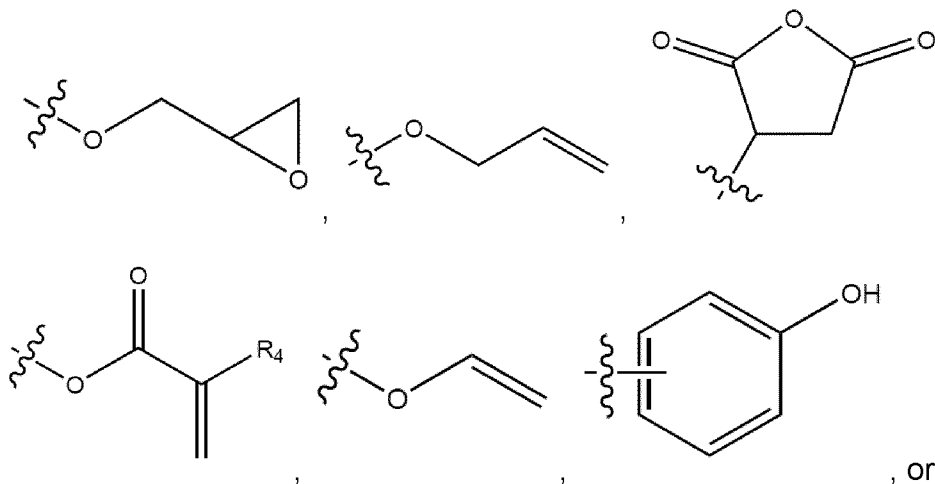


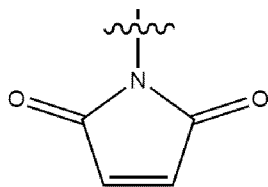
wherein

A is -(CH₂)_m-, -(CH₂CH₂O)_pCH₂CH₂-, or -(SiR₁R₂O)_qSiR₁R₂-,

wherein R₁ and R₂ are each, independently, H or alkyl, typically C₁-C₆ alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20; and

b) optionally, reacting the product of step a) with one or more reagents to convert one or more pendent hydroxyl groups into a moiety selected from the group consisting of -NR₅R₆, -OR₇, -SR₈, -(C=O)OR₉,





wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

R_7 is alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation;

R_8 and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation.

In a third aspect, the present disclosure relates to a polymer comprising a repeating unit derived from the oligomer described herein or derived from the oligomer produced by the process described herein.

In a fourth aspect, the present disclosure relates to a process for producing a polymer described herein, the process comprising:

reacting the oligomer described herein or the oligomer produced by the process described herein with a compound comprising one or more, typically two or more, thiol or amine groups, with a compound comprising one or more acrylate or methacrylate groups, with a compound comprising one or more vinyl ether groups, or with a compound comprising one or more maleimide groups.

In a fifth aspect, the present disclosure relates to an article comprising the polymer described herein or polymer produced according to a process described herein.

Detailed Description

As used herein, the terms “a”, “an”, or “the” means “one or more” or “at least one” and may be used interchangeably, unless otherwise stated.

As used herein, the term “and/or” used in a phrase in the form of “A and/or B” means A alone, B alone, or A and B together.

As used herein, the term “comprises” includes “consists essentially of” and “consists of.” The term “comprising” includes “consisting essentially of” and “consisting of.” “Comprising”, which is synonymous with “including,” “containing,” or “characterized by,” is intended to be inclusive or open-ended and does not exclude additional, unrecited elements or steps. The transitional phrase “consisting essentially of” is inclusive of the specified materials or steps and those that do not materially affect the basic characteristic or function of the composition, process, method, or article of manufacture described. The transitional phrase “consisting of” excludes any element, step, or component not specified.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this specification pertains.

As used herein, and unless otherwise indicated, the term “about” or “approximately” means an acceptable error for a particular value as determined by one of ordinary skill in the art, which depends in part on how the value is measured or determined. In certain embodiments, the term “about” or “approximately” means within 1, 2, 3, or 4 standard deviations. In certain embodiments, the term “about” or “approximately” means within 50%, 20%, 15%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, 0.5%, or 0.05% of a given value or range.

Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

Throughout the present disclosure, various publications may be incorporated by reference. Should the meaning of any language in such publications incorporated by reference conflict with the meaning of the language of the present disclosure, the meaning of the language of the present disclosure shall take precedence, unless
5 otherwise indicated.

As used herein, the terminology "(Cx-Cy)" or "Cx-Cy" in reference to an organic group, wherein x and y are each integers, means that the group may contain from x carbon atoms to y carbon atoms per group.

10 As used herein, the term "aryl" refers to a 5- or 6-membered carbocyclic ring having a delocalized, conjugated π system, with a number of π electrons that is equal to $4n+2$, where n is 0 or a positive integer, or an arrangement of 2 or more of such rings in which the rings are connected by bonds and/or share one or more sides, i.e., are
15 fused. One or more of the ring members may be a heteroatom, typically selected from oxygen, nitrogen, and sulfur, and one or more of the ring members may possess non-hydrogen substituents, typically selected from alkyl, alkoxy, hydroxyalkyl, cycloalkyl, alkoxyalkyl, haloalkyl, aryl, alkaryl, and aralkyl. Exemplary aryl groups include, but are not limited to, those derived from benzene, biphenyl,
20 furan, pyridine, imidazole, thiophene, acridine, cinnoline, quinoline, phenazine, naphthalene, anthracene, phenanthrene, acenaphthylene, pyrene, perylene, and the like.

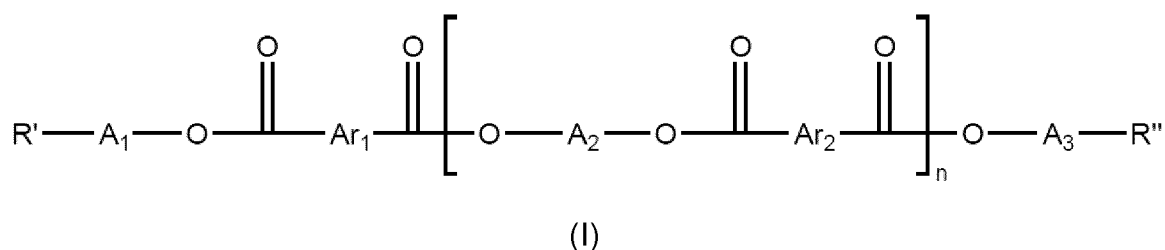
The radicals described herein may be bivalent, i.e., two hydrogen atoms may be
25 replaced by chemical bonds. Such groups are often modified by an "-ene" ending herein. For example, the term "alkylene" means an alkyl radical with an additional hydrogen replaced by a chemical bond. Similarly, the term "arylene" means an aryl radical with an additional hydrogen replaced by a chemical bond.

30 As used herein with reference to an organic compound, the term "aromatic" means that the organic compound comprises one or more aryl or arylene moieties as defined herein.

Any substituent or radical described herein may optionally be substituted at one or more carbon atoms with one or more, same or different, substituents described herein. For instance, an aryl group may be further substituted with another aryl group or an alkyl group. Any substituent or radical described herein may also

- 5 optionally be substituted at one or more carbon atoms with one or more substituents selected from the group consisting of halogen, such as, for example, F, Cl, Br, and I; nitro (NO₂), cyano (CN), and hydroxy (OH).

