

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



WIPO | PCT



(10) International Publication Number

WO 2014/191292 A1

(43) International Publication Date
4 December 2014 (04.12.2014)

- (51) International Patent Classification:
C07C 255/37 (2006.01) C08G 73/10 (2006.01)
C08F 265/06 (2006.01) G02F 1/1337 (2006.01)
- (21) International Application Number:
PCT/EP2014/060508
- (22) International Filing Date:
22 May 2014 (22.05.2014)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13169419.2 28 May 2013 (28.05.2013) EP
- (71) Applicant: ROLIC AG [CH/CH]; Chamerstrasse 50, CH-6300 Zug (CH).
- (72) Inventors: BURY S. PIRES, Izabela; Burgfeldermattweg 63, CH-4123 Allschwil (CH). CHAPPELLET, Sabrina; 37 rue des Jardins, F-68128 Village-Neuf (FR). IBN-EL-HAJ, Mohammed; In den Dürrenmatten 1, CH-4123 Allschwil (CH). LINCKER, Frédéric; 4 rue d'Epemay, F-67300 Schiltigheim (FR).
- (74) Agent: VEENSTRA, Eva; Rolic Technologies Ltd., IP Department, Gewerbestrasse 18, CH-4123 Allschwil (CH).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report (Art. 21(3))

(54) Title: CYANOSTILBENES

(57) Abstract: The present invention relates to novel compounds that are particularly useful for the alignment, especially photo-alignment, of slave material, especially liquid crystals for optical or electro-optical applications, such as security applications, liquid crystal devices or optical or electro-optical films.

WO 2014/191292 A1

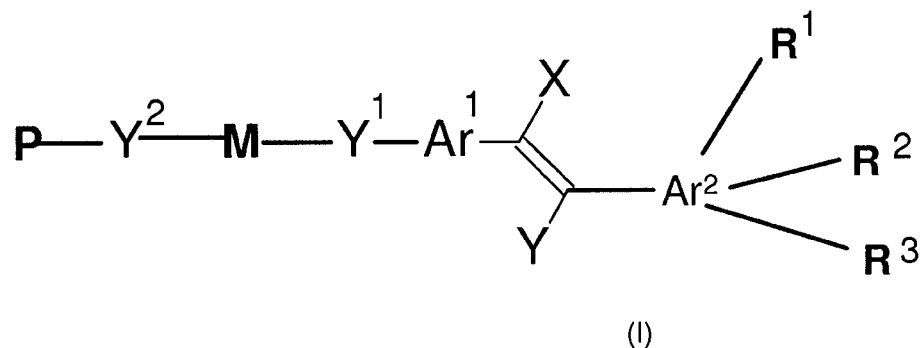
Cyanostilbenes

The present invention relates to compounds that are particularly useful for the alignment, especially photoalignment, of slave material, especially liquid crystals for optical or electro-optical applications, such as security applications, liquid crystal devices or optical or electro-optical films.

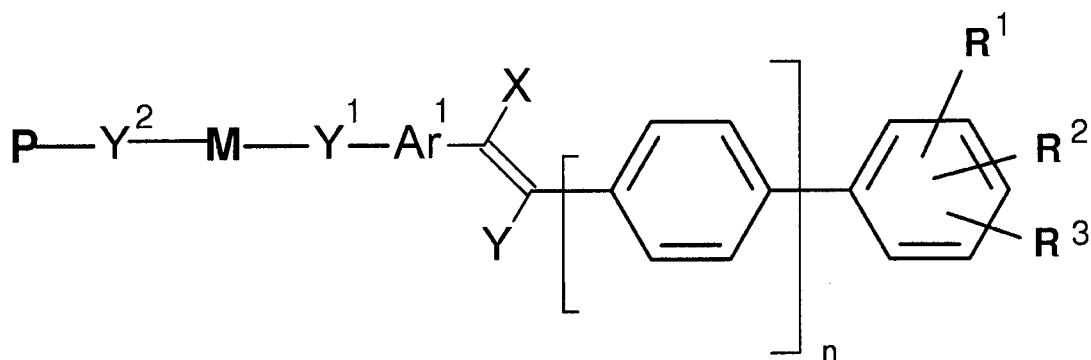
The photoalignment process for the orientation of slave material, especially liquid crystals, is a very economic and ecologic way of manufacturing because it generates nearly any wastage.

Hence, there is a constant growing demand from the market to provide further photoalignment material having advanced properties for the desired application, such as high contrast, good alignment quality, azimuthal stability or high speed of orientation.

Thus, the present invention relates in a first aspect to compounds according to the general formula (I)



preferably



(Ia)

wherein

Ar¹ and Ar² are independently from each other a ring system of 4 to 40 atoms, wherein each ring system includes at least one unsaturation directly connected via electron conjugation (π - π bonding) to the double bond shown in formula (I),
 5 wherein the ring system is unsubstituted or mono- or poly-substituted by a halogen atom and/or a polar group like hydroxy, nitro, nitrile, -CF₃; or by a carboxy group, and/or a cyclic, straight-chain or branched alkyl residue having from 1 to 30 carbon atoms, which is unsubstituted, mono- or poly-substituted by methyl, fluorine and/or chlorine, wherein one or more, preferably non-adjacent -CH₂- groups
 10 independently may be replaced by a group selected from -O-, -CO-, -CO-O-, -O-CO-, -NR^{1'}-, -NR^{1'}-CO-, -CO-NR^{1'}-, -NR^{1'}-CO-O-, -O-CO-NR^{1'}-, -NR^{1'}-CO-NR^{1'}-, -CH=CH-, -C $\equiv$ C-, -O-CO-O- and -Si(CH₃)₂-O-Si(CH₃)₂-, an aromatic or an alicyclic group, wherein R^{1'} is a hydrogen atom or lower alkyl; and/or an acryloyloxy, alkoxy,
 15 alkylcarbonyloxy, alkyloxocarbonyloxy, methacryloyloxy, vinyl, allyl, vinyloxy and/or allyloxy group, having from 1 to 20 carbon atoms, preferably having from 1 to 10 carbon atoms; preferably the ring system is unsubstituted or substituted by an alkoxy group; and wherein;

if X is hydrogen and Y is CN,

20 then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃, with the proviso that R¹, R² or R³ are not simultaneously hydrogen;

if X is CN and Y is hydrogen;

then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃;

M is a single covalent bond or a spacer unit;

25 Y¹, Y² are independently from each other a bridging group,

n is 0, 1, 2 or 3; preferably 0,

P is a hydrogen atom, optionally substituted alkyl, or a polymerizable group.

[0001] In the context of the present application, a "slave material" shall refer to any
 30 material that has the capability to establish anisotropy upon contact with a photo-aligned material. The nature of the anisotropy in the photo-aligned material and in the slave material may be different from each other. For example, the slave material may exhibit light absorption anisotropy for visible light and therefore can act as a polarizer,

whereas the anisotropy of the photo-aligned material may only be related to the molecular orientation. There may be also moieties of the photo-alignable material, for example in a co-polymer, which are not sensitive to aligning light, but create anisotropic properties because of interaction with the photo-sensitive moieties, which
5 undergo a photo-reaction upon exposure to aligning light. Such a material exhibits properties of a photo-alignable material and of a slave material, but shall be included in the meaning of a photo-alignable material.

[0002] A slave material may comprise polymerizable and/or non-polymerizable compounds. Within the context of the present application the terms "polymerizable" and "polymerized" shall include the meaning of "cross-linkable" and "cross-linked",
10 respectively. Likewise, "polymerization" shall include the meaning of "cross-linking".

[0003] Preferably, the slave material is a self organizing material. More preferred is that the slave material is a liquid crystal material and in particular preferred is that the slave material is a liquid crystal polymer material.

15 [0004] A liquid crystal polymer (LCP) material as used within the context of this application shall mean a liquid crystal material, which comprises liquid crystal monomers and/or liquid crystal oligomers and/or liquid crystal polymers and/or cross-linked liquid crystals. In case the liquid crystal material comprises liquid crystal monomers, such monomers may be polymerized, typically after anisotropy has been
20 created in the LCP material due to contact with a photo-aligned material. Polymerization may be initiated by thermal treatment or by exposure to actinic light, which preferably, comprises uv-light. A LCP-material may consist of a single type of liquid crystal compound, but may also be a composition of different polymerizable and/or non-polymerizable compounds, wherein not all of the compounds have to be
25 liquid crystal compounds. Further, an LCP material may contain additives, for example, a photo-initiator or isotropic or anisotropic fluorescent and/or non-fluorescent dyes.

[0005] In the context of this application, an alignment layer comprising compound (I), as a photo-alignable material, is also referred to as a light controlled molecular orientation (LCMO) layer, no matter if it has already been exposed to polarized light or
30 not. Accordingly, an LCMO layer, as used herein, may have no anisotropic property as long as it has not been exposed to aligning light, preferably polarized light and has

anisotropic property after it has been exposed to aligning light. Typically, an LCMO layer may be a thin layer applied to a substrate. It is also possible that the LCMO layer is thick and mechanically stable enough, such that it can be handled without an additional substrate. In the latter case, the LCMO layer has also the function of a substrate.

[0006] In the context of the present application, the term "aligning light" shall mean light, which can induce anisotropy in a photo-alignable material and which is at least partially linearly or elliptically polarized. Preferably, the aligning light is linearly polarized with a degree of polarization of more than 5:1. Wavelengths, intensity and energy of the aligning light are chosen depending on the photosensitivity of the photo-alignable material. Typically, the wavelengths are in the UV-A, UV-B and/or UV-C range or in the visible range. Preferably, the aligning light comprises light of wavelengths less than 450 nm. More preferred is that the aligning light comprises light of wavelengths less than 420 nm.

[0007] If the aligning light is linearly polarized, the polarization plane of the aligning light shall mean the plane defined by the propagation direction and the polarization direction of the aligning light. In case the aligning light is elliptically polarized, the polarization plane shall mean the plane defined by the propagation direction of the light and by the major axis of the polarization ellipse.

In a further aspect, the compound (I) is part of an oligomer, dendrimer, or polymer. In the context of the present invention the term polymer is a homopolymer or a copolymer and/or an oligomer and/or dendrimer. Said polymer may be obtained by polymerization of the monomer of general formula (I) and may be in form of a gel or a network.

The invention relates in a further aspect to alignment layer materials comprising said compounds according to formula (I) in monomeric, oligomeric, dendrimeric or polymeric form. Such alignment layer materials are particularly useful for the alignment of liquid crystals and polymerizable, dimerizable or crosslinkable liquid crystalline materials.

The invention relates in yet a further aspect to optical elements, e.g. polymerized, dimerized or crosslinked films having a nematic, smectic or cholesteric order, and electro-optical elements, e.g. liquid crystal display cells, comprising an alignment layer made of a material comprising a compound according to the general formula (I) in monomeric, oligomeric, dendrimeric or polymeric form.

In specific embodiments, the alignment layer has a pattern of different alignment directions, which pattern advantageously can be formed by photoalignment methods.

In a further aspect the invention also relates to the use of materials containing a compound according to formula (I) for the preparation of alignment layers.

It is understood that the wording "each ring system includes at least one unsaturation directly connected via electron conjugation (π - π bonding) to the double bond" indicates that each ring system Ar^1 and Ar^2 contains at least one unsaturated bond, i.e. double bond, that is directly linked to the double bond in formula (I) thereby extending the electron conjugation.

In a preferred embodiment ring systems Ar^1 and Ar^2 is a carbocyclic or heterocyclic ring group selected from a monocyclic ring of four to six atoms, or two adjacent monocyclic rings of five or six atoms, or a fused bicyclic ring system of eight, nine or ten atoms, or a fused tricyclic ring system of thirteen or fourteen atoms. More preferably ring systems Ar^1 and Ar^2 are selected from pyrimidine, pyridine, thiophenylene, furanylene, phenanthrylene, naphthylene, biphenylene or phenylene. Most preferred Ar^1 is phenylene, which is unsubstituted or substituted with -O-methyl, preferably Ar^1 is unsubstituted. Further most preferred Ar^2 is phenylene or biphenylene, preferably phenylene, which is unsubstituted or substituted by R^1 , R^2 and R^3 within the above given meanings and preferences.

In a further preferred embodiment of the present invention the bridging group is a group selected from but not limited to a single bond, -O-, -CO-, -CO-O-, -O-CO-, -NR^{1'}-, -NR^{1'}-CO-, -CO-NR^{1'}-, -NR^{1'}-CO-O-, -O-CO-NR^{1'}-, -NR^{1'}-CO-NR^{1'}-, -C=C-,

-C≡C-, -O-CO-O- and -Si(CH₃)₂-O-Si(CH₃)₂-, wherein R^{1'} is a hydrogen atom or lower alkyl, preferably single bond, -O-, -CO-, -COO-, -OCO-, -C=C-, -C≡C-. More preferably Y¹ and Y² are single bond, -O-, -CO-, -COO-, -OCO-, and most preferred Y¹ is -O- and Y² is single bond, -O-, -CO-, -COO- or -OCO-.

5

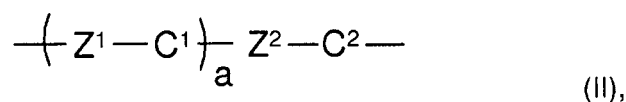
In a further preferred embodiment M is a single bond or a straight-chain or branched alkylene residue having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 or 24, preferably 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16, more preferably 6, 7, 8, 9, 10, 11 or 12 carbon atoms, most preferred 8, 9, 10 or 11, which is unsubstituted, mono-substituted by cyano or halogen, or poly-substituted by halogen and wherein one or more, preferably non-adjacent CH₂ groups independently may be replaced by a heteroatom or a group selected from but not limited to -O-, -CO-
 10 -CO-O-, -O-CO-, -NR^{1'}-, -NR^{1'}-CO-, -CO-NR^{1'}-, -NR^{1'}-CO-O-, -O-CO-NR^{1'}-, -NR^{1'}-CO-NR^{1'}-, -C=C-, -C≡C-, -O-CO-O- and -Si(CH₃)₂-O-Si(CH₃)₂-, preferably
 15 selected from -O-, -CO-, -COO-, -OCO-, -C=C-, -C≡C-, wherein R^{1'} is a hydrogen atom or lower alkyl. Preferably M is unsubstituted.

In a further preferred embodiment the polymerizable group in P is selected from unsubstituted or substituted acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, optionally *N*-lower alkyl substituted acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, vinyl ether and ester, allyl ether and ester, epoxy, carbonic acid ester, acetal, styrene and styrene derivatives, for example alpha-methylstyrene, p-methylstyrene, p-tert-butyl styrene, p-chlorostyrene, etc., siloxanes, silane, diamine, imide monomers, amic acid monomers and their esters, amidimide monomers, maleic
 20 acid and maleic acid derivatives, for example, di-n-butyl maleate, dimethyl maleate, diethyl maleate, etc, maleinimide, norbornene, norbornene derivatives, fumaric acid and fumaric acid derivatives, for example, di-n-butyl fumarate, di-(2-ethylhexyl) fumarate, etc, urea, urethanes or their corresponding homo- and co-polymers and mixtures thereof. More preferably the polymerizable group in P is selected from acrylate,
 25 methacrylate, vinyl ether and ester, epoxy, styrene derivatives, siloxanes, imide monomers, amic acid monomers and their corresponding polymers, homo or copolymers.

30

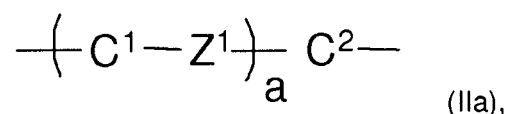
In a yet a further embodiment

Ar¹ is a ring system of formula (II):



and

5 Ar² is a ring system of formula (IIa)



wherein:

C¹, C² each independently are a non-aromatic or aromatic, optionally substituted, carbocyclic or heterocyclic group of 5 to 14 atoms, preferably connected to each other at the opposite positions via the bridging groups Z¹ and Z²,

10 Z¹, Z² each independently are a single bond or a bridging group preferably selected from -CH(OH)-, -O-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -COF₂-, -CF₂CO-, -S-CO-, -CO-S-, -SOO-, -OSO-, -CH₂-CH₂-, -O-CH₂-, -CH₂O-, -CH=CH-, -C≡S-, -SH=CH-COO-, -OCO-CH=CH-, -CH=N-,
15 -C(CH₃)=N-, -O-CO-O-, -N=N-, or a short alkyl spacer of 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms,

a is 0, 1, 2 or 3,

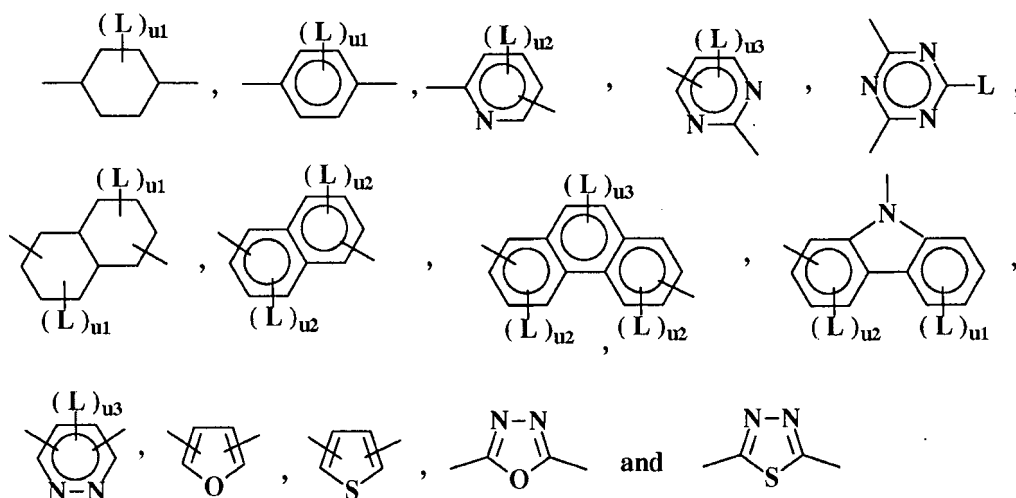
with the proviso that C², which is directly connected to the double bond, is unsaturated and conjugated to it.

20

The term "connected to each other at the opposite positions via the bridging groups Z¹ and Z²" means that five- and six-membered rings are preferably linked in 1,3- or 1,4-position. Analogous linking pattern in other e.g. higher membered rings will be obvious to a skilled person.

25

Preferably C¹, C² in formula (II) independently have one of the following meanings:



wherein

- L is halogen, hydroxyl, and/or a polar group such as nitro, cyano or carboxy, and/or acryloyloxy, alkoxy, such as methoxy, ethoxy, propoxy, alkylcarbonyloxy, alkyloxocarbonyloxy, methacryloyloxy, vinyl, vinyloxy, allyl, allyloxy, and/or a cyclic, straight-chain or branched alkyl residue, which is unsubstituted, mono- or poly-substituted by fluorine and/or chlorine, and/or a silane group, and/or a siloxane group, wherein the alkyl residue has from 1 to 20 C-atoms, wherein one or more, preferably non-adjacent, -CH₂- groups independently may be replaced by a group, preferably selected from -O-, -CO-, -COO-, -OCO-, -C=C-, -C≡C-, -Si(CH₃)₂-, -Si(CH₃)₂-O-Si(CH₃)₂-, preferably L is methoxy
- u₁ is 0, 1, 2, 3, or 4, preferably 0 or 1,
- u₂ is 0, 1, 2, or 3, preferably 0 or 1, and
- u₃ is 0, 1, or 2 preferably 0 or 1,
- with the proviso that C², which is directly connected to the double bond, is unsaturated and conjugated to it.

More preferably C¹, C² are phenanthryl or phenanthrylene, biphenyl or biphenylene, naphthyl or naphthylene, phenyl or phenylene, pyridine or pyridinylene; preferably naphthyl or naphthylene, phenyl or phenylene, pyridine or pyridinylene, and more preferably phenyl or phenylene.

Preferably L is selected from alkoxy, more preferably methoxy, ethoxy or propoxy.

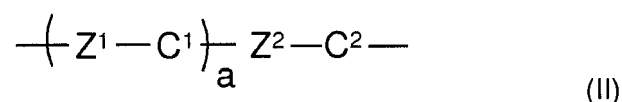
Preferably Z^1 , Z^2 in formulae (II) and (III) each independently are a single bond or a bridging group selected from -CH(OH)-, -O-, -CH₂(CO)-, -COO-, -OCO-, -COF₂-, -CF₂CO-, -CH₂-CH₂-, -O-CH₂-, -CH₂O-, -CH=CH-, -OCO-CH=CH-, -CH=N-, -C(CH₃)=N-, -O-CO-O-, -N=N-, or a short alkyl spacer of 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms.

More preferably Z^1 , Z^2 each independently are a single bond -O-, -CH₂(CO)-, -COO-, -OCO-, -CH₂-CH₂-, -OCO-CH=CH-, -N=N-, or a short alkyl spacer of 1 to 3 carbon atoms.

10

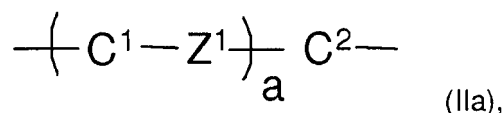
Preferred compounds of formula (I) are those, wherein

Ar^1 is a ring system of formula (II):



and

15 Ar^2 is a ring system of formula (IIa)



wherein:

20 C^1 , C^2 each independently are a non-aromatic or aromatic, optionally substituted, carbocyclic or heterocyclic group of 5 to 14 atoms, preferably connected to each other at the opposite positions via the bridging groups Z^1 and Z^2 ,

Z^1 , Z^2 each independently are a single bond or a bridging group preferably selected from -CH(OH)-, -O-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -COF₂-, -CF₂CO-, -S-CO-, -CO-S-, -SOO-, -OSO-, -CH₂-CH₂-, -O-CH₂-, -CH₂O-, -CH=CH-, -C≡S-, -SH=CH-COO-, -OCO-CH=CH-, -CH=N-, -C(CH₃)=N-, -O-CO-O-, -N=N-, or a short alkyl spacer of 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms,

25 a is 0, 1, 2 or 3, preferably a is 0 or 1, more preferably 0, with the proviso that C^2 , which is directly connected to the double bond, is unsaturated and conjugated to it;

30

or more preferred are compounds of formula (Ia), wherein
and wherein;

if X is hydrogen and Y is CN,

then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃, with
the proviso that R¹, R² or R³ are not simultaneously hydrogen;

or preferably, if X is hydrogen and Y is CN,

then R¹ is fluoro, chloro, bromo or -CF₃, and R² and R³ are hydrogen; or

R¹ and R² is independently from each other fluoro, chloro, bromo or -CF₃, and
R³ is hydrogen; or R¹, R² or R³ are simultaneously fluoro, chloro or bromo;

or

if X is CN and Y is hydrogen;

then R¹ is fluoro, chloro, bromo or -CF₃, and R² and R³ are hydrogen; or

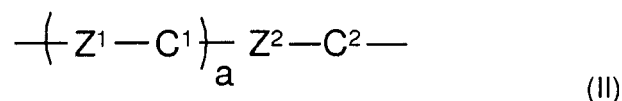
R¹ and R² is independently from each other fluoro, chloro, bromo or -CF₃, and
R³ is hydrogen; or R¹, R² or R³ are simultaneously hydrogen, fluoro, chloro or
bromo;

M is a single bond or a straight-chain or branched alkylene residue having 1, 2, 3,
4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 or 24, preferably 1,
2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16, more preferably 6, 7, 8, 9, 10, 11 or
12 carbon atoms, most preferred 8, 9, 10 or 11, wherein one or more -CH₂- groups
independently may be replaced by a group selected from -O-, -CO-, -COO-, -OCO-,
-C=C-, -C≡C-;

P is a hydrogen atom, optionally substituted alkyl, or a polymerizable
group.

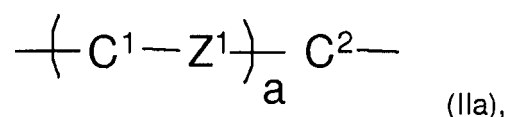
Thus more preferred compounds are compounds according to formula (I) wherein

Ar¹ is a ring system of formula (II):



and

Ar² is a ring system of formula (IIa)



wherein:

C¹, C² each independently are phenyl or phenylene;

Z¹, Z² each independently are a single bond or -O-, -CH₂(CO)-, -COO-,

5 -OCO-, -CH₂-CH₂-, -OCO-CH=CH-, -N=N-, or a short alkyl spacer of 1 to 3 carbon atoms,

a is 0 or 1, preferably 0;

or most preferred are compounds of formula (Ia);

and wherein;

10 if X is hydrogen and Y is CN,

then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃, with the proviso that R¹, R² or R³ are not simultaneously hydrogen;

or preferably, if X is hydrogen and Y is CN,

then R¹ is fluoro, chloro, bromo or -CF₃, and R² and R³ are hydrogen; or

15 R¹ and R² is independently from each other fluoro, chloro, bromo or -CF₃, and R³ is hydrogen; or R¹, R² or R³ are simultaneously fluoro, chloro or bromo;

or

if X is CN and Y is hydrogen;

then R¹ is fluoro, chloro, bromo or -CF₃, and R² and R³ are hydrogen; or

20 R¹ and R² is independently from each other fluoro, chloro, bromo or -CF₃, and R³ is hydrogen; or R¹, R² or R³ are simultaneously hydrogen, fluoro, chloro or bromo;

M is a single bond or a straight-chain or branched alkylene residue having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 or 24, preferably 1,

25 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16, more preferably 6, 7, 8, 9, 10, 11 or 12 carbon atoms, most preferred 8, 9, 10 or 11, wherein one or more -CH₂- groups independently may be replaced by a group selected from -O-, -COO-, -OCO-, -C=C-;

P is a hydrogen atom, optionally substituted alkyl, or a polymerizable group selected from acrylate, methacrylate, vinyl ether and ester, epoxy, siloxanes,

30 silane, diamines, imide monomers, amic acid monomers and their ester, and mixtures thereof, or their corresponding homo- and co-polymers.

The term "alkyl", unless the context requires otherwise, includes straight-chain and branched alkyl, as well as saturated and unsaturated groups.

The term "lower alkyl", as used in the context of the present invention, taken on its own or in a combination such as "lower alkoxy", etc., preferably denotes straight-chain and branched saturated hydrocarbon groups having from 1 to 6, preferably from 1 to 3, carbon atoms. Methyl, ethyl, propyl and isopropyl groups are especially preferred. In case of "lower alkoxy", methoxy, ethoxy, propoxy and isopropoxy groups are especially preferred.

The term "aliphatic", unless the context requires otherwise, includes straight-chain and branched alkyl, as well as saturated and unsaturated groups. Possible substituents include alkyl, aryl (thus giving an araliphatic group) and cycloalkyl, as well as amino, cyano, epoxy, halogen, hydroxy, nitro, oxo etc. Possible heteroatoms which may replace carbon atoms include nitrogen, oxygen and sulphur. In the case of nitrogen further substitution is possible with groups such as alkyl, aryl and cycloalkyl.

The term "alicyclic", as used in the context of the present invention, preferably denotes optionally substituted non-aromatic carbocyclic or heterocyclic ring systems, with 3 to 30 carbon atoms, e.g. cyclopropane, cyclobutane, cyclopentane, cyclopentene, cyclohexane, cyclohexene, cyclohexadiene, decaline, tetrahydrofuran, dioxane, pyrrolidine, piperidine or a steroidal skeleton such as cholesterol.

The term "aromatic", as used in the context of the present invention, preferably denotes optionally substituted carbocyclic and heterocyclic aromatic groups, incorporating five, six, ten or 14 ring atoms, e.g. furan, benzene, pyridine, pyrimidine, naphthalene, phenanthrene, biphenylene or tetraline units.

The term "phenylene", as used in the context of the present invention, preferably denotes a 1,2-, 1,3- or 1,4-phenylene group, which is optionally substituted. It is preferred that the phenylene group is either a 1,3- or a 1,4-phenylene group. 1,4-phenylene groups are especially preferred.

The term "halogen" denotes a chloro, fluoro, bromo or iodo substituent, preferably a chloro or fluoro substituent.

The term "polar group", as used in the context of the present invention primarily denotes a group like hydroxy, nitro, nitrile, $-CF_3$ or a carboxy group.

5 The term "heteroatom", as used in the context of the present invention primarily denotes oxygen, sulphur and nitrogen, preferably oxygen and nitrogen, in the latter case preferably in the form of $-NH-$.

10 The term "optionally substituted" as used in the context of the present invention primarily means substituted by lower alkyl, lower alkoxy, hydroxy, halogen or by a polar group as defined above.

15 With respect to straight or branched alkyl, alkylene, alkoxy, alkoxycarbonyl, alkylcarbonyl, alkylcarbonyloxy groups it is repeatedly pointed out that some or several of the $-CH_2-$ groups may be replaced e.g. by heteroatoms, but also by other groups. In such cases it is generally preferred that such replacement groups are not directly linked to each other. It is alternatively preferred that heteroatoms, and in particular oxygen atoms are not directly linked to each other.

20 The term "polymerizable group" as used in the context of the present invention refers to a functional group that can be subjected to polymerization (optionally with other comonomers) to yield an oligomer, dendrimer or polymer according to the present invention. For a person skilled in the art it will be obvious which functional groups are intended for any specific polymer. Thus for example in case of "imid monomer" as the indicated polymer backbone group it is obvious to a person skilled in the art that the
25 actual monomer units for polymerization to yield a polyimid are e.g. diamines and dianhydrides. Similarly regarding "urethane monomer" the actual monomer units are diols and diisocyanates.

30 The compounds according to the present invention in form of prefinished monomers may be readily prepared using methods that are well known to the person skilled in the art. Suitable methods can for instance be found in Houben-Weyl, Methoden der Organischen Chemie, Thieme-Verlag, Stuttgart.

Subsequently these prefinished monomers are typically subjected to direct polymerisation to obtain an oligomer, dendrimer or polymer. Thus, the compounds of the present invention may also be part of an oligomer, a dendrimer or a polymer, which may be a homopolymer or a copolymer.

5

In a specific embodiment the compounds of formula (I) may be formulated with any other monomers, functional moieties and additives.

10

For the direct polymerisation, the monomers and (optionally) the comonomers are firstly prepared separately from the individual components. Subsequently the formation of the polymers is effected in a manner known *per se* for any given polymer for example under the influence of UV radiation or heat or by the action of radical or ionic catalysts. Potassium peroxodisulfate, dibenzoyl peroxide, azobisisobutyronitrile or di-*tert*-butyl peroxide are examples of radical initiators. Ionic catalysts are alkali-organic compounds such as phenyllithium or naphthylsodium or Lewis acids such as BF₃, AlCl₃, SnCl₃ or TiCl₄. The monomers can be polymerised in solution, suspension, emulsion or substance.

15

If copolymerized with other comonomers the obtained copolymers are consisting of a monomer unit derivating from formula (I) as defined in any of the proceeding meanings and any other known monomer unit that is commercially available or not.

20

Upon polymerization it may further be advantageous to terminate the growing polymer chain after a suitable chain length is reached by capping the polymerizable group present at the chain end by using specific reagents well known in the art.

25

Suitable polymers include polyacrylates, polymethacrylates, polyacrylamides, polymethacrylamides, polyvinylether and polyvinylester, polyallylether and ester, polystyrenes, polysiloxanes, polyimides, polyamic acids and their esters, polyamidimides, polymaleic acids, polyfumaric acids polyurethanes or derivatives thereof or mixtures thereof.

30

These polymers may all be prepared according to well known methods in the art. Thus for example the poly(meth)acrylates described herein may be prepared in line with

methods such as described in Polymer Synthesis Characterization: A Laboratory Manual (Stanley R. Sandler, Wolf Karo, JoAnne Bonesteel, Eli M. Pearce) and Principles of Polymerization (George Odian).

- 5 Thus in the case when the monomer unit is bearing an acrylic or methacrylic end, the comonomer unit can be represented by compounds listed below. Most of them are commercially available from chemical suppliers such as Aldrich, ABCR, ACROS, Fluka.
- 10 2,2,2-trifluoroethyl acrylate, 2-hydroxyethyl acrylate, acrylic acid, glycidyl acrylate, methyl acrylate, tert-butyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 3-sulfopropyl acrylate, potassium salt, 4-hydroxybutyl acrylate, 2-bromoethyl acrylate, 2-cyanoethyl acrylate, tetrahydrofurfuryl acrylate, allyl acrylate, stearyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-hydroxypropyl acrylate, iso-hexadecyl acrylate,
- 15 2-tetrahydrofuryl acrylate, n,n-dimethylaminoethyl acrylate, 1h,1h-perfluorooctyl acrylate, 1h,1h-heptafluorobutyl acrylate, 2,2,3,3,3-pentafluoropropyl acrylate, 1h,1h,5h-octafluoropentyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, d,l-menthyl acrylate, beta-carboxyethyl acrylate, 1h,1h,11h-eicosafluoroundecyl acrylate, 2-fluoroethyl acrylate, 1h,1h,2h,2h-perfluorodecyl acrylate, pentafluorobenzyl
- 20 acrylate, pentafluorophenyl acrylate, 1h,1h,2h,2h-perfluorooctyl acrylate, 2,2,3,3-tetrafluoropropyl acrylate, isobutyl acrylate, lauryl acrylate, n,n-diethylaminoethyl acrylate, 2-ethoxyethyl acrylate, (r)-(+)-alpha-acryloyloxy-beta,beta-dimethyl-gamma-butyrolactone, 2,2,3,4,4,4-hexafluorobutyl acrylate, 2-chloroethyl acrylate, cyclohexyl acrylate, methallyl acrylate, phenyl acrylate, acrylic anhydride,
- 25 benzyl acrylate, 2-methoxyethyl acrylate, cinnamyl acrylate, 3-methoxybutyl acrylate, iso-propyl acrylate, n-decyl acrylate, undecyl acrylate, tridecyl acrylate, 2-ethylbutyl acrylate, n-propyl acrylate, acryloxytri-n-butyltin, 2-n-butoxyethyl acrylate, n-amyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-hydroxy-3-chloropropyl acrylate, 2-phenoxyethyl acrylate, iso-amyl acrylate, sec-butyl acrylate,
- 30 n-(3-acryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, (3-acryloxypropyl)methylbis(trimethylsiloxy)silane, (3-acryloxypropyl)dimethylmethoxysilane, 3-acryloxypropyl tris(trimethylsiloxy) silane, (3-acryloxypropyl)trimethoxysilane, (3-acryloxypropyl)methyldichlorosilane, (3-acryloxypropyl)trichlorosilane, vinyl acrylate, 2,3-dibromopropyl acrylate, mono-(acryloyloxyethyl) phthalate,

3-acryloxypropyl-2-n-phenyl carbamate, 2-hydroxy-3-phenoxypropyl acrylate,
 potassium acrylate, sodium acrylate, [2-(acryloyloxy)ethyl](4-
 benzoylbenzyl)dimethylammonium bromide, n-acryloxysuccinimide, 1h,1h,9h-
 hexadecafluorononyl acrylate, 3,3,5-trimethylcyclohexyl acrylate, n-nonyl acrylate,
 5 cyclopentyl acrylate, perfluorooctyl acrylate, 2-allyloxyethoxyethyl acrylate,
 crotyl acrylate, 4-cumylphenyl acrylate, 2,4,6-tribromophenyl acrylate,
 hexadecyl acrylate, propargyl acrylate, acrylate, ammonium, acrylate, cesium,
 lithium acrylate, acrylate, rubidium, n-(acryloxyethyl) phthalimide, n-(acryloxyethyl)
 succinimide, mono-2-acryloyloxyethyl maleate, 2-allyloxyethyl acrylate
 10 allyloxy propyl acrylate, behenyl acrylate, 1,3-bis(4-benzoyl-3-hydroxyphenoxy)-2-
 propyl acrylate, isobornyl acrylate, 2-(bromo-1-naphthoxy)-ethyl acrylate,
 2-(1-bromo-2-naphthoxy)-ethyl acrylate, p-chlorophenoxyethyl acrylate,
 4-chlorophenyl acrylate, 2-cyanoethoxyethyl acrylate, cyclol acrylate,
 iso-decyl acrylate, dibutyltin acrylate, n,n-diethylaminoethyl acrylate q-salt,
 15 methosulfate, [2-(acryloyloxy)ethyl]trimethylammonium chloride, 3,6-dioxaheptyl
 acrylate, furfuryl acrylate, 2,3-dihydroxypropyl acrylate, hexoxyethyl acrylate,
 3-iodobenzyl acrylate, d-menthyl acrylate, l-menthyl acrylate, 2-methyl butyl acrylate,
 2-n-morpholinoethyl acrylate, alpha-naphthyl acrylate, beta-naphthyl acrylate,
 2-(1-naphthoxy)-ethyl acrylate, 2-(2-naphthoxy)-ethyl acrylate, 2-nitroethyl acrylate,
 20 p-nitrophenyl acrylate, nonylphenyl acrylate, norbornyl acrylate, 2-octyl acrylate,
 isooctyl acrylate, pentabromophenyl acrylate, pentachlorophenyl acrylate, neo-pentyl
 acrylate, (perfluorocyclohexyl)methyl acrylate, 2-phenylethyl acrylate,
 phenylpropyl acrylate, mono-2-acryloyloxyethyl phthalate, 1-piperidineethyl acrylate,
 silver acrylate, sorbitol acrylate, trichloroethyl acrylate,
 25 [2-(acryloyloxy)ethyl]trimethylammonium methyl sulphate, 3,5,5-trimethylhexyl acrylate
 vinylbenzyl acrylate, 2-(n-butylperfluorooctanesulfamido) ethyl acrylate,
 2-(n-ethylperfluorooctanesulfamido) ethyl acrylate,
 3-(trifluoromethyl)benzyl acrylate, 1h,1h,7h-dodecafluoroheptyl acrylate,
 3-dimethylamino neopentyl acrylate, 1h,1h,3h-hexafluorobutyl acrylate,
 30 2-(4-benzoyl-3-hydroxyphenoxy)ethyl acrylate, monoacryloxyethyl phosphate,
 2,2-dinitropropyl acrylate, abitol acrylate, potassium acrylate, hemihydrate,
 2-(acryloxyethoxy)trimethylsilane, (3-acryloxypropyl)methyldimethoxysilane,
 Acryloxytrimethylsilane, acryloxytriphenyltin, sodium acrylate, hemihydrate,
 dicyclopentenyl acrylate, dicaprolactone 2-(acryloyloxy)ethyl ester,