In the first aspect, the present disclosure relates to an oligomer represented by
10 formula I:



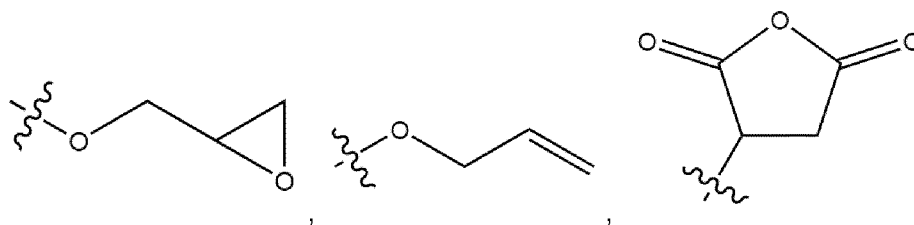
15 wherein

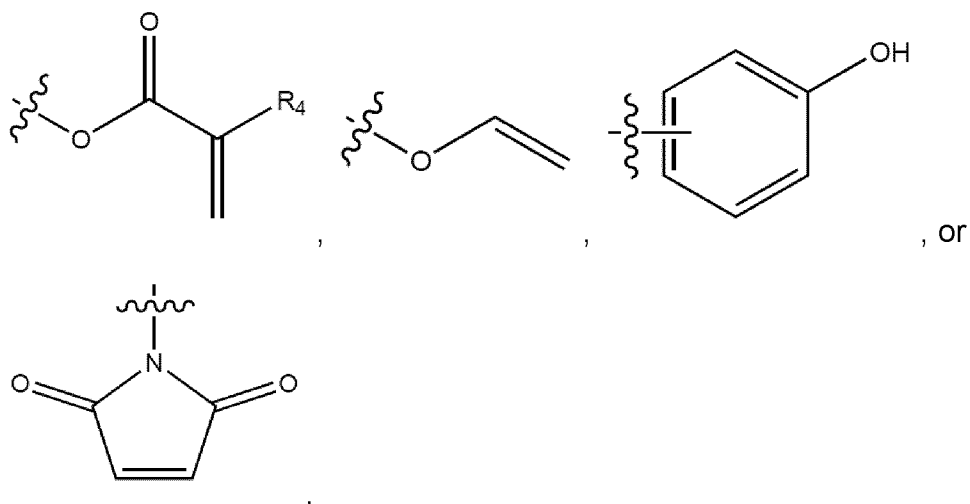
Ar₁ and Ar₂ are each, independently, a C₆-C₁₄ arylene group or -Ar_a-L-Ar_b-, wherein Ar_a and Ar_b are each a C₆-C₁₄ arylene group and L is -(C=O)O-, -(C=S)O-, -(C=S)S-, -(C=O)NH-, -S-, -SO-, -SO₂-, -O-, or -NH-;

20 A₁, A₂, and A₃ are each, independently, -(CH₂)_m-, -(CH₂CH₂O)_pCH₂CH₂-, or - (SiR₁R₂O)_qSiR₁R₂-,

wherein R₁ and R₂ are each, independently, H or alkyl, typically C₁-C₆ alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20;

25 R' and R'' are each, independently, -NR₅R₆-, -OR₇-, -SR₈-, -(C=O)OR₉-,





wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

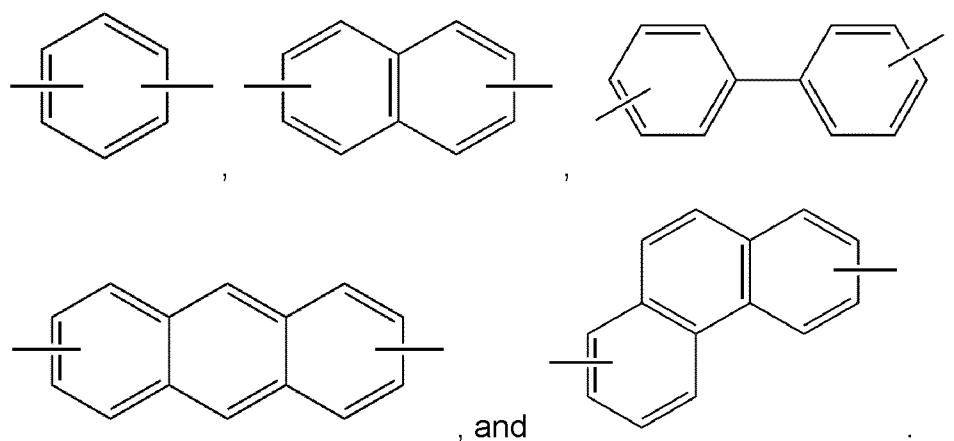
- 5 R_7 , R_8 , and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation; and n is an integer from 1 to 30, typically 2 to 15.

- 10 Ar_1 and Ar_2 are each, independently, a C_6 - C_{14} arylene group or $-Ar_a-L-Ar_b-$, wherein Ar_a and Ar_b are each a C_6 - C_{14} arylene group and L is $-(C=O)O-$, $-(C=S)O-$, $-(C=S)S-$, $-(C=O)NH-$, $-S-$, $-SO-$, $-SO_2-$, $-O-$, or $-NH-$. Suitable C_6 - C_{14} arylene groups include, but are not limited to, those derived from benzene, biphenyl, furan, pyridine, imidazole, thiophene, acridine, cinnoline, quinoline, phenazine, naphthalene, anthracene, phenanthrene, acenaphthylene, pyrene, perylene, and the like.

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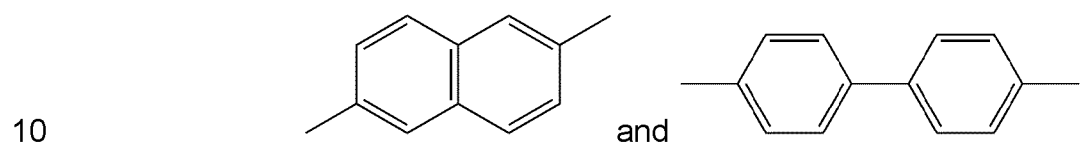
In an embodiment, Ar_1 and Ar_2 are each, independently, a C_6 - C_{14} arylene group, typically selected from the group consisting of those derived from benzene, naphthalene, biphenyl, anthracene, and phenanthrene.

- 20 In an embodiment, Ar_1 and Ar_2 are each, independently, selected from the group consisting of:



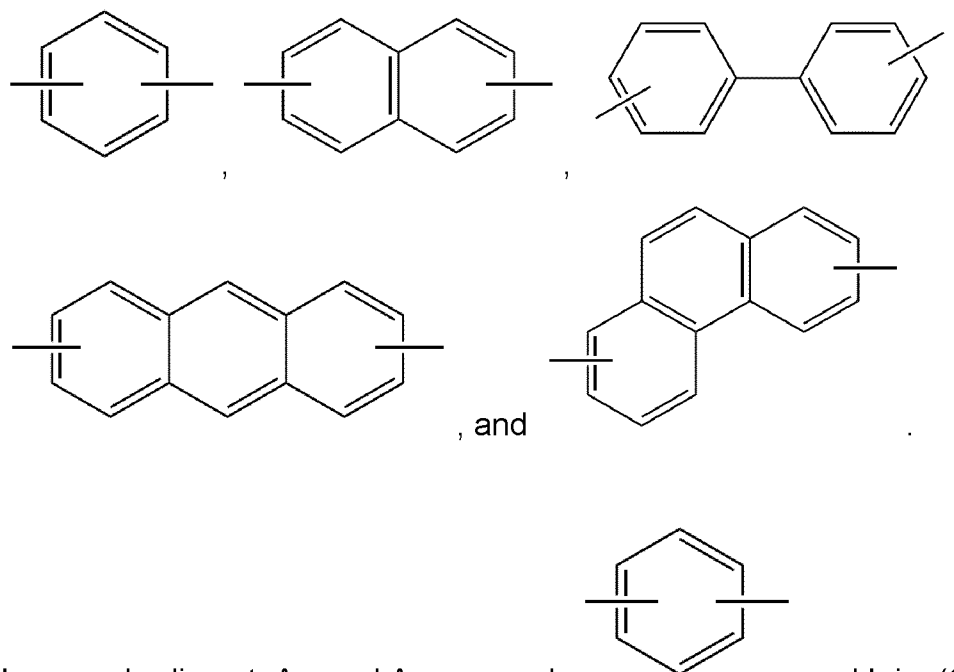
The two bonds connecting the carbonyl carbons to Ar_1 and Ar_2 are not limited and
 5 may be on the same ring or on different rings.

In another embodiment, Ar_1 and Ar_2 are each, independently, selected from the group consisting of:



In an embodiment, Ar_1 and Ar_2 are each, independently, a $-Ar_a-L-Ar_b-$, wherein Ar_a
 and Ar_b are each a C_6-C_{14} arylene group and L is $-(C=O)O-$, $-(C=S)O-$, $-(C=S)S-$, $-(C=O)NH-$, $-S-$, $-SO-$, $-SO_2-$, $-O-$, or $-NH-$. Suitable C_6-C_{14} arylene groups are those
 15 described hereinabove.