di(ethylene glycol) 2-ethylhexyl ether acrylate, dicyclopentenylloxyethyl acrylate,
 3-(dimethylamino)propyl acrylate, 4,4-dimethyl-2-oxotetrahydrofuran-3-yl acrylate,
 2-(perfluorobutyl)ethyl acrylate, 3-(perfluorobutyl)-2-hydroxypropyl acrylate,
 3-(perfluorohexyl)-2-hydroxypropyl acrylate, 3-(perfluorooctyl)-2-hydroxypropyl
 5 acrylate, 2-(perfluorodecyl)ethyl acrylate, 2-(perfluoro-3-methylbutyl)ethyl acrylate,
 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate, 2-(perfluoro-5-methylhexyl)ethyl
 acrylate, 2-(perfluoro-9-methyloctyl)ethyl acrylate, 2-(perfluoro-9-methyldecyl)ethyl
 acrylate, urethane acrylate, mono-2-(acryloyloxy)ethyl succinate,
 heptafluoro-2-propyl acrylate,
 10 (3-(allanoyloxy)-5-[4-(benzoylamino)-2-oxopyrimidin-1(2h)-yl]tetrahydrofuran-2-yl),
 dihydrodicyclopentadienyl acrylate, 2-(acryloyloxy)ethyl acetoacetate
 acrylic acid 3-(1-oxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 4-tert-butylcyclohexyl acrylate,
 acrylic acid 3-(3,5-dioxo-4-aza-tricyclo(5.2.1.0(2,6))dec-8-en-4-yl)-ph ester,
 15 acrylic acid 3-(4-nitro-1,3-dioxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 acrylic acid 3-(4,5,6,7-tetrachloro-1,3-dioxo-1,3-2h-isoindol-2-yl)-phenyl ester
 methyl furyl acrylate, rcl r35,845-2,
 acrylic acid 3-(2,5-dioxo-pyrrolidin-1-yl)-phenyl ester,
 acrylic acid 3-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 20 cobalt acrylate, manganese acrylate, 3-acryloyloxypropyl-2-n-phenyl carbamate,
 acrylated bisphenol "a" glycidyl ether,
 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl acrylate,
 3-(perfluoro-7-methyloctyl)-2-hydroxypropyl acrylate,
 neopentyl glycol acrylate benzoate, 2'-cinnamoyloxyethyl acrylate,
 25 triisopropylsilyl acrylate, uvecryl p 36, 2-[[[(butylamino)carbonyl]oxy]ethyl acrylate,
 1h,1h-perfluoro-n-decyl acrylate, methacrylic acid, 2-hydroxyethyl methacrylate,
 2-hydroxypropyl methacrylate, glycidyl methacrylate, methacrylic anhydride,
 methyl methacrylate, 2-(dimethylamino)ethyl methacrylate, allyl methacrylate,
 3-methacryloxypropyltrimethoxysilane, isobutyl methacrylate, lauryl methacrylate,
 30 ethyl methacrylate, 2-ethoxyethyl methacrylate, n-butyl methacrylate,
 2-ethylhexyl methacrylate, potassium sulfopropylmethacrylate,
 2,2,2-trifluoroethyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl
 methacrylate, 2-(tert-butylamino)ethyl methacrylate, n-hexyl methacrylate,
 1,6-hexanediol dimethacrylate,

- 3-methyl-2-benzothiazolinone, azine with 4'-(2-(me-acryloyl-o)ethoxy)acetophenone
 2-(p-nitrophenoxy) ethyl methacrylate, stearyl methacrylate
 2-hydroxy-3-methacryloxypropyl trimethyl ammonium chloride
 2-phenylethyl methacrylate, 2-(diethylamino)ethyl methacrylate
 5 1h,1h-perfluorooctyl methacrylate, 1h,1h-heptafluorobutyl methacrylate
 2,2,3,3,3-pentafluoropropyl methacrylate, 1h,1h,5h-octafluoropentyl methacrylate
 1,1,1,3,3,3-hexafluoroisopropyl methacrylate,
 n-(3-sulfopropyl)-n-methacryloxyethyl-n,n-dimethylammonium betaine
 3-chloro-2-hydroxypropyl methacrylate, d,l-menthyl methacrylate,
 10 1h,1h,11h-perfluoroundecyl methacrylate, 2-fluoroethyl methacrylate,
 1h,1h,2h,2h-perfluorodecyl methacrylate, 2,2,3,4,4,4-hexafluorobutyl methacrylate,
 pentafluorobenzyl methacrylate, pentafluorophenyl methacrylate,
 2,2,3,3-tetrafluoropropyl methacrylate, 2-bromoethyl methacrylate, methacrylato
 chromic chloride, 2-chloroethyl methacrylate, cyclopentyl methacrylate,
 15 1,4-cyclohexanedimethyl 1,4-dimethacrylate,2-cyanoethyl methacrylate,
 barium methacrylate, potassium methacrylate, magnesium methacrylate,
 sodium methacrylate, zinc methacrylate, furfuryl methacrylate, phenyl methacrylate,
 neopentyl glycol dimethacrylate, methallyl methacrylate, 2-methoxyethyl methacrylate,
 propargyl methacrylate, 3-methoxybutyl methacrylate, tert-butyl methacrylate,
 20 isopropyl methacrylate, iso-amyl methacrylate, n-decyl methacrylate,
 sec-butyl methacrylate, 2-ethylbutyl methacrylate, n-propyl methacrylate,
 2-n-butoxyethyl methacrylate, hydroxypropyl methacrylate,
 Methacryloxypropylmethyldichlorosilane, benzyl methacrylate,
 2-phenoxyethyl methacrylate, methacryloxypropyltris(methoxyethoxy)silane,
 25 3-methacryloxypropyl pentamethyl disiloxane, iso-decyl methacrylate,
 methacryloxytri-n-butyltin, n-amyl methacrylate, n-octyl methacrylate,
 trimethylsilyl methacrylate, 2-(trimethylsiloxy)ethyl methacrylate,
 methacryloxypropylbis(trimethylsiloxy)methylsilane,
 methacryloxypropyltris(trimethylsiloxy)silane,
 30 methacryloxypropyldimethylethoxysilane,
 3-methacryloxypropylmethyldiethoxysilane,
 3-methacryloxypropyldimethylchlorosilane,
 2-methacryloxyethyldimethyl(3-trimethoxysilylpropyl)ammonium chloride,
 acetoacetoxyethyl methacrylate, methacryloxypropyltrichlorosilane,

3-methacryloxypropyltris(vinyldimethylsiloxy)silane, trimethylsilylmethyl methacrylate,
 (methacryloxymethyl) phenyldimethylsilane, methacryloxypropenyl trimethoxysilane,
 methacrylate, calcium, tridecyl methacrylate, vinyl methacrylate,
 methoxyethoxyethyl methacrylate, [2-(methacryloyloxy)ethyl]trimethylammonium
 5 chloride, mono-(2-(methacryloyloxy)-ethyl) phthalate, 2-hydroxy-3-phenoxypropyl
 methacrylate, methacryloxypropyltriethoxysilane, 2-diisopropylaminoethyl methacrylate,
 1h,1h,2h,2h-perfluorooctyl methacrylate, 2-aminoethyl methacrylate hydrochloride
 2-trimethylammonium ethyl methacrylate methosulfate, trityl methacrylate
 perfluorooctyl methacrylate, 2,4,6-tribromophenyl methacrylate,
 10 4-hydroxybutyl methacrylate, hexadecyl methacrylate, undecyl methacrylate,
 n-nonyl methacrylate, 2-allyloxyethoxyethyl methacrylate,
 3,3,5-trimethylcyclohexyl methacrylate, 2,3-dibromopropyl methacrylate,
 cinnamyl methacrylate, crotyl methacrylate,
 1h,1h,9h-hexadecafluorononyl methacrylate, n-heptyl methacrylate
 15 2-allyloxyethyl methacrylate, allyloxy propyl methacrylate,
 neo-pentyl methacrylate, 2-(1-aziridinyl)-ethyl methacrylate,
 behenyl methacrylate, 5-norbornene-2-methanol methacrylate,
 1,3-bis(4-benzoyl-3-hydroxyphenoxy)-2-propyl methacrylate,
 ethoxyethoxyethyl methacrylate, p-chlorophenoxyethyl methacrylate,
 20 4-cumylphenyl methacrylate, dibutyltin methacrylate,
 n,n-diethylaminoethyl methacrylate q-salt, methosulfate,
 diethylene glycol mono-methacrylate, 2,3-dihydroxypropyl methacrylate,
 3,3-dimethyl butanol-2 methacrylate, ethyl triglycol methacrylate,
 ethylidene dimethacrylate, ethylthioethyl methacrylate, hexoxyethyl methacrylate,
 25 2-(1-imidazoloyl) ethyl methacrylate, 3-iodobenzyl methacrylate,
 isocyanatoethyl methacrylate, d-menthyl methacrylate
 l-menthyl methacrylate, aluminum methacrylate,
 n-(methacryloxyethyl) phthalimide, n-(methacryloxyethyl) succinimide,
 4-methacryloxyethyl trimellitic anhydride,
 30 4-methacryloxy-2-hydroxybenzophenone,
 mono-(2-(methacryloyloxy)-ethyl) maleate,
 2-methacryloyloxymethyl-2,3-dihydro-4h-pyran,
 methoxypropyl methacrylate, 3-methyl butanol-2 methacrylate,
 3-methylbuten-2-yl-methacrylate, 2-methyl butyl methacrylate,

- 3-(4-methylphenoxy)-2-hydroxypropyl methacrylate, 2-n-morpholinoethyl methacrylate, alpha-naphthyl methacrylate, 2-naphthyl methacrylate, 2-(1-naphthyloxy)-ethyl methacrylate, 2-(2-naphthyloxy)-ethyl methacrylate, 2-nitroethyl methacrylate, p-nitrophenyl methacrylate, nonylphenyl methacrylate, norbornyl methacrylate,
- 5 iso-octyl methacrylate, pentabromophenyl methacrylate, pentachlorophenyl methacrylate, perfluorocyclohexyl methyl methacrylate, phenylpropyl methacrylate, 1-piperidineethyl methacrylate, sorbitol methacrylate, 2-sulfoethyl methacrylate, tribromoneopentyl methacrylate, trichloroethyl methacrylate, 1h,1h,7h-dodecafluoroheptyl methacrylate,
- 10 3,5,5-trimethylhexyl methacrylate, methacryloxyethoxy tris(trimethylsiloxy) silane, vinylbenzyl methacrylate, 2-(n-ethylperfluorooctanesulfamido) ethyl methacrylate 3-(trifluoromethyl)benzyl methacrylate, isobornyl methacrylate, poly(ethylene glycol) methacrylate, hydroxypropyl methacrylate, lead methacrylate 2-ethylhexanoate, 2-methacryloxyethyl glucoside,
- 15 bis-(2,3-dibromopropyl) 2-(methacryloyloxy)-ethyl phosphate, 3-methyl-2-benzothiazolinone, azine with 4-(2-(methacryloyl-o)eto)-m-anisaldehyde, 2-(methacryloyloxy)ethyl n-(3-bromophenyl)carbamate, 2-(methacryloyloxy)ethyl n-(n-(3,5-dichlorophenyl)carbamoyle)carbamate, 2-(methacryloyloxy)ethyl n-(4-isopropylphenyl)carbamate,
- 20 ethylene glycol methacrylate phosphate, trimethylol propane diallyl ether mono-methacrylate, abitol methacrylate, isocyanatoethyl methacrylate butyl urethane, isocyanatoethyl methacrylate octyl urethane, isocyanatoethyl methacrylate caprolactam adduct
- 25 isocyanatoethyl methacrylate pyrrolidone adduct, methacrylic acid hydroxypropyl ester, calcium methacrylate, hydrate, 2-hydroxy-4-[2-hydroxy-3-(methacryloyloxy)-propoxy]benzophen, Methacryloxydiphenylantimony, (2-methacryloxyethoxy)triisopropoxytitanate, (methacryloxymethyl)bis(trimethylsiloxy)methylsilane,
- 30 (methacryloxymethyl)dimethylethoxysilane, Methacryloxymethyltriethoxysilane, Methacryloxymethyltrimethoxysilane, methacryloxymethyltrimethylgermane, methacryloxymethyltris(trimethylsiloxy)silane, methacryloxypropyldimethylmethoxysilane, methacryloxypropylmethylmethoxysilane, methacryloxypropylsilatrane,

methacryloxytriethylgermane, titanium methacrylate triisopropoxide,
 dicyclopentenyl methacrylate, tetrahydropyranyl methacrylate,
 caprolactone 2-(methacryloyloxy)ethyl ester, 2-methyl-2-nitropropyl methacrylate,
 2-(2-oxo-1-imidazolidinyl)ethyl methacrylate, tetrakis(2-methacryloxyethoxy)silane
 5 2-(methylthio)ethyl methacrylate,
 2-[3-(2-h-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate,
 dicyclopentenylmethoxyethyl methacrylate, 2-methyl-acrylic acid 4-hydroxy-phenyl ester
 2-(perfluorobutyl)ethyl methacrylate, 2-(perfluorodecyl)ethyl methacrylate
 2-(perfluoro-3-methylbutyl)ethyl methacrylate,
 10 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl methacrylate,
 2-(perfluoro-5-methylhexyl)ethyl methacrylate,
 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl methacrylate,
 2-(perfluoro-7-methyloctyl)ethyl methacrylate,
 3-(perfluoro-7-methyloctyl)-2-hydroxypropyl methacrylate,
 15 2-(perfluoro-9-methyldecyl)ethyl methacrylate,
 3-(perfluoro-8-methyldecyl)-2-hydroxypropyl methacrylate,
 (9-anthryl) methacrylate, (9-phenanthryl)methyl methacrylate,
 n-(3-methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane,
 4-(methacryloyloxy) chalcone, mono-2-(methacryloyloxy)ethyl succinate,
 20 2-(sulfooxy)ethyl methacrylate, ammonium salt, ethylene methacrylate phosphate,
 2-methacrylic acid 2-(4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-phenyl)-ethyl ester,
 2-(2'-methacryloxy-5'-methylphenyl)benzotriazole,
 2-methacrylic acid 3-(3,5-dioxo-4-aza-tricyclo(5.2.1.0(2,6))dec-8-en-4-yl)ph ester,
 2-methacrylic acid 4-(4-nitro-1,3-dioxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 25 rcl r35,715-4, 9-anthracenylmethyl methacrylate, 1-pyrenylmethyl methacrylate,
 2-methyl-acrylic acid 3-(1-oxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 2-methacrylic acid 3-(4-nitro-1,3-dioxo-1,3-dihydro-isoindol-2-yl)-phenyl ester,
 2-methyl-acrylic acid 3-(2,5-dioxo-pyrrolidin-1-yl)-phenyl ester,
 2-methyl-acrylic acid 4-(2,5-dioxo-pyrrolidin-1-yl)-phenyl ester,
 30 rcl r35,836-3, 2-methyl-acrylic acid 4-acetyl-amino-phenyl ester,
 (1-pyrene)methyl methacrylate, 2-hydroxypropyl 2-(methacryloyloxy)ethyl phthalate,
 peg monomethacrylate, 3-methylbuten-2-yl-methacrylate,
 (methacryloxymethyl)bis(trimethylsiloxy)-(methylsiloxy)methylsilane,
 (r)-2-hydroxy-2'-methacryloxy-1,1'-bi-2-naphthol,

4-[[6-(methacryloyloxy)hexyl]oxy]benzenecarboxylic acid,
 hexafluoroisopropyl urethane of isocyanato ethyl methacrylate,
 dicyclopentenyl-2-methacrylate, (r)-(-)-isobornylmethacrylate,
 3-perfluorohexyl-2-hydroxypropyl methacrylate,
 5 3-perfluorooctyl-2-hydroxypropyl methacrylate, (1-naphthyl)ethyl methacrylate,
 (1-naphthyl)methyl methacrylate, o-methacryloyl hoechst 33258,
 o-(methacryloxyethyl)-n-(triethoxysilylpropyl) urethane,
 4-[3-(methacryloyloxy)propoxy]benzenecarboxylic acid,
 4-[4-(methacryloyloxy)butoxy]benzenecarboxylic acid,
 10 hexafluoroisopropylurethane-n-ethyl methacrylate,
 2-methyl-acrylic acid 2-(4-(4,5-dihydro-oxazol-2-yl)-phenoxy)-ethyl ester,
 3-methacryloxypropyltris(pentamethyldisiloxy)silane,
 di(propylene glycol) allyl ether methacrylate,
 triacetoneaminoylmethacrylate, 1h,1h-perfluoro-n-decyl methacrylate,
 15 3-(perfluorobutyl)-2-hydroxypropyl methacrylate,
 2-methyl-acrylic acid 4-(3-phenyl-acryloyl)-phenyl ester,
 3-(5-nitro-1,3-dioxo-1,3-dihydro-2h-isoindol-2-yl)phenyl 2-methylacrylate,
 n-(2-hydroxy-3((2-methyl-1-oxo-2-propenyl) oxy)propyl)-n-(4-methyphenyl)-glycine or
 mixtures thereof.

20

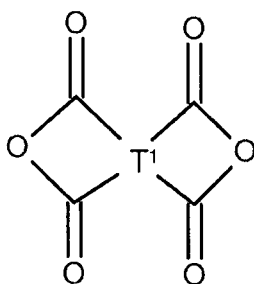
The polyamic acids, polyamic acid esters and polyimides according to the present
 invention may be prepared in line with known methods, such as those described in
 Plast. Eng. 36 (1996), (Polyimides, fundamentals and applications), Marcel Dekker Inc.
 For example, the polycondensation reaction for the preparation of the polyamic acids is
 25 carried out in solution in a polar aprotic organic solvent, such as γ -butyrolactone,
N,N-dimethylacetamide, *N*-methylpyrrolidone or *N,N*-dimethylformamide. In most
 cases equimolar amounts of the dianhydride and the diamine are used, that is to say
 one amino group per anhydride group. If it is desired to stabilise the molecular weight
 of the polymer, it is possible for that purpose to add an excess or a less-than-
 30 -stoichiometric amount of one of the two components or to add a monofunctional com-
 pound in the form of a dicarboxylic acid monoanhydride or in the form of a monoamine.
 Examples of such monofunctional compounds are maleic anhydride, phthalic

anhydride, aniline and so on. The reaction is carried out preferably at a temperature of less than 100 °C.

5 The cyclisation of the polyamic acids to form the polyimides can be carried out by heating, that is to say by condensation with removal of water or by other imidisation reactions with reagents. When carried out purely thermally, the imidisation of the polyamic acids is not always complete, that is to say the resulting polyimides may still contain proportions of polyamic acid. The imidisation reactions are generally carried out at a temperature of from 60 to 250 °C, but preferably at less than 200 °C. In order
10 to achieve imidisation at rather lower temperatures there are additionally mixed into the reaction mixture reagents that facilitate the removal of water. Such reagents are, for example, mixtures consisting of acid anhydrides, such as acetic acid anhydride, propionic acid anhydride, phthalic acid anhydride, trifluoroacetic acid anhydride, and tertiary amines, such as triethylamine, trimethylamine, tributylamine, pyridine,
15 *N,N*-dimethylaniline, lutidine, collidine etc.. The amount of reagents used in that case is preferably at least two equivalents of amine and four equivalents of acid anhydride per equivalent of polyamic acid to be condensed.

20 The imidisation reaction can be carried out before or alternatively only after application to a support. The latter variant is preferred especially when the polyimide in question has poor solubility in the customary solvents.

25 Thus the polymer material or oligomer material from the class of polyamic acids, polyamic acid esters or polyimides (and any mixtures thereof) may be obtained by or obtainable by the reaction of at least one compound represented by the general formula (I) wherein G represents a diamine group and optionally one or more additional other diamines (as e.g. given above), with one or more tetracarboxylic acid anhydrides of the general formula (IV)



(IV)

wherein:

T¹ represents a tetravalent organic radical.

- 5 The tetravalent organic radical T¹ is preferably derived from an aliphatic, alicyclic or aromatic tetracarboxylic acid dianhydride.

Preferred examples of aliphatic or alicyclic tetracarboxylic acid dianhydrides are:

- 1,1,4,4-butanetetracarboxylic acid dianhydride,
 10 ethylenemaleic acid dianhydride,
 1,2,3,4-cyclobutanetetracarboxylic acid dianhydride,
 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride,
 2,3,5-tricarboxycyclopentylacetic acid dianhydride,
 3,5,6-tricarboxynorbornylacetic acid dianhydride,
 15 2,3,4,5-tetrahydrofuran-tetracarboxylic acid dianhydride,
 rel-[1S,5R,6R]-3-oxabicyclo[3.2.1]octane-2,4-dione-6-spiro-3'- (tetrahydrofuran-2',5'-
 dione), 4-(2,5-dioxotetrahydrofuran-3-yl)tetrahydronaphthalene-1,2-dicarboxylic acid
 dianhydride, 5-(2,5-dioxotetrahydrofuran-3-yl)-3-methyl-3-cyclohexene-1,2-dicarboxylic-
 acid dianhydride, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride,
 20 bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic acid dianhydride,
 1,8-dimethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid
 dianhydride, and the like.

Preferred examples of aromatic tetracarboxylic acid dianhydrides are:

- 25 pyromellitic acid dianhydride,
 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride,
 4,4'-oxydiphthalic acid dianhydride,

3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride,
 1,4,5,8-naphthalenetetracarboxylic acid dianhydride,
 2,3,6,7-naphthalenetetracarboxylic acid dianhydride,
 3,3',4,4'-dimethyldiphenylsilanetetracarboxylic acid dianhydride,
 5 3,3',4,4'-tetraphenylsilanetetracarboxylic acid dianhydride,
 1,2,3,4-furantetracarboxylic acid dianhydride,
 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride,
 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride,
 4,4'-bis(3,4-dicarboxyphenoxy)diphenylpropane dianhydride,
 10 3,3',4,4'-biphenyltetracarboxylic acid dianhydride,
 ethylene glycol bis(trimellitic acid) dianhydride,
 4,4'-(1,4-phenylene)bis(phthalic acid) dianhydride,
 4,4'-(1,3-phenylene)bis(phthalic acid) dianhydride,
 4,4'-(hexafluoroisopropylidene)diphthalic acid dianhydride,
 15 4,4'-oxydi(1,4-phenylene)bis(phthalic acid) dianhydride,
 4,4'-methylenedi(1,4-phenylene)bis(phthalic acid) dianhydride,
 and the like.

More preferably the tetracarboxylic acid dianhydrides used to form the tetravalent
 20 organic radical T¹ are selected from:

1,2,3,4-cyclobutanetetracarboxylic acid dianhydride,
 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride,
 2,3,5-tricarboxycyclopentylacetic acid dianhydride,
 25 5-(2,5-dioxotetrahydrofuran-3-yl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid
 dianhydride,
 4-(2,5-dioxotetrahydrofuran-3-yl)tetrahydronaphthalene-1,2-dicarboxylic acid
 dianhydride,
 4,4'-(hexafluoroisopropylidene)diphthalic acid dianhydride and
 30 bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride.

The term "diamine" or "diamine compound" is to be understood as designating a
 chemical structure which has at least two amino groups, i.e. which may also have 3 or
 more amino groups.

The diamine represents an optionally substituted aliphatic, aromatic or alicyclic diamino group having from 1 to 40 carbon atoms and preferably made from or selected from the following group of structures: aniline, p-phenylenediamine, m-phenylenediamine, benzidine, diaminofluorene, or their derivatives, with the proviso that compounds listed which do not carry two amino groups are taken as derivatives with at least one additional amino group, and more preferably made from or selected from the following commercially available amino compounds (example of suppliers: Aldrich, ABCR, ACROS, Fluka) which can also be used as comonomers:

10

4-amino-2,3,5,6-tetrafluorobenzoic acid
4-amino-3,5-diiodobenzoic acid, 3,4-diaminobenzoic acid
4-amino-3-methylbenzoic acid,
4-amino-2-chlorobenzoic acid

15

4-aminosalicylic acid
4-aminobenzoic acid
4-aminophthalic acid
1-(4-aminophenyl)ethanol
4-aminobenzyl alcohol

20

4-amino-3-methoxybenzoic acid
4-aminophenyl ethyl carbinol
4-amino-3-nitrobenzoic acid
4-amino-3,5-dinitrobenzoic acid
4-amino-3,5-dichlorobenzoic acid

25

4-amino-3-hydroxybenzoic acid
4-aminobenzyl alcohol hydrochloride
4-aminobenzoic acid hydrochloride
pararosaniline base

30

4-amino-5-chloro-2-methoxybenzoic acid
4-(hexafluoro-2-hydroxyisopropyl)aniline
piperazine-p-amino benzoate
4-amino-3,5-dibromobenzoic acid
isonicotinic acid hydrazide p-aminosalicylate salt
4-amino-3,5-diiodosalicylic acid

- 4-amino-2-methoxybenzoic acid
2-[2-(4-aminophenyl)-2-hydroxy-1-(hydroxymethyl)ethyl]isoindoline-1,3-dione
4-amino-2-nitrobenzoic acid
2,4-diaminobenzoic acid
5 p-aminobenzoic acid,
[3,5-3h]-4-amino-2-methoxybenzoic acid
L-(+)-threo-2-amino-1-(4-aminophenyl)-1,3-propanediol
L-(+)-threo-2-(N,N-dimethylamino)-1-(4-aminophenyl)-1,3-propanediol
ethyl 2-(4-aminophenyl)-3,3,3-trifluoro-2-hydroxypropanoate
10 ethyl 2-(4-amino-3-methylphenyl)-3,3,3-trifluoro-2-hydroxypropanoate
ethyl 2-(4-amino-3-methoxyphenyl)-3,3,3-trifluoro-2-hydroxypropanoate
3,4-diaminobenzyl alcohol dihydrochloride
4-aminonaphthalene-1,8-dicarboxylic acid
4-amino-3-chloro-5-methylbenzoic acid
15 4-amino-2,6-dimethylbenzoic acid
4-amino-3-fluorobenzoic acid
4-amino-5-bromo-2-methoxybenzenecarboxylic acid
2,7-diaminofluorene
4,4'-diaminooctafluorobiphenyl
20 3,3'-diaminobenzidine
3,3',5,5'-tetramethylbenzidine
3,3'-dimethoxybenzidine
o-tolidine
3,3'-dinitrobenzidine
25 2-nitrobenzidine
3,3'-dihydroxybenzidine
o-tolidine sulfone
benzidine,
3,3'-dichlorobenzidine
30 2,2',5,5'-tetrachlorobenzidine,
benzidine-3,3'-dicarboxylic acid
4,4'-diamino-1,1'-binaphthyl
4,4'-diaminodiphenyl-3,3'-diglycolic acid
dihydroethidium

- o-dianisidine
 2,2'-dichloro-5,5'-dimethoxybenzidine
 3-methoxybenzidine
 3,3'-dichlorobenzidine (diphenyl-d6),
 5 2,7-diamino-9-fluorenone
 3,5,3',5'-tetrabromo-biphenyl-4,4'-diamine
 2,2'-bis(trifluoromethyl)benzidine
 2,2'-dichloro[1,1'-biphenyl]-4,4'-diamine
 3,9-diamino-1,11-dimethyl-5,7-dihydro-dibenzo(a,c)cyclohepten-6-one
 10 3,3'-bis(trifluoromethyl)benzidine
 dibenzo(1,2)dithiine-3,8-diamine
 3,3'-tolidine-5-sulfonic acid
 3,3'-dichlorobenzidine-d6
 tetramethylbenzidine
 15 3,3'-diaminobenzophenone, 3,3'-diaminodiphenylmethane,
 4,4-bis-(3-amino-4-hydroxyphenyl)-valeric acid
 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane
 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane
 tetrabromo methylenedianiline
 20 2,7-diamino-9-fluorenone
 2,2-bis(3-aminophenyl)hexafluoropropane
 bis-(3-amino-4-chloro-phenyl)-methanone
 bis-(3-amino-4-dimethylamino-phenyl)-methanone
 3-[3-amino-5-(trifluoromethyl)benzyl]-5-(trifluoromethyl)aniline
 25 1,5-diaminonaphthalene

or their derivatives, again with the proviso that compounds listed which do not carry two amino groups are taken as derivatives with at least one additional amino group.

30

Preferred examples of additional other diamines are:

ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, 1,5-pentylenediamine, 1,6-hexylenediamine, 1,7-heptylenediamine, 1,8-oxylenediamine,

1,9-nonylenediamine, 1,10-decylenediamine, 1,11-undecylenediamine,
 1,12-dodecylenediamine, α,α' -diamino-*m*-xylene, α,α' -diamino-*p*-xylene,
 (5-amino-2,2,4-trimethylcyclopentyl)methylamine, 1,2-diaminocyclohexane,
 4,4'-diaminodicyclohexylmethane, 1,3-bis(methylamino)cyclohexane,
 5 4,9-dioxadodecane-1,12-diamine, 3,5-diaminobenzoic acid methyl ester,
 3,5-diaminobenzoic acid hexyl ester, 3,5-diaminobenzoic acid dodecyl ester,
 3,5-diaminobenzoic acid isopropyl ester, 4,4'-methylenedianiline, 4,4'-ethylenedianiline,
 4,4'-diamino-3,3'-dimethyldiphenylmethane, 3,3',5,5'-tetramethylbenzidine,
 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, 1,5-diaminonaphthalene,
 10 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,4'-diaminodiphenyl ether,
 3,3'-diaminobenzophenone, 4,4'-diaminobenzophenone,
 4,4'-diamino-2,2'-dimethylbibenzyl, bis[4-(4-aminophenoxy)phenyl] sulfone,
 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene,
 1,3-bis(3-aminophenoxy)benzene, 2,7-diaminofluorene,
 15 9,9-bis(4-aminophenyl)fluorene, 4,4'-methylene-bis(2-chloroaniline),
 4,4'-bis(4-aminophenoxy)biphenyl, 2,2',5,5'-tetrachloro-4,4'-diaminobiphenyl,
 2,2'-dichloro-4,4'-diamino-5,5'-dimethoxybiphenyl, 3,3'-dimethoxy-4,4'-diaminobiphenyl,
 4,4'-(1,4-phenyleneisopropylidene)bis(aniline),
 4,4'-(1,3-phenyleneisopropylidene)bis(aniline),
 20 2,2-bis[4-(4-aminophenoxy)phenyl]propane,
 2,2-bis[3-(4-aminophenoxy)phenyl]hexafluoropropane,
 2,2-bis[3-amino-4-methylphenyl]hexafluoropropane,
 2,2-bis(4-aminophenyl)hexafluoropropane,
 2,2'-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane,
 25 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl, and
 4,4'-bis[(4-amino-2-trifluoromethyl)phenoxy]-2,3,5,6,2',3',5',6'-octafluorobiphenyl.

The polymers of the present invention have a molecular weight M_W between 1 000
 and 5 000 000, preferably however between 5 000 and 2 000 000, especially
 30 advantageously however between 10 000 and 1 000 000.

The number of monomer building blocks from which the polymer chains according to
 the invention are synthesised can vary within a wide range. It is generally from 2 to
 2000, but especially from 3 to 200.

The polymers according to the invention may further contain additives such as silane-containing compounds and epoxy-containing crosslinking agents for further improving the adhesion of the polymer to a substrate. Example for silane adhesion promoters were described in the literature, for example *Plast. Eng.* **36** (1996) (Polyimides, fundamentals and applications). The above epoxy-containing crosslinking agent preferably includes 4,4'-methylenebis(*N,N*-diglycidylaniline), trimethylolpropane triglycidyl ether, benzene-1,2,4,5-tetracarboxylic acid 1,2:4,5-*N,N'*-diglycidyl diimide, polyethylene glycol diglycidyl ether, *N,N*-diglycidylcyclohexylamine and the like.

10

The polymers according to the invention may contain additives such a photosensitiser, a photoradical generator and/or a cationic photoinitiator. Example for such additives were 2,2-dimethoxyphenylethanone, mixture of diphenylmethanone and *N,N*-dimethylbenzenamine or ethyl 4-(dimethylamino)benzoate, xanthone, thioxanthone, IRGACURE™ 184, 369, 500, 651 and 907 (Ciba), Michler's ketone, triaryl sulfonium salt and the like.

15

The polymers according to the invention may be used as a single polymer or as mixture with other polymers, oligomers, monomers, photoactive polymers, photoactive oligomers and/or photoactive monomers. Thus the properties of the layer may be modified to give what is sought. For example, an induced pretilt angles, good surface wetting, high voltage holding ratio, a specific anchoring energy etc. may be obtained.

20

The polymers according to the invention can then be applied to a support and, after any imidisation step which may be necessary, crosslinked by irradiation with aligning light, preferably with linearly polarised light, that is to say by cycloaddition of their side-chains containing the photoreactive group, there being obtained, depending upon the direction of polarisation of the light radiated in, a preferred direction of orientation and of the angle of tilt for liquid crystals that are brought into contact with the alignment layer. By spatially selective irradiation of the molecular units according to the invention it is hence possible for very specific regions of a surface to be aligned and provided with a defined angle of tilt. At the same time the alignment layer so produced is also stabilised by the cycloaddition.

25

30

Such alignment layers can be produced, for example, by first preparing a solution of the resulting polymer material, which is applied to a support, which is optionally coated with an electrode (for example a glass plate coated with indium–tin oxide (ITO)), in a spin-coating apparatus, so that homogeneous layers of 5 nanometer to 2 micrometer thickness are produced. Then, or optionally after prior imidisation, the regions to be oriented can be irradiated, for example, with a high-pressure mercury vapour lamp, a xenon lamp or a pulsed UV laser, using a polariser and optionally a mask for creating images of structures. The irradiation time is dependent upon the output of the individual lamps and can vary from a few seconds to several hours. The photoreaction can also be carried out, however, by irradiation of the homogeneous layer using filters that, for example, allow only the radiation suitable for the crosslinking reaction to pass through.

Such alignment layers of the invention may be used in the production of optical or electro-optical devices having at least one orientation layer as well as unstructured and structured optical elements and multi-layer systems. Thus the invention further relates to an optical or electro-optical device comprising one or more oligomers, dendrimers or polymers according to the present invention; preferably in cross-linked form.

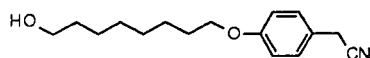
The technical advantage of the novel compounds of the present invention is their high contrast, in several application for the orientation for polymerizable and movable liquid crystals, In addition, high speed of orientation can be accesses and good azimuthal stability. The latter property is important for the provion of structured retarders such a optical films for 3 D, security devices, functional foils such as barrier layers.

The examples which follow further illustrate the invention. They are given by way of illustration and not by way of limitation. Variations on these examples falling within the scope of the invention will be apparent to a person skilled in the art.

EXAMPLES

Definitions used in the examples:

- 5 LC/MS: Liquid chromatography/Mass spectrometry
[M+Na] = Molecular Mass plus sodium
[M+H] = Molecular Mass plus proton
[M+NH₄] = Molecular Mass plus ammonium
¹H NMR = ¹H nuclear magnetic resonance spectroscopy
- 10 DMSO-d₆ = dimethylsulfoxid deuterated
THF-d₈ = Tetrahydrofuran deuterated
300MHz = 300 Megahertz
m = multiplet
d = doublet
- 15 dd = doublet doublet
t = triplet
s = singlet
q = quintet
br = broad
- 20 δ = chemical shift
HCl = hydrogen chloride
MeOH: methanol
EtOAc: ethyl acetate
NMP: N-methyl-2-pyrrolidone
- 25 THF: tetrahydrofuran
TBME: tert. butyl methyl ether
DMF: N,N-dimethylformamide
RT : room temperature, usually in the range of 18 °C to 28 °C
[η]: viscosity
- 30 v.t.% : volume percent
MLC7067: is a mixture of liquid crystal available from Merck KGA with a Dielectric anisotropy of 10.3, an optical anisotropy of 0.1025 and a rotational viscosity of 81 m.Pa.s.
- 35 Example 1: Preparation of {4-[(8-hydroxyoctyl)oxy]phenyl}acetonitrile 1A



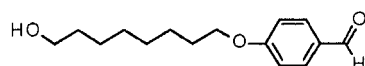
20.0 g (150 mmol) of (4-hydroxyphenyl)acetonitrile and 29.5 g (179 mmol) of 8-chlorooctan-1-ol are dissolved in 400 mL of N,N-dimethylformamide. 41.5 g (300 mmol) of potassium carbonate and 5.0 g (30 mmol) of potassium iodide are added and the suspension is heated to 80 °C. After 48h, the excess of potassium carbonate is filtered off and the resulting filtrate is poured to icy water. The aqueous layer is extracted twice with ethyl acetate. Combined organic layers are washed with brine and evaporated to dryness. The crude is purified twice on SiO₂ column chromatography with Heptane/ethyl acetate: 7/3 as eluant and dried overnight at 40 °C. 24.5 g of {4-[(8-hydroxyoctyl)oxy]phenyl}acetonitrile are obtained as a yellow solid (62% yield).