In an embodiment, Ar_a and Ar_b are each, independently, selected from the group consisting of:



In an embodiment, Ar_a and Ar_b are each

and L is $-(C=O)O-$.

5

A_1 , A_2 , and A_3 provide functionalities that act as flexible spacers in polymers made from the oligomer of formula I. A_1 , A_2 , and A_3 are each, independently, $-(CH_2)_m-$, $-(CH_2CH_2O)_pCH_2CH_2-$, or $-(SiR_1R_2O)_qSiR_1R_2-$, wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, each

10 occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20.

In an embodiment, A_1 , A_2 , and A_3 are each, independently, $-(CH_2)_m-$, wherein each occurrence of m is an integer from 5 to 20, typically 10 to 15.

15

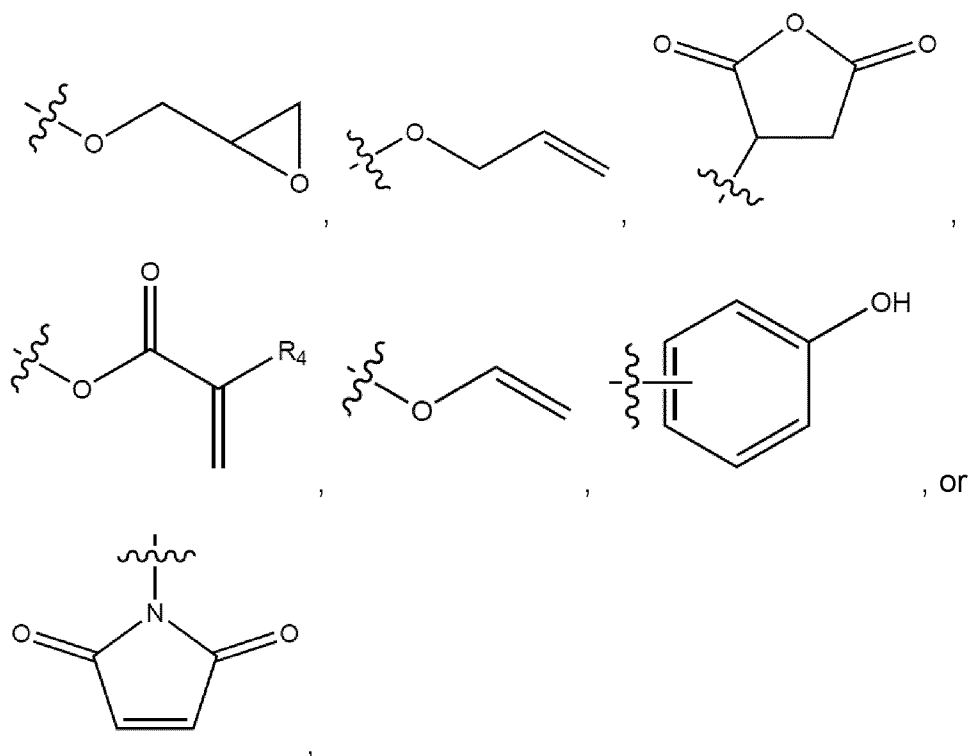
In another embodiment, A_1 , A_2 , and A_3 are each, independently, $-(CH_2CH_2O)_pCH_2CH_2-$, wherein each occurrence of p is an integer from 2 to 10, typically 3 to 8.

20 In another embodiment, A_1 , A_2 , and A_3 are each, independently, $-(SiR_1R_2O)_qSiR_1R_2-$, wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, and each occurrence of q is an integer from 2 to 18.

In an embodiment, A_1 , A_2 , and A_3 are unsubstituted.

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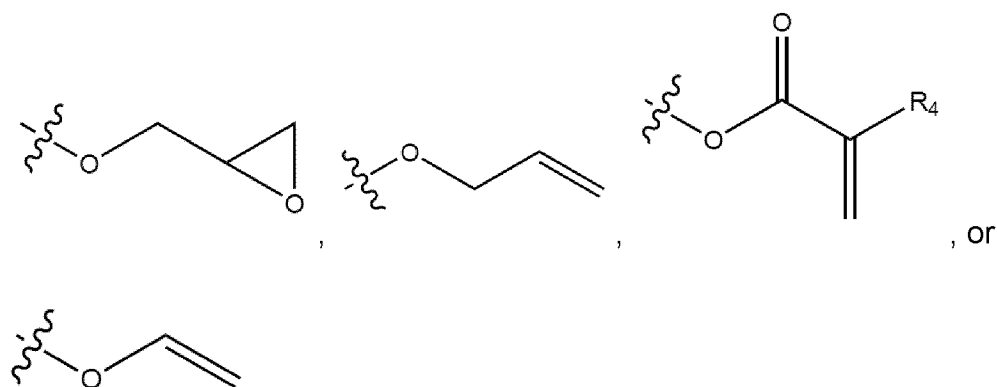
R' and R'' provide the reactive functionality used for producing polymers from the oligomer of formula I. Suitable reactive moieties are -NR₅R₆, -OR₇, -SR₈, - (C=O)OR₉,



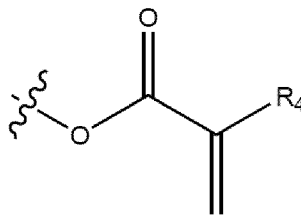
wherein R₄, R₅, and R₆ are each, independently, H or alkyl, typically C₁-C₆ alkyl, more typically methyl;

R₇, R₈, and R₉ are each, independently, H, alkyl, typically C₁-C₆ alkyl, more typically methyl, or M⁺, wherein M⁺ is a monovalent cation.

In an embodiment, R' and R'' are each, independently,



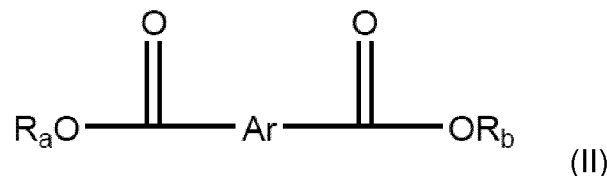
, wherein R₄ is H or alkyl, typically C₁-C₆ alkyl, more typically methyl.



In an embodiment, R' and R'' are each alkyl, typically C₁-C₆ alkyl, more typically methyl. , wherein R₄ is H or

- 5 In the second aspect, the present disclosure relates to a process for producing the oligomer described herein, the process comprising:

a) reacting a compound represented by formula II:



10

wherein

Ar is a C₆-C₁₄ arylene group or -Ar_a-L-Ar_b-, wherein Ar_a and Ar_b are each a C₆-C₁₄ arylene group and L is -(C=O)O-, -(C=S)O-, -(C=S)S-, -(C=O)NH-, -S-, -SO-, -SO₂-, -O-, or -NH-;

15

R_a and R_b are each, independently H, alkyl, typically C₁-C₆ alkyl, more typically methyl, or M⁺, wherein M⁺ is a monovalent cation;

with a compound represented by formula III:

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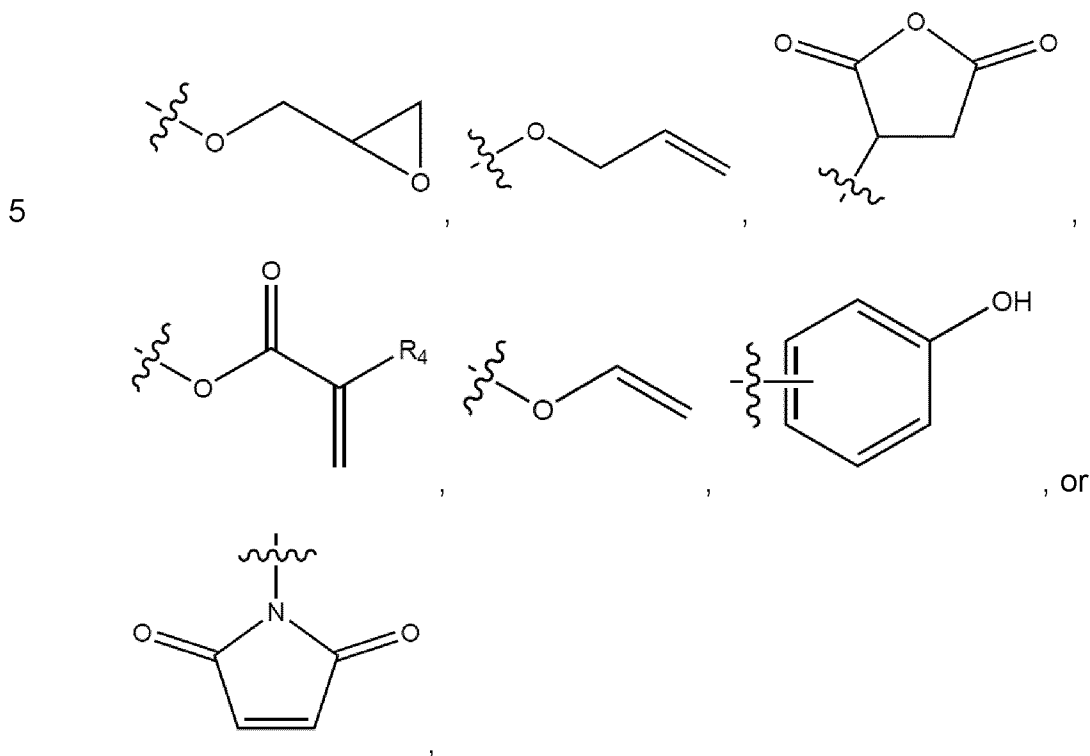
wherein