The compounds 1B, 1C are prepared according to the process described in example 1 for compound 1A with the proviso that 8-chlorooctan-1-ol is replaced by 6-bromohexan-1-ol, respectively 11-bromoundecan-1-ol.

The compounds 1D is prepared according to the process described in example 1 for compound 1C with the proviso that (4-hydroxyphenyl)acetonitrile is replaced by [4-hydroxy-3-methoxy-phenyl]acetonitrile

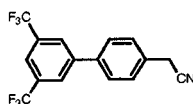
The compounds 1E is prepared according to the process described in example 1 for compound 1D with the proviso that 11-bromoundecan-1-ol is replaced by 8-chlorooctan-1-ol.

Example 2: Preparation of 4-[(8-hydroxyoctyl)oxy]benzaldehyde



4-[(8-hydroxyoctyl)oxy]benzaldehyde is prepared starting from 4-hydroxybenzaldehyde and 8-chlorooctan-1-ol according to the procedure described example 1 in 62% yield.

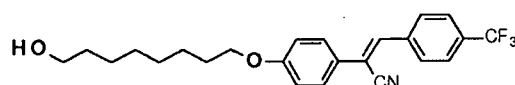
Example 4: Preparation of [3',5'-bis(trifluoromethyl)-1,1'-biphenyl-4-yl]acetonitrile



0.664 g (3.4 mmol) of (4-bromophenyl)acetonitrile, 0.645 g (3.4 mmol) of [3,5-bis(trifluoromethyl)phenyl]boronic acid and 937 mg (6.8 mmol) of potassium carbonate are dissolved in 20 mL of tetrahydrofuran and 5 mL of water. The solution is purged with argon and 78 mg of tetrakis(triphenylphosphine)palladium(0) are added. The solution is purged with argon and heated to 80 °C. After 12h at 80 °C, the reaction

mixture is cooled to room temperature, and the aqueous layer is extracted twice with ethyl acetate. Combined organic layers are washed with brine and evaporated to dryness. The crude is purified twice on SiO₂ column chromatography with Heptane/ethyl acetate 3/2 as eluant and dried overnight at 30 °C. 527 mg of Example 4 are obtained as a white solid.

Example 6: Preparation of (2Z)-2-{4-[(8-hydroxyoctyl)oxy]phenyl}-3-[4-(trifluoromethyl)phenyl]prop-2-enenitrile 6A



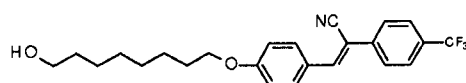
5.0 g (19.1 mmol) of Example 1A, 3.5 g (19.1 mmol) of 4-(trifluoromethyl)benzaldehyde are dissolved in 50 mL of propan-2-ol. The solution is heated to 60 °C and 1.9 mL (1.9 mmol) of a 1M solution of tetrabutylammoniumhydroxyde in methanol are added dropwise. After 2h at 60 °C, the reaction mixture is cooled down to 0 °C. The precipitate is filtered off, washed with cold propan-2-ol and recrystallized in propan-2-ol. 4.7 g of Example 6A are obtained as a white solid (59% yield).

The compounds 6B, 6E, 6H, 6X, 6U, 6V, 6AA, 6AB is prepared according to the process described in example 6 for compound 6A with the proviso that 4-(trifluoromethyl)benzaldehyde is replaced by 3,5-(trifluoromethyl)benzaldehyde, respectively 3-(trifluoromethyl)benzaldehyde, respectively 4-fluorobenzaldehyde, respectively benzaldehyde, respectively 4-chlorobenzaldehyde, respectively 4-bromobenzaldehyde, respectively 3,4,5-trifluorobenzaldehyde, respectively 4,6-difluorobenzaldehyde.

The compounds 6J, 6K, 6L is prepared according to the process described in example 6 for compound 6A with the proviso that Example 1A is replaced by Example 1E, respectively by Example 1B, respectively by Example 1D.

The compounds 6N is prepared according to the process described in example 6 for compound 6B with the proviso that Example 1A is replaced by Example 1C.

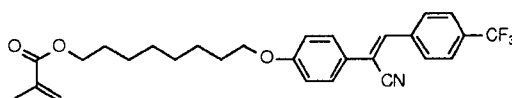
Example 7: Preparation of (2Z)-3-{4-[(8-hydroxyoctyl)oxy]phenyl}-2-[4-(trifluoromethyl)phenyl]prop-2-enenitrile 7A



Example 7A is prepared starting from Example 2 and [(4-trifluoromethyl)phenyl]acetonitrile according to the procedure described in example 6 in 76% yield.

The compounds 7B, 7D, 7E, 7W, 7Y are prepared according to the process described in example 7 for compound 7A with the proviso that [(4-trifluoromethyl)phenyl]acetonitrile is replaced by [(3,5-bis(trifluoromethyl))phenyl]acetonitrile, respectively Example 4, respectively [(4-fluoro)phenyl]acetonitrile, respectively [(4-chloro)phenyl]acetonitrile, respectively [(4-bromo)phenyl]acetonitrile, respectively [(3,4,5-Trifluoro)phenyl]acetonitrile, respectively [(4,6-difluoro)phenyl]acetonitrile.

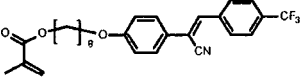
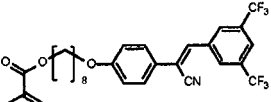
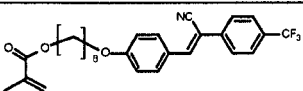
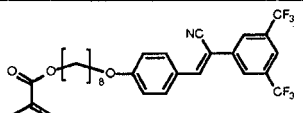
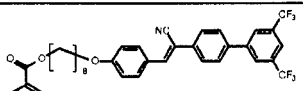
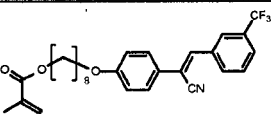
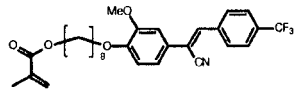
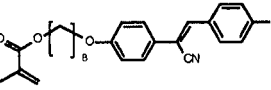
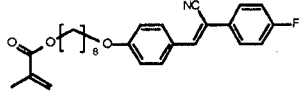
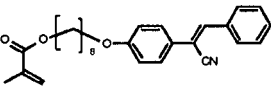
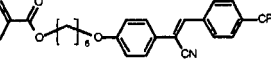
Example 10: Preparation of 8-(4-[(Z)-1-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl]phenoxy)octyl 2-methylacrylate 10A

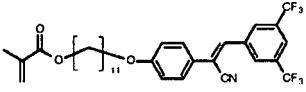
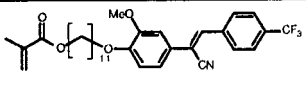
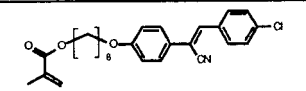
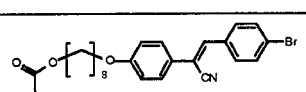
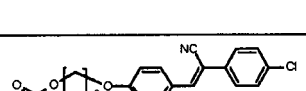
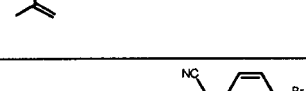
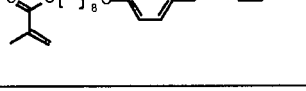
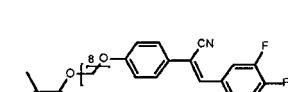


2.03 g (4.9 mmol) of Example 6A, 59 mg (0.49 mmol) of 4-dimethylaminopyridine and 1.48 g (14.69 mmol) of triethylamine are dissolved in 40 mL of tetrahydrofurane. The solution is cooled down to 0°C and a solution 0.9 g (5.8 mmol) of methacrylic anhydride in 10 mL of tetrahydrofuran is added dropwise in 1h at 0°C. After 2h at 0°C, the reaction mixture is then allowed to heat up to room temperature. After 15h, the reaction mixture is poured onto icy water. The precipitate is filtered off, dried at 30°C and recrystallized in methanol with a small amount of 2,6-di-*tert*-buthyl-4-methylphenol. 1.4 g of Example 10A are obtained as a white solid (61% yield).

The compounds 10B, 10E, 10F, 10H, 10I, 10L, 10M, 10N, 10O, 10P, 10R, 10S, 10U, 10V, 10W, 10Y, 10AA, 10AB are prepared according to the process described in example 10 for compound 10A with the proviso that Example 6A is replaced by Example 6B, respectively, respectively Example 7A, respectively Example 7B, respectively Example 7D, respectively Example 6E, respectively Example 6J, respectively Example 6H, respectively Example 7E, respectively Example 6X, respectively Example 6K, respectively Example 6N, respectively Example 6L, respectively Example 6U, respectively Example 6V, respectively Example 7W, respectively Example 7Y, respectively 6AA, respectively 6AB.

Analytical data of compounds are given in the following table:

	Structure	Analytical data
10A		LC/MS: $[M+H]^+ = 486.2$
10B		LC/MS: $[M+Na]^+ = 576.7$
10E		LC/MS: $[M+Na]^+ = 508.2$
10F		LC/MS: $[M+Na]^+ = 576.1$
10H		LC/MS: $[M+NH_4]^+ = 647.2$
10I		LC/MS: $[M+Na]^+ = 508.2$
10L		LC/MS: $[M+Na]^+ = 538.1$
10M		LC/MS: $[M+Na]^+ = 458.1$
10N		LC/MS: $[M+H]^+ = 436.2$
10O		LC/MS: $[M+Na]^+ = 440.5$
10P		LC/MS: $[M+Na]^+ = 480.1$

10R		LC/MS: $[M+Na]^+ = 618.1$
10S		LC/MS: $[M+Na]^+ = 580.2$
10U		LC/MS: $[M+Na]^+ = 474.1$
10V		LC/MS: $[M+Na]^+ = 518.1$
10W		LC/MS: $[M+Na]^+ = 474.1$
10Y		LC/MS: $[M+Na]^+ = 518.1$
10AA		^1H NMR DMSO- d_6 (300MHz): 7.89 (s, 1H), 7.81 (m, 2H), 7.67 (d, 2H), 7.08 (d, 2H), 6.01 (s, 1H), 5.66 (s, 1H), 4.09 (dd, 2H), 4.02 (dd, 2H), 1.87 (s, 3H), 1.73 (m, 2H), 1.62 (m, 2H), 1.33 (m, 8H).
10AB		^1H NMR DMSO- d_6 (300MHz): 8.04 (dd, 1H), 7.82 (s, 1H), 7.69 (dd, 2H), 7.45 (dd, 1H), 7.29 (dd, 1H), 7.06 (d, 2H), 6.01 (s, 1H), 5.66 (s, 1H), 4.09 (m, 2H), 4.02 (m, 2H), 1.87 (s, 3H), 1.72 (m, 2H), 1.61 (m, 2H), 1.33 (m, 8H).

Example 11: Preparation of 8-(4-((Z)-1-cyano-2-[4-

(trifluoromethyl)phenyl]ethenyl)phenoxy)octyl poly-2-methylacrylate 11A

2.00 g (4.1 mmol) of Example 10A are dissolved in 10 mL of degassed cyclohexanone.

- 5 The solution is purged with argon and heated to 60°C. A solution of 20.0 mg (0.14 mmol) of 2,2'-Azobis(2-methylpropionitrile) in 2 mL of cyclohexanone is added dropwise. After 36h at 60°C, the reaction mixture is cooled down to room temperature,

diluted with 5 mL of tetrahydrofuran, and precipitated in 200 mL of cold methanol. The precipitate is filtered off, washed with methanol and dried overnight at 30°C. 1.50 g of Example 11A are obtained as a white solid (75% yield).

The compounds 11B, 11E, 11F, 11H, 11I, 11L, 11M, 11N, 11O, 11P, 11R, 11S, 11U,
 5 11V, 11W, 11Y, 11AA, 11AB are prepared according to the process described in
 example 11 for compound 11A with the proviso that Example 10A is replaced by
 Example 10B, respectively Example 10E, respectively Example 10F, respectively
 Example 10H, respectively Example 10I, respectively Example 10L, respectively
 Example 10M, respectively Example 10N, respectively Example 10O, respectively
 10 Example 10P, respectively Example 10R, respectively Example 10S, respectively
 Example 10U, respectively Example 10V, respectively Example 10W, respectively
 Example 10Y, respectively Example 10AA, respectively Example 10AB.

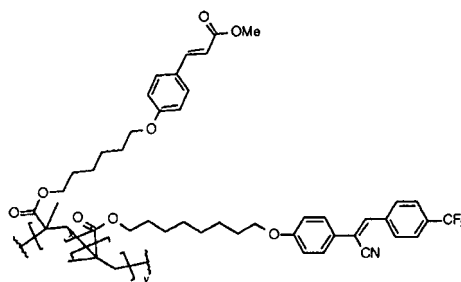
	Name	¹ H NMR (300MHz) in THF-d ₈	Mw GPC-PS- equivalent
11A	8-(4-((Z)-1-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl)phenoxy)octyl poly-2-methylacrylate	7.98 (d, 2H), 7.70 (d, 2H), 7.64 (m, 3H), 6.94 (d, 2H), 3.96 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	166 000
11B	8-(4-((Z)-2-[3,5-bis(trifluoromethyl)phenyl]-1-cyanoethenyl)phenoxy)octyl poly-2-methylacrylate	8.43 (s, 2H), 8.04 (s, 1H), 7.78 (s, 1H), 7.67 (d, 2H), 6.97 (d, 2H), 4.00 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	101 900
11E	8-(4-((Z)-2-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl)phenoxy)octyl poly-2-methylacrylate	7.92 (d, 2H), 7.81 (d, 2H), 7.74 (s, 1H), 7.68 (d, 2H), 6.96 (d, 2H), 3.98 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	79 000
11F	8-(4-((Z)-2-[3,5-bis(trifluoromethyl)phenyl]-2-cyanoethenyl)phenoxy)octyl	8.19 (m, 2H), 7.97 (m, 2H), 7.93 (m, 2H), 6.98 (dd, 2H), 4.00 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m,	66 300

	poly-2-methylacrylate	2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	
11H	8-(4-((Z)-2-[3',5'-bis(trifluoromethyl)-1,1'-biphenyl-4-yl]-2-cyanoethenyl)phenoxy)octyl poly-2-methylacrylate	8.17 (m, 2H), 7.92 (m, 3H), 7.77 (m, 5H), 6.94 (d, 2H), 3.97 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 16H), 1.15-0.79 (m, 3H)	66 000
11I	8-(4-((Z)-1-cyano-2-[3-(trifluoromethyl)phenyl]ethenyl)phenoxy)octyl poly-2-methylacrylate	8.15 (d, 2H), 8.09 (s, 1H), 7.80-7.50 (m, 5H), 6.94 (d, 2H), 3.96 (m, 4H), 1.86-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.20-0.80 (m, 3H)	62 000
11L	of 8-(4-((Z)-1-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl)-2-methoxyphenoxy)octyl poly-2-methylacrylate	7.98 (d, 2H), 7.70 (d, 2H), 7.66 (s, 1H), 7.23 (m, 2H), 6.90 (d, 1H), 3.96 (m, 4H), 3.83 (s, 3H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	24 200
11M	8-{4-[(Z)-1-cyano-2-(4-fluorophenyl)ethenyl]phenoxy}octyl poly-2-methylacrylate	7.91 (d, 2H), 7.59 (d, 2H), 7.54 (s, 1H), 7.15 (m, 2H), 6.92 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	89 000
11N	8-(4-((Z)-2-cyano-2-[4-(fluoro)phenyl]ethenyl)phenoxy)octyl poly-2-methylacrylate	7.86 (d, 2H), 7.66 (dd, 2H), 7.54 (s, 1H), 7.12 (dd, 2H), 6.94 (d, 2H), 3.97 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	121 000
11O	8-{4-[(Z)-1-cyano-2-phenylethenyl]phenoxy}octyl poly-2-methylacrylate	7.86 (d, 2H), 7.51 (d, 2H), 7.56 (s, 1H), 7.38 (m, 3H), 6.93 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	349 000
11P	6-(4-((Z)-1-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl)phenoxy)hexyl poly-2-methylacrylate	7.97 (d, 2H), 7.69 (d, 2H), 7.63 (m, 1+2H), 6.93 (d, 2H), 3.96 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 6H), 1.25-0.80 (m, 3H)	66 000
11R	11-(4-((Z)-2-[3,5-bis(trifluoromethyl)phenyl]-1-	8.43 (s, 2H), 8.04 (s, 1H), 7.78 (s, 1H), 7.67 (d, 2H), 6.97 (d, 2H), 3.99 (m, 4H),	111 700

	cyanoethenyl]phenoxy)undecyl poly-2-methylacrylate	2.00-1.55 (m, 4H), 1.55-1.25 (m, 16H), 1.25-0.80 (m, 3H)	
11S	11-(4-{{(Z)-1-cyano-2-[4-(trifluoromethyl)phenyl]ethenyl}-poly-2-methoxyphenoxy)undecyl poly-2-methylacrylate	7.99 (d, 2H), 7.73 (s, 1H), 7.69 (d, 2H), 7.26 (m, 2H), 6.91 (d, 1H), 3.96 (m, 4H), 3.83 (s, 3H), 2.00-1.55 (m, 4H), 1.55-1.25 (m, 16H), 1.25-0.80 (m, 3H)	63 700
11U	8-(4-{{(Z)-1-cyano-2-[4-(chloro)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	7.90 (d, 2H), 7.65 (m, 3H), 7.45 (d, 2H), 7.05 (m, 2H), 4.01 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.30 (m, 9H), 1.25-0.80 (m, 3H)	58700
11V	8-(4-{{(Z)-1-cyano-2-[4-(bromo)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	7.95 (d, 2H), 7.65 (m, 5H), 6.95 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	62200
11W	8-(4-{{(Z)-2-cyano-2-[4-(chloro)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	7.95 (d, 2H), 7.66 (m, 3H), 7.44 (d, 2H), 7.05 (d, 2H), 4.05 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	64600
11Y	8-(4-{{(Z)-2-cyano-2-[4-(bromo)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	7.95 (d, 2H), 7.66 (m, 5H), 7.05 (m, 2H), 4.05 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	44800
11AA	8-(4-{{(Z)-1-cyano-2-[3,4,5-(trifluoro)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	7.49 (m, 4H), 7.20 (s, 1H), 6.87 (m, 2H), 3.93 (m, 4H), 2.10-1.20 (m, 12H), 1.20-0.70 (m, 3H)*	58000
11AB	8-(4-{{(Z)-1-cyano-2-[4-(4,6 difluoro)phenyl]ethenyl]phenoxy)octyl poly-2-methylacrylate	20 (dd, 1H), 7.53 (d, 1H), 7.48 (s, 1H), 6.89 (m, 4H), 3.93 (m, 4H), 2.10-1.20 (m, 12H), 1.20-0.70 (m, 3H)*	53000

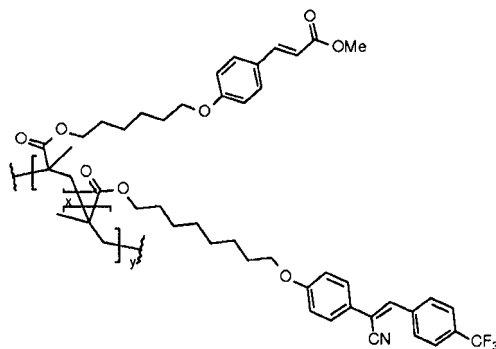
*: NMR made in CDCl₃

Example 12: Preparation of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl poly-2-methylacrylate-Co-8-{4-[(Z)-1-cyano-2-phenylethenyl]phenoxy}octyl poly-2-methylacrylate (98:2 ratio)



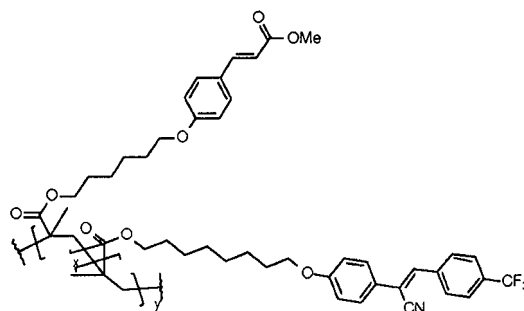
990 mg (2.858 mmol) of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl 2-methylacrylate (example 4 of US 6,107,427) and 28.6 mg (0.059 mmol) of Example 10A are dissolved in 5.0 mL of degassed cyclohexanone. The solution is purged with argon and heated to 60°C. A solution of 9.0 mg (0.055 mmol) of 2,2'-Azobis(2-methylpropionitrile) in 1 mL of cyclohexanone is added dropwise. After 17h at 60°C, the reaction mixture is cooled down to room temperature, diluted with 5 mL of tetrahydrofuran, and precipitated in 150 mL of cold methanol. The precipitate is filtered off, washed with methanol and dried overnight at 30°C. 864 mg of Example 12 are obtained as a white solid (85% yield). Size-exclusion chromatography (PS-equivalent): Mw 62,700.

Example 13: Preparation of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl poly-2-methylacrylate-Co-8-{4-[(Z)-1-cyano-2-phenylethenyl]phenoxy}octyl poly-2-methylacrylate (95:5 ratio)



Example 13 is prepared starting 987 mg (2.849 mmol) of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl 2-methylacrylate (example 4 of US 6,107,427) and 73.8 mg (0.152 mmol) of Example 10A according to the procedure described for Example 12. Size-exclusion chromatography (PS-equivalent): Mw 60,800.

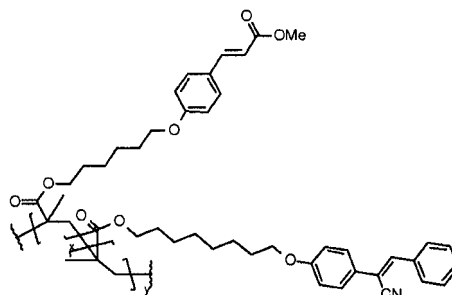
Example 14: Preparation of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl poly-2-methylacrylate-Co-8-{4-[(Z)-1-cyano-2-phenylethenyl]phenoxy}octyl poly-2-methylacrylate (90:10 ratio)



- 5 Example 14 is prepared starting 1000 mg (2.887 mmol) of example 4 of US 6,107,427 and 156 mg (0.321 mmol) of Example 10A according to the procedure described for Example 12.

Size-exclusion chromatography (PS-equivalent), Mw 53,100.

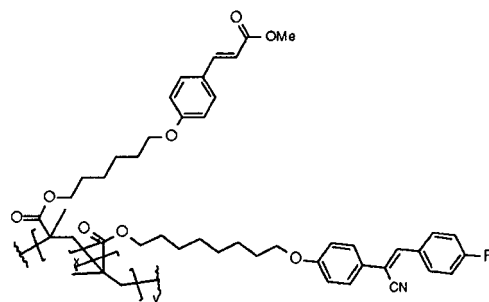
- 10 Example 15: Preparation of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl poly-2-methylacrylate-Co-8-{4-[(Z)-1-cyano-2-phenylethenyl]phenoxy}octyl poly-2-methylacrylate (90:10 ratio)



- 15 Example 15 is prepared starting 1000 mg (2.887 mmol) of example 4 of US 6,107,427 and 134mg (0.321 mmol) of Example 10O according to the procedure described for Example 12.

Size-exclusion chromatography (PS-equivalent) Mw 75,400.

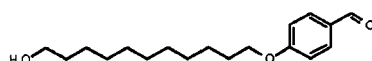
- 20 Example 16: Preparation of 6-{4-[(1E)-3-methoxy-3-oxoprop-1-enyl]phenoxy}hexyl poly-2-methylacrylate-Co-8-{4-[(Z)-1-cyano-2-(4-fluorophenyl)ethenyl]phenoxy}octyl poly-2-methylacrylate (90:10 ratio)



Example 16 is prepared starting 1000 mg (2.887 mmol) of Example 4 of US 6,107,427) and 140mg (0.321 mmol) of Example 10M according to the procedure described for Example 12.

5 Size-exclusion chromatography (PS-equivalent) Mw 78,900.

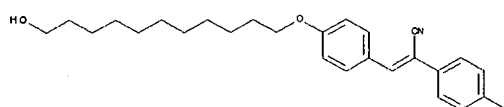
Example 17: Preparation of 4-[(11-hydroxyundecyl)oxy]benzaldehyde 17A



Example 17A is prepared starting from 4-hydroxybenzaldehyde and 11-bromoundecan-1-ol according to the procedure described for Example 2 in 57% yield.

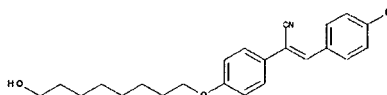
10 Example 17B is prepared starting from 4-hydroxy-3-methoxybenzaldehyde and 11-bromoundecan-1-ol according to the procedure described for Example 2 in 97% yield.

Example 18: Preparation of (Z)-2-(4-fluorophenyl)-3-[4-(11-hydroxyundecoxy)phenyl]prop-2-enenitrile



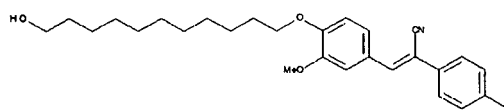
15 Example 18A is prepared starting from Example 17A and [(4-fluoro)phenyl]acetonitrile according to the procedure described in Example 7.

Example 20: (Z)-2-(4-fluorophenyl)-3-[4-(11-hydroxyundecoxy)phenyl]prop-1-enenitrile



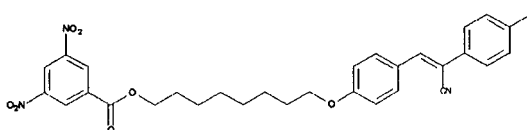
20 Example 20 is prepared starting from Example 1A and 4-Fluorobenzaldehyde according to the procedure described in Example 7.

Example 21: Preparation of (Z)-2-(4-fluorophenyl)-3-[4-(11-hydroxyundecoxy)-3-methoxy-phenyl]prop-2-enenitrile



Example 21 is prepared starting from Example 17B and [(4-fluoro)phenyl]acetonitrile according to the procedure described in Example 6.

Example 22: Preparation of 8-[4-[(Z)-2-cyano-2-(4-fluorophenyl)vinyl]phenoxy]octyl 3,5-dinitrobenzoate 22A



3290 mg (14.2 mmol) of 3,5-dinitrobenzoyl chloride is dissolved in 30 mL of toluene and 2 drops DMF. A solution of 5000 mg (13.6 mmol) of Example 19B, 160 mg (1.3 mmol) of 4-dimethylaminopyridine and 3240 mg (41.0 mmol) of pyridine in 10 mL of toluene are added slowly. The mixture is stirred at room temperature for 96 hours. The solution is then heated up to 80°C and 10 ml of MeOH are added. The suspension is stirred at room temperature for 1 hour and at 0°C for 1 hour. The precipitate is filtered off. The solid is dispersed in a mixture of 40 mL of MeOH and 10 mL of HCl 1N and is stirred 1h at room temperature. The suspension is filtered off, washed several time with cold MeOH and dried under high vacuum 12h to give 9600 mg (71%) of Example 22A.

Example 22B is prepared starting from Example 20 according to the procedure described in Example 22A.

Example 22C is prepared starting from Example 18A according to the procedure described in Example 22A

Example 22F is prepared starting from Example 21 according to the procedure described in Example 22A.

Example 23: Preparation of 8-[4-[(Z)-2-cyano-2-(4-fluorophenyl)vinyl]phenoxy]octyl 3,5-diaminobenzoate 23A

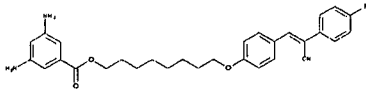
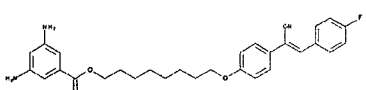
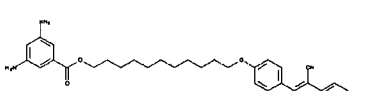
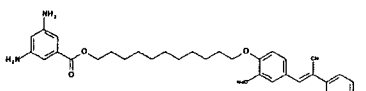
4.8 g (5.55 mmol) of Example 22A are dissolved in a mixture of 63 ml of DMF and 7 ml of water. 13.8 g (51.3 mmol) of ferric chloride hexahydrate are added. 5.58 g (85.5 mmol) of zinc powder are added portionwise within 30 min. The mixture is allowed to react for 2 hours. The reaction mixture is then partitioned between ethyl acetate and water and filtered. The organic phase is washed repeatedly with water, dried over sodium sulfate, filtered and concentrated by rotary evaporation. Filtration of the residue

on silica gel using toluene:ethyl acetate (1:3) as eluant and yields 3.56 g (99%) of Example 23A as a white powder.

The compounds 23B, 23C, 23F are prepared according to the process described in example 23 for compound 23A with the proviso that Example 22A is replaced by

5

Example 22B, respectively Example 22C, respectively Example 22F.

	Name	Structure	¹ H NMR (300MHz) in DMSO-d ₆
23A	8-[4-[(Z)-2-cyano-2-(4-fluorophenyl)vinyl]phenoxy]octyl 3,5-diaminobenzoate		7.92 (d, 2H), 7.91 (s, 1H), 7.80-7.73 (m, 2H), 7.35 (dd, 2H), 7.09 (d, 2H), 6.43 (d, 2H), 6.02 (dd, 1H), 4.98 (s broad, 4H), 4.16 (t, 2H), 4.05 (t, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.36 (m, 8H)
23B	8-[4-[(Z)-1-cyano-2-(4-fluorophenyl)vinyl]phenoxy]octyl 3,5-diaminobenzoate		7.96 (m, 2H), 7.91 (s, 1H), 7.65 (d, 2H), 7.38 (dd, 2H), 7.04 (d, 2H), 6.43 (d, 2H), 6.03 (dd, 1H), 4.99 (s, 4H), 4.16 (t, 2H), 4.02 (t, 2H), 1.70 (m, 4H), 1.36 (m, 8H)
23C	11-[4-[(Z)-2-cyano-2-(4-fluorophenyl)vinyl]phenoxy]undecyl 3,5-diaminobenzoate		7.92 (d, 2H), 7.91 (s, 1H), 7.80-7.73 (m, 2H), 7.35 (dd, 2H), 7.09 (d, 2H), 6.43 (d, 2H), 6.02 (dd, 1H), 4.99 (s broad, 4H), 4.16 (t, 2H), 4.05 (t, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.36 (m, 14H)
23F	11-[4-[(Z)-2-cyano-2-(4-fluorophenyl)vinyl]-2-methoxyphenoxy]undecyl 3,5-diaminobenzoate		7.91 (s, 1H), 7.79 (m, 2H), 7.66 (d, 1H), 7.55 (dd, 1H), 7.38 (m, 2H), 7.13 (d, 1H), 6.42 (d, 2H), 6.02 (t, 1H), 4.98 (s, 4H), 4.14 (t, 2H), 4.03 (t, 2H), 3.81 (s, 3H), 1.73 (m, 2H), 1.64 (m, 2H), 1.29 (m, 14H).

Example 24: Preparation of PAA1

469 mg (2.4 mmol) of 1,2,3,4-cyclobutanetetracarboxylic acid is added to a solution of 1200 mg (2.4 mmol) of Example 23A in 6.6 g of NMP. Stirring is then carried out at 0°C for 2 hours. The mixture is subsequently allowed to react for 21 hours at room temperature. The polymer mixture is diluted with 4.4 mL of NMP and precipitated into 150 mL of water to yield, after drying at 40°C under vacuum, 1700.mg of PAA-1 in the form of a white powder. $\eta=0.38$ dL/g

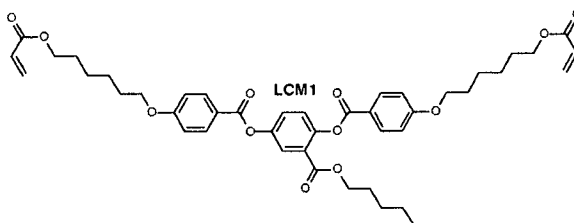
Example 25: Preparation of PAA-2 to PAA-7

In analogy to the preparation of PAA-1 (Example 24), PAA-2 to PAA-7 are prepared from diamine (see below table) with 2,3,5-tricarboxycyclopentylacetic-1,2:3,4-dianhydride. Analytical data are given in below table.

Diamines	Polyamic acid	Viscosity (dL/g)
Example 23A	PAA-4	0.52
Example 23B	PAA-2	0.38
Example 23C	PAA-3	0.37
Example 23F	PAA-7	0.42

Example 26: Preparation of liquid crystal photo-polymerisable monomer formulation S2.

15 A solution of 29.1 wt% LCM1, 0.3 wt% photoinitiator IRGACURE™ 369 from Ciba SC, 0.3 wt% of Tinuvin 123, and 0.3 wt% of BHT, is prepared using anisole as solvent. The solution is stirred for 30 minutes at room temperature and filtered on 0.20 µm PTFE hi-cap.



20 Example 27: Application as photoalignment material

A two percent by weight solution S1 of material of the photoreactive polymer is prepared in cyclopentanone. The solution is stirred for 30 minutes at room temperature and filtered on 0.20 μm PTFE hi-cap. The solution is spin-coated at 2000 rpm onto a glass substrate, which is then dried for 5 minutes at 180°C. The substrate is

subsequently irradiated with polarized UVA light from a mercury high-pressure lamp, the direction of incidence being perpendicular to the substrate surface. For the polarization a Moxtec polarizer is used. The exposure energy of the polarised UVA, using a Moxtec polariser, varied from 0.2 to 250 mJ.cm⁻². The formulation S2 (Example 26) is spin-coated at 800 rpm onto the substrate exposed with linearly polarised light, which is then dried for 30 seconds at 50°C. The resulting substrate is subsequently purged with nitrogen atmosphere for 30 seconds and then exposed with 1J.cm⁻² of isotropic UV light under nitrogen atmosphere. The devices prepared are placed under Leitz microscope with crossed polarizers and the light intensity is measured separately in clear and dark state by a photomultiplier connected with the microscope and sending the results to a digital voltmeter. Contrast ratios are calculated from a following equation:

Contrast = $[I_{45^\circ} - I_{\text{offset}}] / [I_{0^\circ} - I_{\text{offset}}]$, where:

I_{0° (V) is the minimal light intensity, *i.e.* the dark state

I_{45° (V) is the maximal light intensity, *i.e.* the clear state

I_{offset} (V) is the light intensity measured without coating of S2 solution

The minimum energy needed to obtain a good alignment (contrast > 800) is determined for each compound. Contrasts at this specific energy are measured. The following table resumes the results obtained for photoreactive polymers from Examples 11A, Examples 11B, Examples 11F, Examples 11M, Examples 11N, Examples 11O, Examples 11P, Examples 11U, Examples 11V, Examples 11W, Examples 11Y, Examples 11I, Examples 11S.

From examples	E min for orientation (mJ.cm ²)	Contrast with Emin.
11O	1.6	1800
11N	1.6	2600
11U	<0.6	4310
11V	<0.6	1190
11W	1	3400
11Y	1	900
11F	12	1100

11B	8	2220
11A	1.3	3200
11R	8	2300
11I	4	1200
11M	0.6	1600
11S	8	1400
11P	1.6	1300
11AA	1	1480
11AB	1.6	1470

Example 28:

The high contrasts of devices prepared in Example 27 from Examples 11O, Examples 11N, Examples 11F, Examples 11E, Examples 11M are measured for an exposure energy of the polarised UVA of 150 mJ.cm^{-2} and presented in the following table.

From examples	Contrast
11O	5500
11N	8600
11F	7800
11E	6000
11M	5000

5

10

15

Example 29: The azimuthal angle stability illustrates the stability of the first exposure E1 applied on photoalignment material with linearly polarized UV light and subsequently exposed with E2=E1 of this same light after the rotation of the sample at 45° according to the first irradiation direction. The method of double exposure at 0 and 45° defines the stability of LPP orientation through applied energy to be deviated if supplemental exposure is done at another planar angle. A two percent by weight solution made from photoreactive polymers formulation is prepared using cyclopentanone as solvent. The solution is stirred for 30 minutes at room temperature and filtered on $0.20 \mu\text{m}$ PTFE hi-cap. The solution is spin-coated at 2000 rpm onto a glass substrate, which is then dried for 5 minutes at 180°C . The substrate is subsequently irradiated with polarized UVA light from a mercury high-pressure lamp, the direction of incidence being perpendicular to the substrate surface. For the

polarization a Moxtec polarizer is used. The exposure energy of the polarised UVA light, using a Moxtec polariser, was 128 mJ.cm^{-2} . Then the sample was rotated 45° from starting position with a help of moving stage. The first zone of exposure was masked to keep the reference exposure results done at 0° . The rest of the substrate was irradiated with this same polarized UVA light with energy of 128 mJ.cm^{-2} . The formulation S2 (Example 26) is spin-coated at 800 rpm onto the substrate exposed with linearly polarised light, which is then dried for 30 seconds at 50°C . The resulting substrate is subsequently purged with nitrogen atmosphere for 30 seconds and then exposed with 1 J.cm^{-2} of isotropic UV light under nitrogen atmosphere. The prepared device is placed under polarized microscope on rotating stage and the dark state of the first zone exposed with E1 is defined as reference (0°) position. The sample is next shifted to the zone exposed with $E1(0^\circ)+E2(45^\circ)$, when $E2=E1$. The dark state position is found with the help of rotating stage. The angle difference between reference position and second position, *i.e* the deviation of azimuthal angle is measured and reported in the table below for the following photoreactive polymers.