A is -(CH₂)_m-, -(CH₂CH₂O)_pCH₂CH₂-, or -(SiR₁R₂O)_qSiR₁R₂-,

25

wherein R₁ and R₂ are each, independently, H or alkyl, typically C₁-C₆ alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20; and

b) optionally, reacting the product of step a) with one or more reagents to convert one or more pendent hydroxyl groups into a moiety selected from the group consisting of $-\text{NR}_5\text{R}_6$, $-\text{OR}_7$, $-\text{SR}_8$, $-(\text{C}=\text{O})\text{OR}_9$,



wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

10 R_7 is alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation;

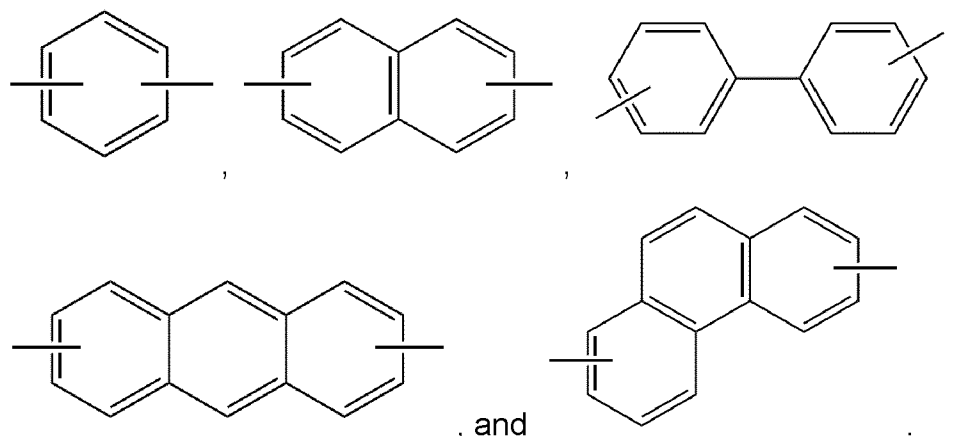
R_8 and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation.

15 The compound represented by formula II is an aromatic diacid, aromatic diester, or salt form thereof, in which Ar is a C_6 - C_{14} arylene group or $-\text{Ar}_a-\text{L}-\text{Ar}_b-$, wherein Ar_a and Ar_b are each a C_6 - C_{14} arylene group and L is $-(\text{C}=\text{O})\text{O}-$, $-(\text{C}=\text{S})\text{O}-$, $-(\text{C}=\text{S})\text{S}-$, $-(\text{C}=\text{O})\text{NH}-$, $-\text{S}-$, $-\text{SO}-$, $-\text{SO}_2-$, $-\text{O}-$, or $-\text{NH}-$. Suitable C_6 - C_{14} arylene groups are those already described hereinabove.

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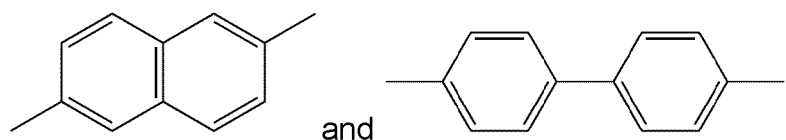
In an embodiment, Ar is a C₆-C₁₄ arylene group, typically selected from the group consisting of those derived from benzene, naphthalene, biphenyl, anthracene, and phenanthrene.

- 5 In an embodiment, Ar is selected from the group consisting of:



- 10 The two bonds connecting the carbonyl carbons to Ar are not limited and may be on the same ring or on different rings.

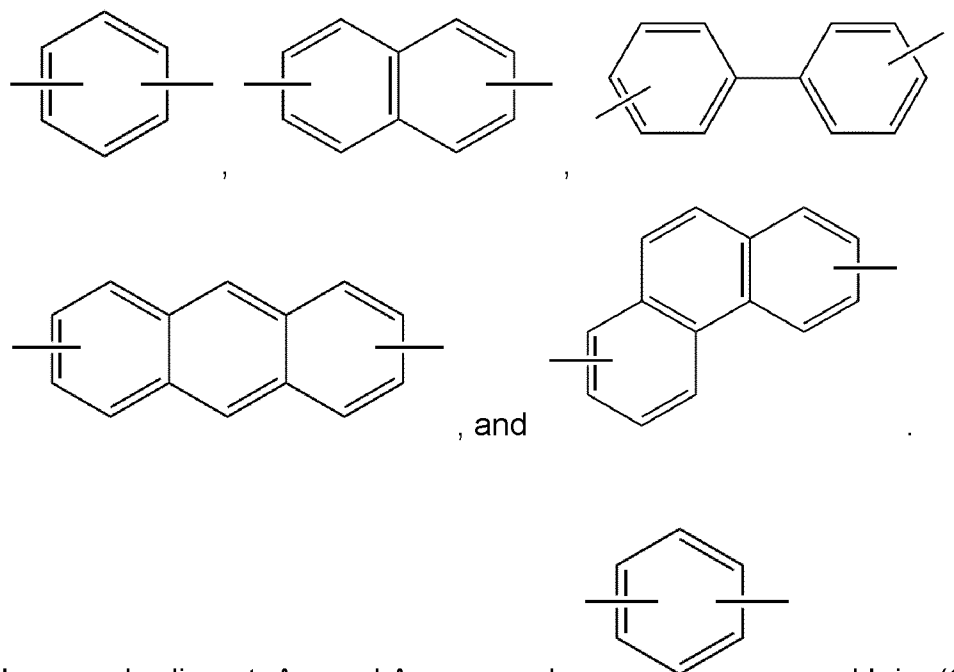
In another embodiment, Ar is selected from the group consisting of:

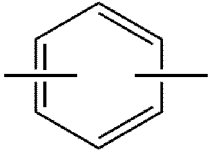


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In an embodiment, Ar is -Ar_a-L-Ar_b-, wherein Ar_a and Ar_b are each a C₆-C₁₄ arylene group and L is -(C=O)O-, -(C=S)O-, -(C=S)S-, -(C=O)NH-, -S-, -SO-, -SO₂-, -O-, or -NH-. Suitable C₆-C₁₄ arylene groups are those described hereinabove.

- 20 In an embodiment, Ar_a and Ar_b are each, independently, selected from the group consisting of:



In an embodiment, Ar_a and Ar_b are each  and L is $-(C=O)O-$.

5

The compound of formula II is reacted with a compound represented by formula III:



10 wherein

A is $-(CH_2)_m-$, $-(CH_2CH_2O)_pCH_2CH_2-$, or $-(SiR_1R_2O)_qSiR_1R_2-$,

wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20.

15

In an embodiment, A is $-(CH_2)_m-$, wherein each occurrence of m is an integer from 5 to 20, typically 10 to 15. In this embodiment, the compounds of formula III are alkanediols. Suitable alkanediols include, but are not limited to, 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, and so on.

20

In another embodiment, A is $-(CH_2CH_2O)_pCH_2CH_2-$, wherein each occurrence of p is an integer from 2 to 10, typically 3 to 8. In this embodiment, the compounds of

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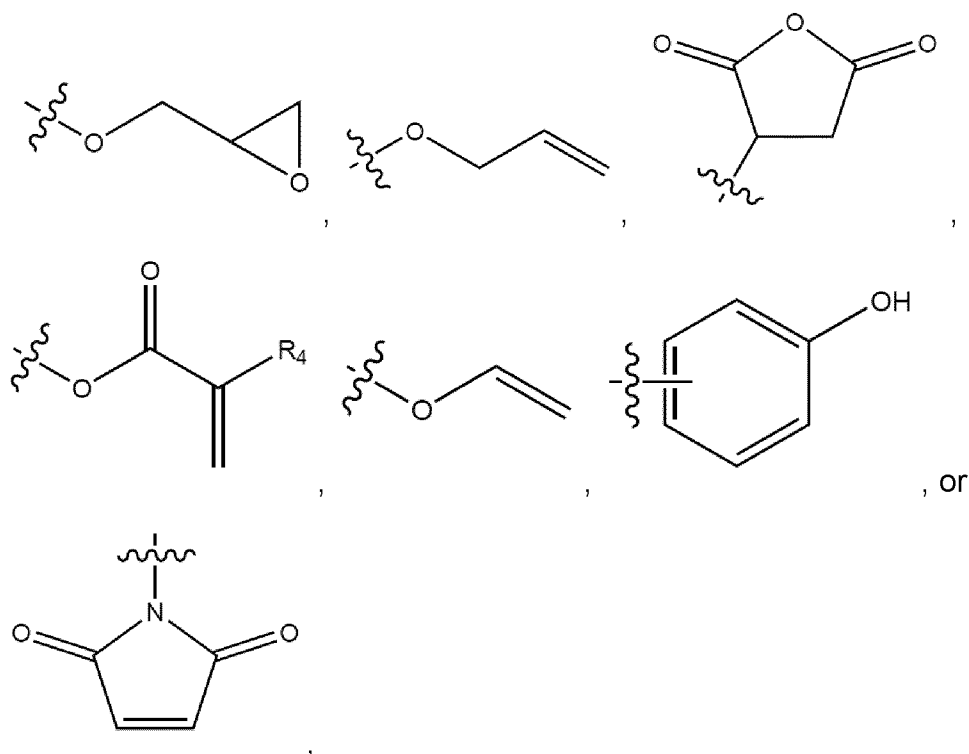
formula III are polyethylene glycols produced from the polymerization of ethylene oxide. Suitable polyethylene glycols include, but are not limited to, diethylene glycol, triethylene glycol, tetraethylene glycol, and so on.

- 5 In yet another embodiment, A is $-(\text{SiR}_1\text{R}_2\text{O})_q\text{SiR}_1\text{R}_2-$, wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, and each occurrence of q is an integer from 2 to 18. In this embodiment, the compounds of formula III are polysiloxanes. An exemplary polysiloxane is polydimethylsiloxane.
- 10 In an embodiment, A_1 , A_2 , and A_3 are unsubstituted.

The compounds of formula II and III may be obtained from commercial sources or synthesized according to published methods.

- 15 The reaction between the compound of formula II with the compound of formula III is an apparent transesterification reaction in which ester linkages are formed between the compound of formula II and the compound of formula III. Such reactions are known and may be conducted by those of ordinary skill in the art according to known methods. However, in a favorable embodiment, the esterification reaction
- 20 between the compound of formula II and the compound of formula III is conducted in the presence of a titanium compound, typically a titanium(IV) compound, more typically a titanium(IV) alkoxide. In a particular embodiment, titanium tetraisopropoxide is used. The reaction conditions are not particularly limited. However, in an embodiment, the reaction is conducted at a temperature in the range
- 25 of $150\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$, typically $200\text{ }^{\circ}\text{C}$ to $240\text{ }^{\circ}\text{C}$. In an embodiment, the reaction is conducted under inert atmosphere and/or vacuum.

- Optionally, the product from step a) of the process may be reacted with one or more reagents to convert one or more pendent hydroxyl groups into a moiety selected
- 30 from the group consisting of $-\text{NR}_5\text{R}_6$, $-\text{OR}_7$, $-\text{SR}_8$, $-(\text{C}=\text{O})\text{OR}_9$,

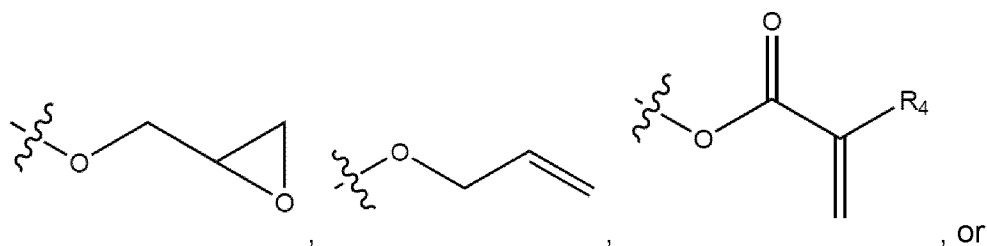


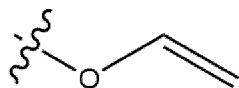
wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

R_7 is alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation;

R_8 and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation.

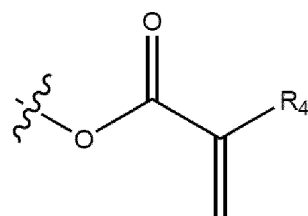
In an embodiment, the product from step a) of the process is reacted with one or more reagents to convert one or more pendent hydroxyl groups into a moiety selected from the group consisting of





, wherein R_4 is H or alkyl, typically C_1 - C_6 alkyl, more typically methyl.

In an embodiment, the product from step a) of the process is reacted with one or more reagents to convert one or more pendent hydroxyl groups into



, wherein R_4 is H or alkyl, typically C_1 - C_6 alkyl, more typically methyl.

Reactions for transforming hydroxyl groups into various functional groups are well-known to those of ordinary skill in the art. Such transformations are described in detail in March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, M. B. Smith and J. March, 5th Edition, John Wiley & Sons, 2001, Comprehensive Organic Transformations, R. C. Larock, 2nd Edition, John Wiley & Sons, 1999, and Protecting Groups in Organic Synthesis, T. W. Greene and P. G. M. Wuts, 3rd edition, John Wiley & Sons, 1999, the entirety of each of which is hereby incorporated herein by reference.

In the third aspect, the present disclosure relates to a polymer comprising a repeating unit derived from the oligomer described herein or derived from the oligomer produced by the process described herein.

In an embodiment, the polymer comprises 1 to 100 %, typically 20 to 95 %, more typically 50 to 90 %, still more typically 65 to 80 %, by weight of the repeating unit derived from the oligomer described herein or derived from the oligomer produced by the process described herein, relative to the weight of the polymer.

The polymer may be a thermoplastic or thermoplastic-like linear or branched polymer. In some cases, the polymer may be a thermoset or thermoset-like polymer, typically with crosslinked structure. In an embodiment, the polymer is a liquid crystalline polymer. As used herein, a liquid crystalline polymer, or "LCP", refers to a type of thermoplastic polymer that exhibits properties between highly ordered solid crystalline materials and amorphous disordered liquids over a well-defined temperature range.

In the fourth aspect, the present disclosure relates to a process for producing a polymer described herein, the process comprising:

reacting the oligomer described herein or the oligomer produced by the process described herein with a compound comprising one or more, typically two or more, thiol or amine groups, with a compound comprising one or more acrylate or methacrylate groups, with a compound comprising one or more vinyl ether groups, or with a compound comprising one or more maleimide groups.

The polymerization reaction may be carried out according to methods known to those of ordinary skill in the art.

In the fifth aspect, the present disclosure relates to an article comprising the polymer described hereinabove or polymer produced according to the process described hereinabove.

The article may be produced according to any method known to those of ordinary skill in the art, typically from the polymer or compositions comprising the polymer described herein. Exemplary methods for manufacturing the article include, but are not limited, injection molding, extrusion, compression molding, thermoforming, such as sheet thermoforming, vacuum forming, pressure forming, trapped sheet forming, steam pressure forming; liquid resin casting, transfer molding, and additive manufacturing, such as 3D printing.

The polymer or compositions comprising the polymer used to produce the articles described herein may further comprise optional materials, such as fibers, fillers, colorants, additives, and the like, that impart beneficial properties to the final article.