The azimuthal stability is defined to be very good, if the deviation of azimuthal angle is below 6° . The azimuthal stability is defined to be good if the deviation of azimuthal angle is between 7° and 15° . The azimuthal stability is defined to be medium if the deviation of azimuthal angle is between 16° and 20° . The azimuthal stability is defined to be bad if the deviation of azimuthal angle is above 21° . The results are summarized in the below table.

From examples	Azimuthal stability
11O	Very good
11B	Very good
11A	Very good
11E	Medium
11R	Very good
11I	Very good
11M	Very good
11N	Good
11L	Very good

11S	Very good
11W	Good
11Y	Good
11AA	Very good
11AB	Very good

Example 30: Application of PAA-1 (Example 24) as photoalignment material for IPS mode.

5 A liquid crystal cell 1 is prepared, wherein the liquid crystal is aligned by photoreactive polyamic acid PAA-1 and the electric field is applied between two plan electrodes on each side of the cell gap.

10 A 4.0% solution of polyamic acid PAA-1 is prepared by mixing the solid polyamic acid PAA-1 in NMP and stirred thoroughly till the solid polyamic acid PAA-1 is dissolved and a second solvent butyl cellulose (BC) is added and the whole composition is stirred thoroughly to obtain final solution. The solvent ratio between NMP and butyl cellulose is 1:1. The above polymer solution was spin-coated onto the two ITO coated glass substrates at a spin speed of 1700 rpm for 30seconds. After spin coating the substrates are subjected to baking procedure consisting of pre-baking for 1.5 minutes at 130°C and post-baking for 40 minutes at a temperature of 200°C. The resulting layer

15 thickness is around 70nm. This substrate is exposed so that the angle between the direction of linearly polarized UV light (LPUV) and the direction of electrode stripes is 78°. The incidence angle of the LPUV, relative to the normal of the substrate surface, was 0°. The plane of polarization was within the plane spanned by the substrate normal and the propagation direction of the light. The applied exposure dose is 500

20 mJ/cm². After LPUV exposure a cell is assembled with the 2 substrates, the exposed polymer layers facing to the inside of the cell. The substrates are adjusted relative to each other such that the induced alignment directions are parallel to each other (corresponds to the anti-parallel, i.e 180°, rubbed configuration in case of alignment by rubbing procedure). The cell is capillary filled with liquid crystal MLC7067 (Merck KGA). After that, the cell is optionally annealed at about 92°C for 10 minutes and

25 slowly cooled down to room temperature. The liquid crystal in the cell showed well defined and homogeneous planar orientation after thermal annealing of the cell.

Example 31: Cells are prepared with PAA-1, PAA-2, PAA-3, PAA-4, PAA-7 as in Example 30. Alignment quality of the liquid crystal in the cell is checked by placing the cell between two crossed polarizers and adjusted to obtain dark state. The alignment quality is defined to be very good, if the dark state show no defects and the liquid crystal is very well oriented. The alignment quality is defined to be medium if the dark state has light leakage because of slight inhomogeneous orientation of liquid crystal in some areas of the cell. The alignment quality is defined to be worse, if liquid crystal is not oriented with absence of dark state. The contrast of cells were measured in the NB mode (crossed polarizers) using a white light source. The polarisers are rotated until a minimum transmission T_{min} is measured, then the maximum transmission T_{max} is determined between parallel polarizers.

$$\text{Contrast Ratio} = T_{max}/T_{min}$$

The results show high contrast values for cells made according to the present invention. The results are summarized in the Table below.

Compound	Alignment quality	Contrast Ratio
PAA-1	Very good	1750-1850
PAA-2	Very good	1750-1850
PAA-3	Very good	1650-1750
PAA-4	Very good	1750-1850
PAA-7	Very good	1600-1700

Example 32: Application as photoalignment material

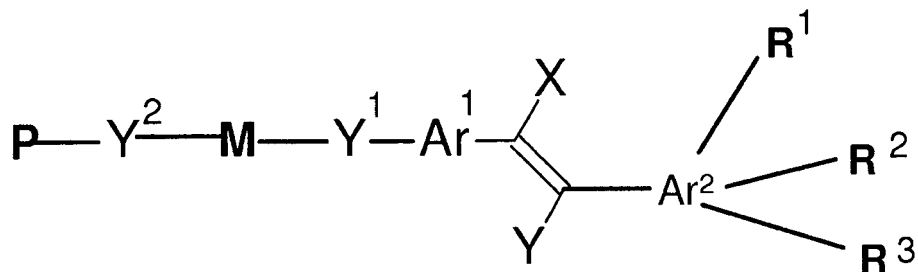
Alignment layers are prepared as in Examples 27 except that materials from Example 12 to Example 17 are used and the substrates are subsequently irradiated with polarized UVB and UVA. The minimum energy needed to obtain a good alignment quality without defects in LCP film is determined for each compound. The azimuthal stability is also measured as in Example 29. The results are given in the following table.

From examples	E min for orientation with UVA (mJ.cm ²)	E min for orientation with UVB (mJ.cm ²)	Azimuthal stability

12	32	4	Good
13	12	4	Good
14	12	4	Good
15	16	4	Medium
16	8	4	Good

Claims:

1. Compounds according to the general formula (I)



(I)

5 wherein

Ar¹ and Ar² are independently from each other a ring system of 4 to 40 atoms, wherein each ring system includes at least one unsaturation directly connected via electron conjugation (π - π bonding) to the double bond shown in formula (I), wherein the ring system is unsubstituted or mono- or poly-substituted by a halogen atom and/or a polar group like hydroxy, nitro, nitrile, -CF₃; or by a carboxy group, and/or a cyclic, straight-chain or branched alkyl residue having from 1 to 30 carbon atoms, which is unsubstituted, mono- or poly-substituted by methyl, fluorine and/or chlorine, wherein one or more, preferably non-adjacent -CH₂- groups independently may be replaced by a group selected from -O-, -CO-, -CO-O-, -O-CO-, -NR^{1'}-, -NR^{1'}-CO-, -CO-NR^{1'}-, -NR^{1'}-CO-O-, -O-CO-NR^{1'}-, -NR^{1'}-CO-NR^{1'}-, -CH=CH-, -C $\equiv$ C-, -O-CO-O- and -Si(CH₃)₂-O-Si(CH₃)₂-, an aromatic or an alicyclic group, wherein R^{1'} is a hydrogen atom or lower alkyl; and/or an acryloyloxy, alkoxy, alkylcarbonyloxy, alkyloxocarbonyloxy, methacryloyloxy, vinyl, allyl, vinyloxy and/or allyloxy group, having from 1 to 20 carbon atoms, preferably having from 1 to 10 carbon atoms; preferably the ring system is unsubstituted or substituted by an alkoxy group; and wherein;

if X is hydrogen and Y is CN,

then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃, with the proviso that R¹, R² or R³ are not simultaneously hydrogen;

25 if X is CN and Y is hydrogen;

then R¹, R² or R³ are independently from each other hydrogen, halogen or -CF₃;

M is a single covalent bond or a spacer unit;

Y¹, Y² are independently from each other a bridging group,

- P is a hydrogen atom, optionally substituted alkyl, or a polymerizable group.
2. Oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, comprising at least one compound according to claim 1 as monomer unit.
- 5 3. Oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2 in form of a gel or a network.
- 10 4. Oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2 further comprising additives such as silane-containing compounds, acrylate- or epoxy-containing crosslinking agents, a photosensitiser, a photoradical generator and/or a cationic photoinitiator.
- 15 5. Oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2 further comprising in admixture other polymers, oligomers, monomers, photoactive polymers, photoactive oligomers and/or photoactive monomers.
- 20 6. Oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2 which is applied to a support and crosslinked by irradiation with aligning light.
- 25 7. Composition comprising an oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claims 2 to 6.
- 30 8. Use of one or more oligomers, dendrimers or a polymer, which polymer is especially a copolymer or homopolymer, according to claims 2 as an alignment layer for liquid crystals.

9. Alignment layer comprising one or more oligomer, dendrimer or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2.
- 5 10. Alignment layer according to claim 9 having a pattern of different alignment directions.
- 10 11. Method for the preparation of an alignment layer according to claim 9, wherein one or more oligomers, dendrimers or a polymer, which polymer is especially a copolymer or homopolymer, according to claim 2 preferably in solution is applied to a support, which is optionally provided with an electrode, and optionally after prior imidisation, said applied oligomers, dendrimers or polymers are crosslinked by irradiation with aligning light.
- 15 12. Optical and electro-optical unstructured or structured constructional elements preferably liquid crystal display cells, multi-layer and hybrid layer elements comprising at least one alignment layer according to claim 9.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/060508

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C255/37 C08F265/06 C08G73/10 G02F1/1337
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)

C07C C08F C08G G02F C09K

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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/033506 A1 (ROLIC AG [CH]; CHERKAoui ZOUBAIR MOHAMMED [CH]; STUDER PEGGY [FR]; REI) 29 March 2007 (2007-03-29) examples A11, A13 claims 18-29	1-12
X	WO 2013/026691 A1 (ROLIC AG [CH]; LINCKER FREDERIC [FR]; BURY S PIRES IZABELA [CH]; CHAPP) 28 February 2013 (2013-02-28) examples 2,4,6,8-12 page 95, lines 21-25 claims 6-17	1-12
	----- -/-	

☒ 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

18 June 2014

Date of mailing of the international search report

26/06/2014

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

Fitz, Wolfgang

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/060508

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/050121 A1 (ROLIC AG [CH]) 11 April 2013 (2013-04-11) page 111; example 56S page 117; compounds PAA-31 page 123, table 3, PAA-31 page 124, table 4, PAA-31 claims 13-16 -----	1-12
X	LEE, JEONGHWAN ET AL: "Polarized Light Emission in a Liquid Crystalline Copolymer Film Comprised of Fluorenevinylene and Photo-Cross-Linkable Mesogenic Side Groups", MOLECULAR CRYSTALS AND LIQUID CRYSTALS , 529, 20-24 CODEN: MCLCD8; ISSN: 1542-1406, 2010, XP008165369, page 21, Materials page 21; figure 1 pages 20 - 21, Introduction page 24 - last paragraph abstract -----	1-12
X	AHMED, A. M. ET AL: "A new class of main-chain liquid - crystalline polymers based on an unsymmetrically disubstituted cyanostilbene", POLYMER , 34(6), 1297-302 CODEN: POLMAG; ISSN: 0032-3861, 1993, XP002714768, page 1298, scheme 1: compounds I and II page 1298; table 1 abstract -----	1-5,7
X	MIHARA, TAKASHI ET AL: "Synthesis and thermal properties of combined liquid", JOURNAL OF APPLIED POLYMER SCIENCE , 68(12), 1979-1990 CODEN: JAPNAB; ISSN: 0021-8995, 1998, XP008165366, page 1980, scheme 1, diepoxy monomer page 1981, line 6 page 1989, column 1, line 18 - column 2 -----	1-7
X	MARTIN, S. J. ET AL: "Linear electrooptic effect in a new class of main-chain liquid -", SPECIAL PUBLICATION - ROYAL SOCIETY OF CHEMISTRY , 137(ORGANIC MATERIALS FOR NON-LINEAR OPTICS III), 295-9 CODEN: SROCD0; ISSN: 0260-6291, 1993, XP008165368, page 295; figure 1 page 296; table 1 abstract -----	1-5,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/060508

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007033506	A1	29-03-2007	AT 424442 T 15-03-2009
		CN 101268168 A 17-09-2008	
		EP 1764405 A1 21-03-2007	
		EP 1928979 A1 11-06-2008	
		JP 2009511431 A 19-03-2009	
		KR 20080050583 A 09-06-2008	
		TW 1324632 B 11-05-2010	
		US 2008274304 A1 06-11-2008	
		WO 2007033506 A1 29-03-2007	
-----	-----	-----	-----
WO 2013026691	A1	28-02-2013	AU 2012299729 A1 13-02-2014
		CN 103748192 A 23-04-2014	
		EP 2748280 A1 02-07-2014	
		KR 20140054346 A 08-05-2014	
		WO 2013026691 A1 28-02-2013	
-----	-----	-----	-----
WO 2013050121	A1	11-04-2013	CN 103842329 A 04-06-2014
		WO 2013050121 A1 11-04-2013	
-----	-----	-----	-----



(12) 发明专利申请

(10) 申请公布号 CN 105377811 A

(43) 申请公布日 2016. 03. 02

(21) 申请号 201480030496. 5 *C08F 265/06*(2006. 01)

(22) 申请日 2014. 05. 22 *C08G 73/10*(2006. 01)

(30) 优先权数据 *G02F 1/1337*(2006. 01)

13169419. 2 2013. 05. 28 EP

(85) PCT国际申请进入国家阶段日

2015. 11. 27

(86) PCT国际申请的申请数据

PCT/EP2014/060508 2014. 05. 22

(87) PCT国际申请的公布数据

W02014/191292 EN 2014. 12. 04

(71) 申请人 罗利克有限公司

地址 瑞士楚格

(72) 发明人 I · 巴里斯皮埃尔斯 S · 查贝雷特

M · 伊本一艾耳哈吉 F · 林克尔

(74) 专利代理机构 中国国际贸易促进委员会专

利商标事务所 11038

代理人 任宗华

(51) Int. Cl.

C07C 255/37(2006. 01)

权利要求书2页 说明书38页

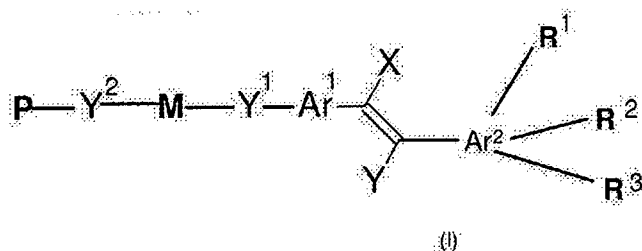
(54) 发明名称

氰基芪类

(57) 摘要

本发明涉及尤其可用于校准,特别地光校准从动材料,特别地用于光学或光电应用,例如安防应用的液晶,液晶器件或光学或光电薄膜的新的化合物。

1. 通式 (I) 的化合物：



其中：

Ar^1 和 Ar^2 彼此独立地为4-40个原子的环系，其中每一环系包括借助电子共轭($\pi-\pi$ 键合)直接与式(I)中所示双键连接的至少一个不饱和度，

其中该环系统未取代或者被下述单-或多-取代：

卤素原子和/或极性基团，例如羟基，硝基，腈， $-CF_3$ ；或羧基和/或未取代或者被甲基、氟和/或氯单-或多-取代的具有1-30个碳原子的环状、直链或支链烷基，其中一个或多个，优选不相邻的 $-CH_2-$ 基独立地可以被选自下述中的基团替代： $-O-$ ， $-CO-CO-O-$ ， $-O-CO-$ ， $-NR^1-$ ， $-NR^1-CO-$ ， $-CO-NR^1-$ ， $-NR^1-CO-O-$ ， $-O-CO-NR^1-$ ， $-NR^1-CO-NR^1-$ ， $-CH=CH-$ ， $-C\equiv C-$ ， $-O-CO-O-$ 和 $-Si(CH_3)_2-O-Si(CH_3)_2-$ ，芳族或脂环族基团，其中 R^1 是氢原子或低级烷基，和/或丙烯酰氧基，烷氧基，烷基羰基氧基，烷基氧代羰基氧基，甲基丙烯酰氧基，乙烯基，烯丙基，乙烯基氧基和/或烯丙基氧基，其具有1-20个碳原子，优选具有1-10个碳原子；优选该环系统未取代或者被烷氧基取代；和其中：

若X是氢和Y是CN，

则 R^1 ， R^2 或 R^3 彼此独立地为氢，卤素或 $-CF_3$ ，条件是 R^1 ， R^2 或 R^3 不同时为氢；

若X是CN和Y是氢；

则 R^1 ， R^2 或 R^3 彼此独立地为氢，卤素或 $-CF_3$ ；

M是单一共价键或间隔基单元；

Y^1 ， Y^2 彼此独立地为桥连基团，

P是氢原子，任选取代的烷基，或可聚合基团。

2. 低聚物、枝状体或聚合物，所述聚合物特别地为共聚物或均聚物，其包括权利要求1的至少一种化合物作为单体单元。

3. 低聚物、枝状体或聚合物，所述聚合物特别地为凝胶或网络形式的权利要求2的共聚物或均聚物。

4. 低聚物、枝状体或聚合物，所述聚合物特别地为权利要求2的共聚物或均聚物，它进一步包括添加剂，例如含硅烷的化合物，含丙烯酸酯或环氧基的交联剂，光敏剂，光自由基生成剂和/或阳离子光引发剂。

5. 低聚物、枝状体或聚合物，所述聚合物特别地为权利要求2的共聚物或均聚物，它进一步包括混合其他聚合物，低聚物，单体，光活性聚合物，光活性低聚物和/或光活性单体。

6. 低聚物、枝状体或聚合物，所述聚合物特别地为权利要求2的共聚物或均聚物，它被施加载体上并通过用校准光辐照而交联。

7. 一种组合物，它包括低聚物，枝状体或聚合物，所述聚合物特别地为权利要求2-6任何一项的共聚物或均聚物。

8. 一种或多种低聚物, 枝状体或聚合物作为液晶校准层的用途, 所述聚合物特别地为权利要求 2 的共聚物或均聚物。

9. 校准层, 它包括一种或多种低聚物, 枝状体或聚合物, 所述聚合物特别地为权利要求 2 的共聚物或均聚物。

10. 权利要求 9 的校准层, 其具有不同校准方向的图案。

11. 制备权利要求 9 的校准层的方法, 其中将优选在溶液中的一种或多种低聚物, 枝状体或聚合物被施加到载体上, 所述聚合物特别地为权利要求 2 的共聚物或均聚物, 所述载体任选地提供有电极, 和任选地在在前的酰亚胺化之后, 所述施加的低聚物, 枝状体或聚合物通过用校准光辐照而交联。

12. 一种光学和光电的未结构化或结构化的构造元件, 优选液晶显示器盒, 多层和混杂层元件, 其包括权利要求 9 的至少一层校准层。

氰基芪类

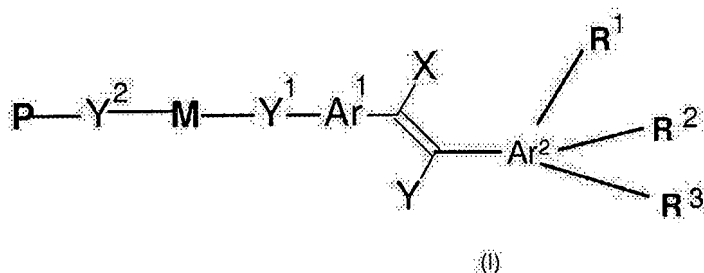
[0001] 本发明涉及化合物,所述化合物尤其可用于校准,特别是光校准从动(slave)材料,特别是用于光学或光电应用,例如安防应用的液晶,液晶器件或光学或光电薄膜。