Fibers may serve as reinforcing media and include, but are not limited to, carbon fiber, synthetic polymeric fibers, silicate fibers, such as aluminum silicate fibers, metal oxide fibers, such as alumina fibers, titania fibers, and magnesia fibers, wollastonite, rock wool fibers, silicon carbide fibers, etc. Exemplary polymeric fibers

5 include fibers formed from high temperature engineering polymers such as, for example, poly(benzothiazole), poly(benzimidazole), polyarylates, poly(benzoxazole), polyaryl ethers and the like, and may include mixtures comprising two or more such fibers.

10 Other optional materials include glass, calcium silicate, silica, clays, such as kaolin, talc, chalk, mica, potassium titanate, and other mineral fillers; colorants, including pigments such as carbon black, titanium dioxide, zinc oxide, iron oxide, cadmium red, iron blue; and other additives such as alumina trihydrate, sodium aluminum carbonate, barium ferrite, etc.

15 Still further, the polymer or compositions comprising the polymer may further include additional additives commonly employed by those of ordinary skill in the art, such as thermal stabilizers, ultraviolet light stabilizers, oxidative stabilizers, plasticizers, lubricants, and mold release agents, such as polytetrafluoroethylene (PTFE) powder,

20 and the like.

In an embodiment, the article is:

- an injection molded article ;
- an extruded article, such as a film, fiber, sheet stock, rod stock, tubing or
- 25 profile ;
- a compression molded article ;
- a valve component or a related part thereof such as a seal ring ;
- a compressor or a pump component;
- a sealing component;
- 30 ■ an electronic component;
- a hard drive platter component, or a head component ;
- a component useful in semi-conductor manufacturing;
- a component of a semi-conductor test equipment;
- a fitting and/or coupling of a fluid delivery system;

- a matrix for structural continuous fiber composites ;
- a cookware or bakeware;
- a downhole abrasion tape or a flexible riser abrasion tape ;
- an under-the-hood automotive component, that may be exposed to high heat ;
- an article useful in lighting applications;
- a thermally dissipative heat sink;
- an aerospace electrical or electronic connector component or housing ;
- a friction and wear component such as a bushing, a bearing or a thrust washer,
- a gear ;
- a mechanical drive component;
- an electrical or electronic, wire or cable insulation or coating ;
- a bushing, bearing or another frictional component of an elevator door component, or other sliding mechanism ; or
- a bushing, bearing or another frictional component of a high temperature conveyor system;
- a plate for turbo components and/or air induction ;
- an hydraulic component, a seal, a poppet or a piston ring of an agricultural or construction equipment ;
- an anti-wear layer of a push-pull cable ;
- a glide ring, a tappet, a gear, an electronically driven pad, a control valve, a pump component, a bushing or a check ball of a brake system ;
- a seal ring, a thrust washer, or a ball of a transmission component ;
- a gear, a bushing or a bearing of a steering system component ;
- a ramp button, a torque roller, a thrust button of a CVT (Continuous Variable transmissions) or clutch.
- a pump component, a gear, or a sensor of an emission system ;
- a pump or a G-rotor of an oil system ;
- a swash plate of a compressor;
- an air bag sensor;
- a friction plate, a door sleeve or a bracket or another sliding component of a train door;
- an automotive chassis component; or

- a motor thrust washer or film for seat adjustment mechanisms.

In another embodiment, the article is:

- a 3D-printed article;
- 5 ■ a foam article;
- a coating;
- an adhesive or component of an adhesive;
- a component of a composite article;
- a component of a multi-layer article; or
- 10 ■ a medical device component.

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
15 shall take precedence.

The oligomers, polymers, methods and processes, and articles according to the present disclosure are further illustrated by the following non-limiting examples.

20 **Example 1. Synthesis of an oligomer of formula I (NDA-TEG).**

The reaction was performed in a dry two-neck 500-mL round-bottomed flask utilizing an overhead stirrer, nitrogen inlet, and distillation apparatus. 2,6-naphthalenedimethyl ester (24.35 g, 0.099 mol equiv), tetraethylene glycol (21.95 g,
25 0.113 mol equiv), and titanium tetraisopropoxide (catalytic, 50 μ L) were introduced to a flask. Oxygen-free reaction conditions were achieved by subsequent degassing with vacuum and purging with N_2 gas (3 $\times$). The reaction progressed at 200 $^{\circ}$ C for 1 hour, 1 $^{\circ}$ C/min ramp from 200 $^{\circ}$ C to 225 $^{\circ}$ C, 225 $^{\circ}$ C for 1 hour, 1 $^{\circ}$ C/min ramp from 225 $^{\circ}$ C to 235 $^{\circ}$ C, 235 $^{\circ}$ C for 1 hour, and lastly 235 $^{\circ}$ C for 1 hour under a vacuum of
30 75-100 mmHg at a constant stirring rate of 75 rpm and N_2 gas purge. Methanol condensate was collected in a liquid nitrogen cooled round-bottomed flask. Once the oligomerization was completed, the reaction flask was cooled down to ambient temperature and a small aliquot was taken out for characterization, confirming the formation of the desired oligomer. The desired oligomer was characterized by

nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and polarized optical microscopy (POM).

- 5 The resulting oligomer was then dissolved in 250 mL of dichloroethane (15 wt%) and cooled down to 5 °C in an ice-water bath. Once the reaction flask was cooled, triethylamine (5.79 mL, 0.057 mol) was added and stirred for 1 hour. After an hour, acryloyl chloride (5.17 mL, 0.057 mol) was added dropwise over a period of 20 minutes and stirred for 24 hours. The cloudy solution was concentrated under
10 reduced pressure to a solid. The resulting white solid was washed with 400 mL of cold deionized water (DI-H₂O) to exhaust excess acryloyl chloride and dissolve salts. The white solid was collected by vacuum filtration and washed three times with 500 mL of cold DI-H₂O. The resulting oligomer was placed to dry in a vacuum oven at room temperature (30 mmHg) for 48 hours.

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Example 2. Synthesis of a compound of formula I (NDA-C12).

NDA-C12 was made according to the procedure of Example 1, except that 1,12-dodecanediol was used instead of tetraethylene glycol.

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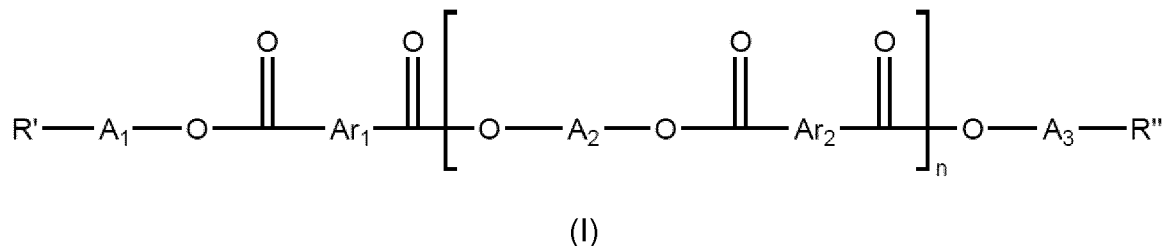
Example 3. Synthesis of a compound of formula I (BB-TEG).

BB-TEG was made according to the procedure of Example 1, except that 4,4'-biphenyldimethyl ester was used instead of 2,6-naphthalenedimethyl ester.

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WHAT IS CLAIMED IS:

1. An oligomer represented by formula I:



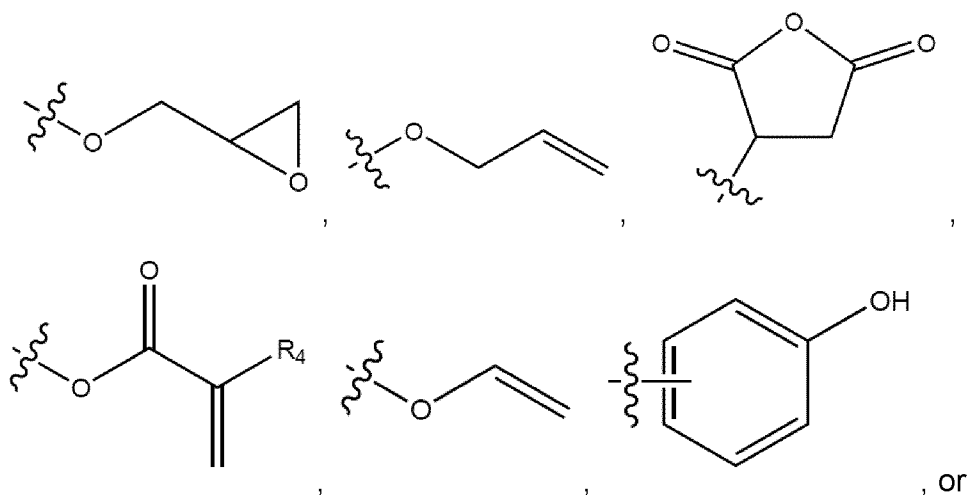
wherein

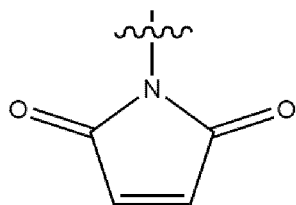
Ar_1 and Ar_2 are each, independently, a C_6 - C_{14} arylene group or $-Ar_a-L-Ar_b-$, wherein Ar_a and Ar_b are each a C_6 - C_{14} arylene group and L is $-(C=O)O-$, $-(C=S)O-$, $-(C=S)S-$, $-(C=O)NH-$, $-S-$, $-SO-$, $-SO_2-$, $-O-$, or $-NH-$;

A_1 , A_2 , and A_3 are each, independently, $-(CH_2)_m-$, $-(CH_2CH_2O)_pCH_2CH_2-$, or $-(SiR_1R_2O)_qSiR_1R_2-$,

wherein R_1 and R_2 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20;

R' and R'' are each, independently, $-NR_5R_6$, $-OR_7$, $-SR_8$, $-(C=O)OR_9$,



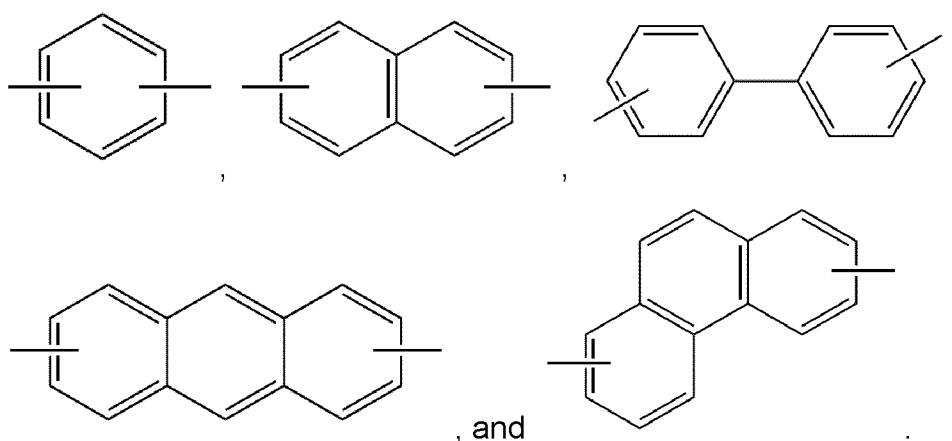


wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

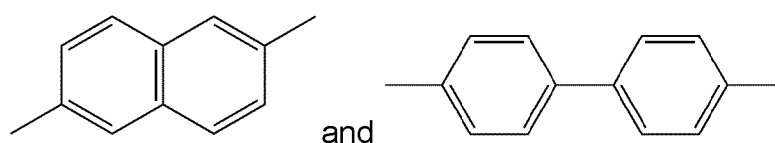
R_7 , R_8 , and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation; and

n is an integer from 1 to 30.

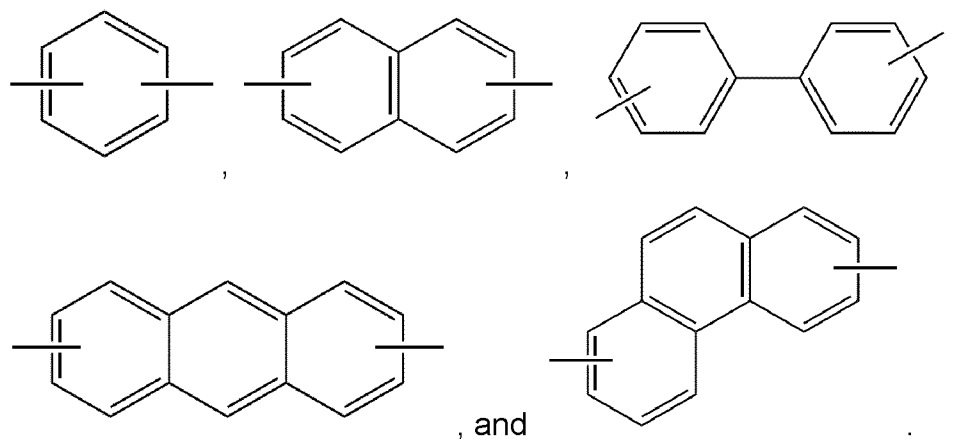
2. The oligomer according to claim 1, wherein Ar_1 and Ar_2 are each, independently, selected from the group consisting of:



3. The oligomer according to claim 1 or 2, wherein Ar_1 and Ar_2 are each, independently, selected from the group consisting of:



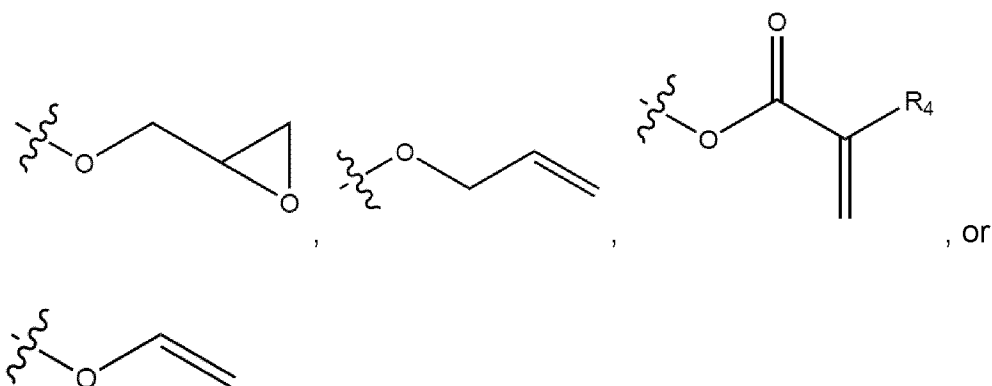
4. The oligomer according to claim 1, wherein Ar_1 and Ar_2 are each $-Ar_a-L-Ar_b-$, wherein Ar_a and Ar_b are each, independently, selected from the group consisting of:



5. The oligomer according to any one of claims 1-4, wherein A_1 , A_2 , and A_3 are each, independently, $-(CH_2)_m-$, wherein each occurrence of m is an integer from 5 to 20, typically 10 to 15.

6. The oligomer according to any one of claims 1-4, wherein A_1 , A_2 , and A_3 are each, independently, $-(CH_2CH_2O)_pCH_2CH_2-$, wherein each occurrence of p is an integer from 2 to 10, typically 3 to 8.

7. The oligomer according to any one of claims 1-6, wherein R' and R'' are each, independently,

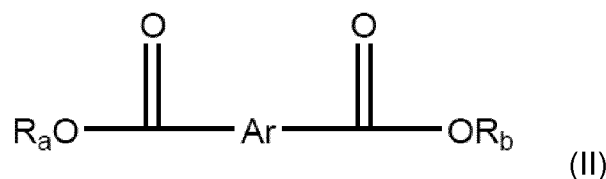


, wherein R_4 is H or alkyl, typically C₁-C₆ alkyl, more typically methyl.

8. The oligomer according to any one of claims 1-7, wherein n is an integer from 2 to 15.

9. A process for producing the oligomer according to any one of claims 1-8, the process comprising:

a) reacting a compound represented by formula II:



wherein

Ar is a C₆-C₁₄ arylene group or -Ar_a-L-Ar_b-, wherein Ar_a and Ar_b are each a C₆-C₁₄ arylene group and L is -(C=O)O-, -(C=S)O-, -(C=S)S-, -(C=O)NH-, -S-, -SO-, -SO₂-, -O-, or -NH-;

R_a and R_b are each, independently H, alkyl, typically C₁-C₆ alkyl, more typically methyl, or M⁺, wherein M⁺ is a monovalent cation;

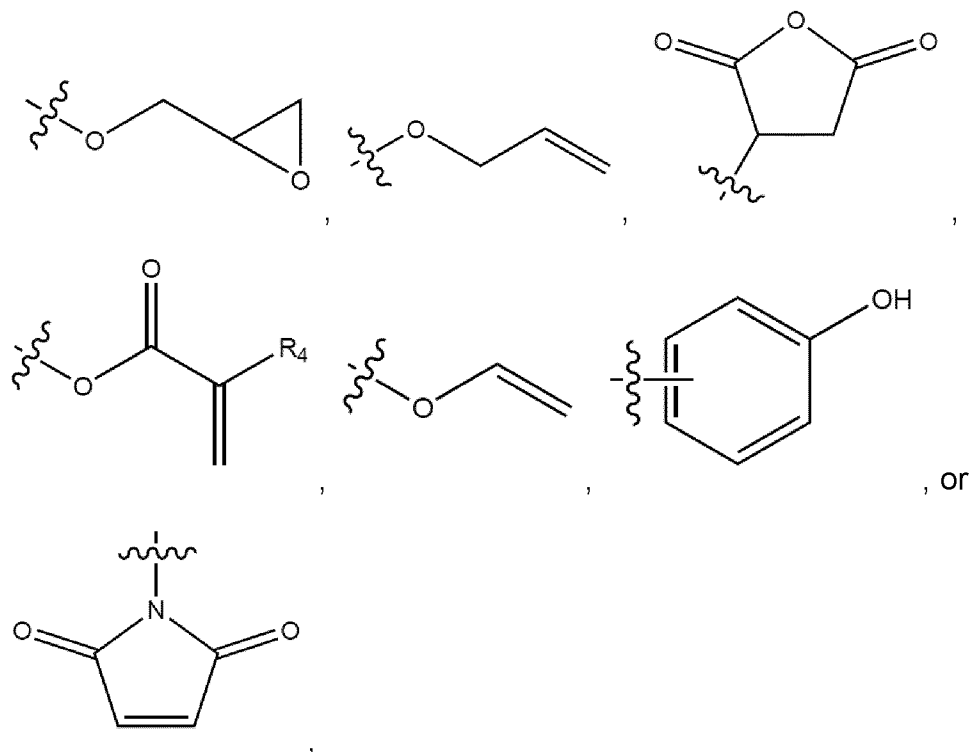
with a compound represented by formula III:



wherein

A is -(CH₂)_m-, -(CH₂CH₂O)_pCH₂CH₂-, or -(SiR₁R₂O)_qSiR₁R₂-,
wherein R₁ and R₂ are each, independently, H or alkyl, typically C₁-C₆ alkyl, more typically methyl, each occurrence of m is an integer from 1 to 20, each occurrence of p is an integer from 1 to 10, and each occurrence of q is an integer from 1 to 20; and

b) optionally, reacting the product of step a) with one or more reagents to convert one or more pendent hydroxyl groups into a moiety selected from the group consisting of -NR₅R₆-, -OR₇-, -SR₈-, -(C=O)OR₉-,



wherein R_4 , R_5 , and R_6 are each, independently, H or alkyl, typically C_1 - C_6 alkyl, more typically methyl;

R_7 is alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation;

R_8 and R_9 are each, independently, H, alkyl, typically C_1 - C_6 alkyl, more typically methyl, or M^+ , wherein M^+ is a monovalent cation.

10. The process according to claim 9, wherein the step a) is conducted in the presence of a titanium compound, typically a titanium(IV) compound, more typically a titanium(IV) alkoxide.

11. The process according to claim 9 or 10, wherein step a) is conducted at a temperature in the range of 150 °C to 250 °C, typically 200 °C to 240 °C.

12. The process according to any one of claims 9-11, wherein step a) is conducted under inert atmosphere and/or vacuum.

13. A polymer comprising a repeating unit derived from the oligomer according to any one of claims 1-8 or derived from the oligomer produced by the process according to any one of claims 9-12.

14. The polymer according to claim 13, wherein the polymer comprises 1 to 100 %, typically 20 to 95 %, more typically 50 to 90 %, still more typically 65 to 80 %, by weight of the repeating unit derived from the oligomer according to any one of claims 1-8 or derived from the oligomer produced by the process according to any one of claims 9-12, relative to the weight of the polymer.

15. The polymer according to claim 13 or 14, wherein the polymer is a liquid crystalline polymer.

16. A process for producing a polymer according to any one of claims 13-15, the process comprising:

reacting the oligomer according to any one of claims 1-8 or the oligomer produced by the process according to any one of claims 9-12 with a compound comprising one or more, typically two or more, thiol or amine groups, with a compound comprising one or more acrylate or methacrylate groups, with a compound comprising one or more vinyl ether groups, or with a compound comprising one or more maleimide groups.

17. An article comprising the polymer according to any one of claims 13-15 or polymer produced according to claim 16.

18. The article according to claim 17, wherein the article is:

- an injection molded article ;
- an extruded article, such as a film, fiber, sheet stock, rod stock, tubing or profile;
- a compression molded article;
- a valve component or a related part thereof such as a seal ring;
- a compressor or a pump component;
- a sealing component;
- an electronic component;

- a hard drive platter component, or a head component;
- a component useful in semi-conductor manufacturing;
- a component of a semi-conductor test equipment;
- a fitting and/or coupling of a fluid delivery system;
- a matrix for structural continuous fiber composites;
- a cookware or bakeware;
- a downhole abrasion tape or a flexible riser abrasion tape;
- an under-the-hood automotive component, that may be exposed to high heat;
- an article useful in lighting applications;
- a thermally dissipative heat sink;
- an aerospace electrical or electronic connector component or housing;
- a friction and wear component such as a bushing, a bearing or a thrust washer,
- a gear;
- a mechanical drive component;
- an electrical or electronic, wire or cable insulation or coating;
- a bushing, bearing or another frictional component of an elevator door component, or other sliding mechanism; or
- a bushing, bearing or another frictional component of a high temperature conveyor system;
- a plate for turbo components and/or air induction;
- an hydraulic component, a seal, a poppet or a piston ring of an agricultural or construction equipment;
- an anti-wear layer of a push-pull cable;
- a glide ring, a tappet, a gear, an electronically driven pad, a control valve, a pump component, a bushing or a check ball of a brake system;
- a seal ring, a thrust washer, or a ball of a transmission component;
- a gear, a bushing or a bearing of a steering system component;
- a ramp button, a torque roller, a thrust button of a CVT (Continuous Variable transmissions) or clutch.
- a pump component, a gear, or a sensor of an emission system;
- a pump or a G-rotor of an oil system;
- a swash plate of a compressor;

- an air bag sensor;
- a friction plate, a door sleeve or a bracket or another sliding component of a train door;
- an automotive chassis component; or
- a motor thrust washer or film for seat adjustment mechanisms.

19. The article according to claim 17, wherein the article is:

- a 3D-printed article;
- a foam article;
- a coating;
- an adhesive or component of an adhesive;
- a component of a composite article;
- a component of a multi-layer article; or
- a medical device component.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/081782

A. CLASSIFICATION OF SUBJECT MATTER INV. C08F290/06 C08G63/181 C08G63/185 C08G63/189 C08G63/91 C08L67/02 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) C08F C09J C08G 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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 355 738 B2 (MITSUI CHEMICALS INC [JP]) 12 March 2002 (2002-03-12) compound B1 compounds B2, B3 claims 1-21 -----	1-6, 9-17
X	EP 2 931 798 B1 (RESINATE MAT GROUP INC [US]) 16 October 2019 (2019-10-16) example 19 claims 1-10 -----	1, 2, 7, 8, 13, 14, 17-19
X	US 9 790 321 B2 (ESTER IND LTD [IN]) 17 October 2017 (2017-10-17) examples 3, 4 claims 1-13 -----	1, 2, 8, 9, 11-14, 17-19
☐ 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 17 February 2023		Date of mailing of the international search report 27/02/2023
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 Popescu, Teodora

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/081782

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