[0002] 从动材料,特别是液晶的取向用的光校准方法是一种非常经济和生态的制造方式,因为它几乎不产生任何浪费。

[0003] 因此,市场上存在持续的增长需求以提供进一步的光校准材料,其具有所需应用的高级性能,例如高对比度,良好的校准质量,方位角稳定性或高速取向。

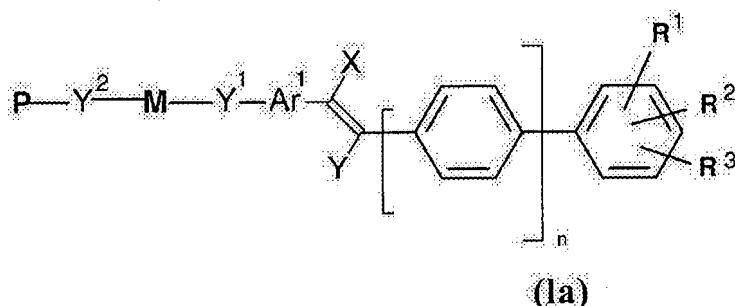
[0004] 因此,在第一方面中,本发明涉及根据通式(I)的化合物:

[0005]



[0006] 优选

[0007]



[0008] 其中

[0009] Ar^1 和 Ar^2 彼此独立地为4-40个原子的环系统,其中每一环系包括借助电子共轭($\pi-\pi$ 键合)直接与式(I)中所示双键连接的至少一个不饱和度,

[0010] 其中该环系未取代或者被下述单-或多-取代:

[0011] 卤素原子和/或极性基团,例如羟基,硝基,腈, $-CF_3$;或羧基和/或未取代或者被甲基、氟和/或氯单-或多-取代的具有1-30个碳原子的环状、直链或支链烷基,其中一个或多个,优选不相邻的 $-CH_2-$ 基独立地可以被选自下述中的基团替代: $-O-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-NR^{1'}-$, $-NR^{1'}-CO-$, $-CO-NR^{1'}-$, $-NR^{1'}-CO-O-$, $-O-CO-NR^{1'}-$, $-NR^{1'}-CO-NR^{1'}-$, $-CH=CH-$, $-C\equiv C-$, $-O-CO-O-$ 和 $-Si(CH_3)_2-O-Si(CH_3)_2-$,芳族或脂环族基团,其中 $R^{1'}$ 是氢原子或低级烷基,和/或丙烯酰氧基,烷氧基,烷基羰基氧基,烷基氧代羰基氧基,甲基丙烯酰氧基,乙烯基,烯丙基,乙烯基氧基和/或烯丙基氧基,其具有1-20个碳原子,优选具有1-10个碳原子;优选该环系未取代或者被烷氧基取代;和其中:

[0012] 若X是氢和Y是CN,

[0013] 则 R^1 , R^2 或 R^3 彼此独立地为氢, 卤素或 $-CF_3$, 条件是 R^1 , R^2 或 R^3 不同时为氢;

[0014] 若 X 是 CN 和 Y 是氢;

[0015] 则 R^1 , R^2 或 R^3 彼此独立地为氢, 卤素或 $-CF_3$;

[0016] M 是单一共价键或间隔基单元;

[0017] Y^1 , Y^2 彼此独立地为桥连基团,

[0018] n 为 0, 1, 2 或 3; 优选 0,

[0019] P 是氢原子, 任选取代的烷基, 或可聚合基团。

[0020] 在本申请的上下文中, “从动材料” 应当指代经与光校准材料接触, 则具有建立各向异性能力的任何材料。在光校准材料内和在从动材料内各向异性的性质可以彼此不同。例如, 从动材料可显示出对于可见光的光吸收的各向异性和因此可充当偏振器, 而光校准材料的各向异性可仅仅与分子取向有关。也可存在例如在共聚物内的可光校准材料的部分, 所述部分对校准光不敏感, 但因与光敏部分相互作用而产生各向异性的性能, 所述光敏部分经曝露于校准光下则经历光反应。这一材料显示出可光校准材料和从动材料的性能, 但应当包括在可光校准材料的含义以内。

[0021] 从动材料可包括可聚合和 / 或不可聚合的化合物。在本申请范围内, 术语 “可聚合” 和 “聚合的” 应当分别包括 “可交联” 和 “交联的” 的含义。同样, “聚合” 应当包括 “交联” 的含义。

[0022] 优选地, 从动材料是一种自组织材料。更优选的是, 从动材料为液晶材料, 和特别优选的是, 从动材料为液晶聚合物材料。

[0023] 在本申请上下文中所使用的液晶聚合物 (LCP) 材料应当是指液晶材料, 所述液晶材料包括液晶单体和 / 或液晶低聚物和 / 或液晶聚合物和 / 或交联液晶。在液晶材料包括液晶单体的情况下, 典型地在因与光校准材料接触导致 LCP 材料内产生各向异性之后, 这种单体可以被聚合。可通过热处理或者通过曝露于光化光下而引发聚合, 所述光化光优选包括紫外光。LCP 材料可由单一类型的液晶化合物组成, 但也可以是不同的可聚合和 / 或不可聚合的化合物的组合物, 其中并非所有化合物必须是液晶化合物。进一步地, LCP 材料可含有添加剂, 例如光引发剂或各向同性或各向异性的荧光和 / 或非 - 荧光染料。

[0024] 在本申请的上下文中, 含化合物 (I) 作为可光校准材料的校准层也称为光控分子取向 (LCMO) 层, 不管它是否已经曝露于偏振光下。因此, 本文中所使用的 LCMO 层可以不具有各向异性的性能, 只要它尚未曝露于校准光, 优选偏振光下且在已经曝露于校准光下之后具有各向异性的性能即可。典型地, LCMO 层可以是施加到基底上的薄层。还可能的是 LCMO 层厚且足够机械稳定, 结果它可在没有额外基底情况下处理。在后一情况下, LCMO 层还具有基底的功能。

[0025] 在本申请的上下文中, 术语 “校准光” 应当是指在可光校准材料内可诱导各向异性且至少部分线性或椭圆偏振的光。优选地, 在大于 5:1 的偏振度下, 校准光被线性偏振。取决于可光校准材料的光敏性而选择校准光的波长, 强度和能量。典型地, 波长在 UV-A, UV-B 和 / 或 UV-C 范围内或者在可见光范围内。优选地, 校准光包括波长小于 450nm 的光。更优选的是校准光包括波长小于 420nm 的光。

[0026] 若校准光被线性偏振, 则校准光的偏振平面应当是指由校准光的传播方向和偏振方向定义的平面。在校准光椭圆偏振的情况下, 偏振平面应当是指由该光的传播方向和由

偏振椭圆的主轴确定的平面。

[0027] 在进一步的方面中,化合物(I)是低聚物、枝状体或聚合物的一部分。在本发明的上下文中术语聚合物是均聚物或共聚物和/或低聚物和/或枝状体。可通过聚合通式(I)的单体,获得所述聚合物,且它可以是凝胶或网络形式。

[0028] 在进一步的方面中,本发明涉及含单体、低聚物、枝状体或聚合物形式的式(I)的所述化合物的校准层材料。这种校准层材料尤其可用于校准液晶和可聚合的、可二聚化或可交联的液晶材料。

[0029] 在再进一步的方面中,本发明涉及具有向列型、近晶型或胆甾型序列的光学元件,例如聚合的、二聚化的或交联的薄膜,和光电元件,例如液晶显示器盒,其包括由含单体、低聚物、枝状体或聚合物形式的通式(I)的化合物的材料制成的校准层。

[0030] 在具体的实施方案中,校准层具有不同校准方向的图案,所述图案有利地可通过光校准方法形成。

[0031] 在进一步的方面中,本发明还涉及含有式(I)的化合物的材料用于制备校准层的用途。

[0032] 要理解,措辞“每一环系包括借助电子共轭($\pi-\pi$ 键合)与双键直接相连的至少一个不饱和度”表示每一环系 Ar^1 和 Ar^2 含有与式(I)中双键直接连接,从而延伸电子共轭的至少一个不饱和键,即双键。

[0033] 在优选的实施方案中,环系 Ar^1 和 Ar^2 是选自下述中的碳环或杂环的环基:4-6个原子的单环,或者5或6个原子的两个相邻的单环,或者8、9或10个原子的稠合双环的环系,或者13或14个原子的稠合三环的环系。更优选环系 Ar^1 和 Ar^2 选自噻吩,吡啶,亚噻吩基,亚呋喃基,亚菲基,亚萘基,亚联苯基或亚苯基。最优选的 Ar^1 是未取代或被 $-O-$ 甲基取代的亚苯基,优选地, Ar^1 未取代。进一步最优的 Ar^2 是亚苯基或亚联苯基,优选亚苯基,它未取代或者被以上给出的含义和优选范围内的 R^1 , R^2 和 R^3 取代。

[0034] 在本发明的进一步优选的实施方案中,桥连基团是选自但不限于下述中的基团:单键, $-O-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-NR^{1'}-$, $-NR^{1'}-CO-$, $-CO-NR^{1'}-$, $-NR^{1'}-CO-O-$, $-O-CO-NR^{1'}-$, $-NR^{1'}-CO-NR^{1'}-$, $-C=C-$, $-C\equiv C-$, $-O-CO-O-$ 和 $-Si(CH_3)_2-O-Si(CH_3)_2-$,其中 $R^{1'}$ 是氢原子或低级烷基,优选单键, $-O-$, $-CO-$, $-COO-$, $-OCO-$, $-C=C-$, $-C\equiv C-$ 。更优选 Y^1 和 Y^2 是单键, $-O-$, $-CO-$, $-COO-$, $-OCO-$,以及最优选 Y^1 是 $-O-$,和 Y^2 是单键, $-O-$, $-CO-$, $-COO-$ 或 $-OCO-$ 。

[0035] 在进一步优选的实施方案中, M 是单键,或是未取代,或者被氰基或卤素单取代或者被卤素多取代的具有1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23或24,优选1,2,3,4,5,6,7,8,9,10,11,12,13,14,15或16,更优选6,7,8,9,10,11或12个碳原子,最优8,9,10或11的直链或支链亚烷基残基,和其中一个或多个,优选不相邻的 CH_2 基团可独立地被杂原子或者选自但不限于下述中的基团: $-O-$, $-CO--CO-O-$, $-O-CO-$, $-NR^{1'}-$, $-NR^{1'}-CO-$, $-CO-NR^{1'}-$, $-NR^{1'}-CO-O-$, $-O-CO-NR^{1'}-$, $-NR^{1'}-CO-NR^{1'}-$, $-C=C-$, $-C\equiv C-$, $-O-CO-O-$ 和 $-Si(CH_3)_2-O-Si(CH_3)_2-$,优选选自 $-O-$, $-CO-$, $-COO-$, $-OCO-$, $-C=C-$, $-C\equiv C-$ 中的基团取代,其中 $R^{1'}$ 是氢原子或低级烷基。优选地 M 未取代。

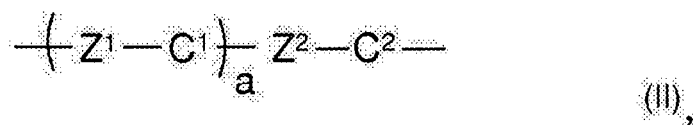
[0036] 在进一步优选的实施方案中, P 中的可聚合基团选自未取代或取代的丙烯酸酯,甲基丙烯酸酯,2-氯丙烯酸酯,2-苯基丙烯酸酯,任选地 N -低级烷基取代的丙烯酰胺,甲基丙烯酰胺,2-氯丙烯酰胺,2-苯基丙烯酰胺,乙烯基醚和酯,烯丙基醚和酯,环氧基,碳酸

酯,乙缩醛 (acetal), 苯乙烯和苯乙烯衍生物, 例如 α -甲基苯乙烯, 对甲基苯乙烯, 对叔丁基苯乙烯, 对氯苯乙烯等, 硅氧烷, 硅烷, 二胺, 酰亚胺单体, 酰胺酸单体及其酯, 酰胺酰亚胺单体, 马来酸和马来酸衍生物, 例如, 马来酸二正丁酯, 马来酸二甲酯, 马来酸二乙酯等, 马来酰亚胺, 降冰片烯, 降冰片烯衍生物, 富马酸和富马酸衍生物, 例如富马酸二正丁酯, 富马酸二-(2-乙基己酯) 等, 脲, 聚氨酯或其相应的均聚物和共聚物及其混合物。更优选在 P 中的可聚合基团选自丙烯酸酯, 甲基丙烯酸酯, 乙烯基醚和酯, 环氧基, 苯乙烯衍生物, 硅氧烷, 酰亚胺单体, 酰胺酸单体及其相应的聚合物、均聚物或共聚物。

[0037] 在仍然进一步的实施方案中,

[0038] Ar^1 是式 (II) 的环系:

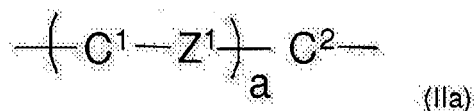
[0039]



[0040] 和

[0041] Ar^2 是式 (IIa) 的环系:

[0042]



[0043] 其中:

[0044] C^1, C^2 各自独立地为 5-14 个原子的非芳族或芳族的, 任选取代的碳环或杂环基团, 所述基团优选借助桥连基团 Z^1 和 Z^2 在相对的位置处彼此连接,

[0045] Z^1, Z^2 各自独立地为单键, 或者优选选自下述中的桥连基团: $-\text{CH}(\text{OH})-$, $-\text{O}-$, $-\text{CH}_2(\text{C}(\text{O})-)$, $-\text{SO}-$, $-\text{CH}_2(\text{SO})-$, $-\text{SO}_2-$, $-\text{CH}_2(\text{SO}_2)-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{COF}_2-$, $-\text{CF}_2\text{CO}-$, $-\text{S-CO}-$, $-\text{CO-S}-$, $-\text{SOO}-$, $-\text{OSO}-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{O-CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{S}-$, $-\text{SH}=\text{CH-COO}-$, $-\text{OCO-CH}=\text{CH}-$, $-\text{CH}=\text{N}-$, $-\text{C}(\text{CH}_3)=\text{N}-$, $-\text{O-CO-O}-$, $-\text{N}=\text{N}-$ 或 1-6 个碳原子, 优选 1-3 个碳原子的短烷基间隔基,

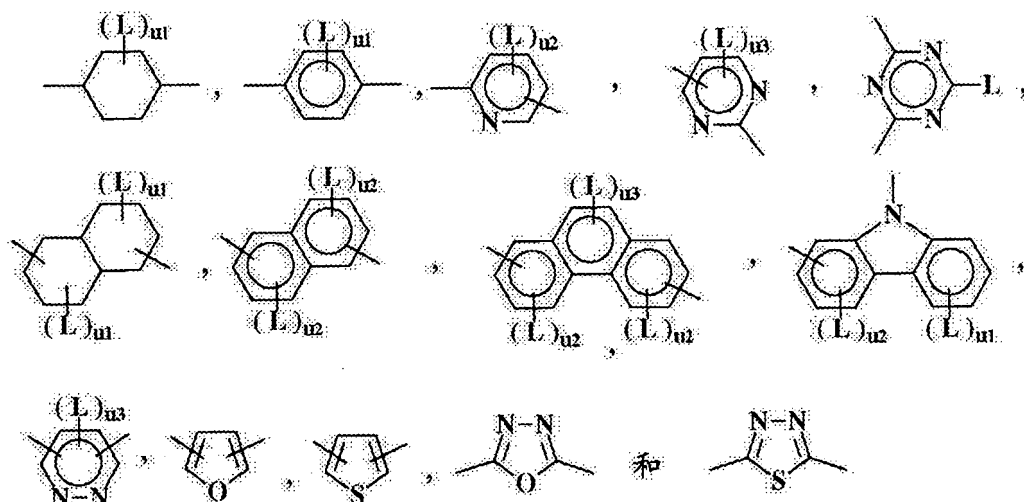
[0046] a 是 0, 1, 2 或 3,

[0047] 条件是与双键直接相连的 C^2 是不饱和的且共轭到它之上。

[0048] 术语“借助桥连基团 Z^1 和 Z^2 在相对的位置处彼此连接”是指 5- 和 6- 元环优选在 1, 3- 或 1, 4- 位连接。在其他, 例如更高元的环内类似的连接图案对于本领域技术人员来说是显而易见的。

[0049] 优选地, 在式 (II) 中的 C^1, C^2 独立地具有下述含义之一:

[0050]



[0051] 其中

[0052] L 是卤素, 羟基和 / 或极性基团, 例如硝基, 氰基或羧基, 和 / 或丙烯酰氧基, 烷氧基, 例如甲氧基, 乙氧基, 丙氧基, 烷基羰基氧基, 烷基氧代羰基氧基, 甲基丙烯酰氧基, 乙烯基, 乙烯基氧基, 烯丙基, 烯丙基氧基, 和 / 或未取代, 被氟和 / 或氯, 和 / 或硅烷基, 和 / 或硅氧烷基单 - 或多 - 取代的环状, 直链或支链烷基残基, 其中烷基残基具有 1-20 个碳原子, 其中一个或多个, 优选不相邻的 $-CH_2-$ 基团独立地可以被一个基团, 优选选自下述中的基团取代: $-O-$, $-CO-$, $-COO-$, $-OCO-$, $-C=C-$, $-C\equiv C-$, $-Si(CH_3)_2-$, $-Si(CH_3)_2-O-Si(CH_3)_2-$, 优选 L 是甲氧基,

[0053] u_1 是 0, 1, 2, 3, 或 4, 优选 0 或 1,

[0054] u_2 是 0, 1, 2, 或 3, 优选 0 或 1, 和

[0055] u_3 是 0, 1, 或 2, 优选 0 或 1,

[0056] 条件是与双键直接相连的 C^2 是不饱和的且共轭到它之上。

[0057] 更优选 C^1 , C^2 是菲基或亚菲基, 联苯基或亚联苯基, 萘基或亚萘基, 苯基或亚苯基, 吡啶或亚吡啶基; 优选萘基或亚萘基, 苯基或亚苯基, 吡啶或亚吡啶基, 和更优选是苯基或亚苯基。

[0058] 优选 L 选自烷氧基, 更优选甲氧基, 乙氧基或丙氧基。

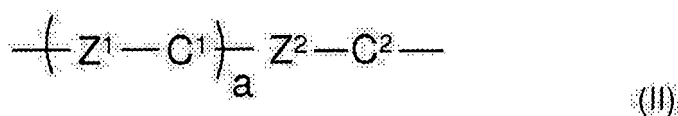
[0059] 优选地, 在式 (II) 和 (III) 中的 Z^1 , Z^2 各自独立地为单键或选自下述中的桥连基团: $-CH(OH)-$, $-O-$, $-CH_2(CO)-$, $-COO-$, $-OCO-$, $-COF_2-$, $-CF_2CO-$, $-CH_2-CH_2-$, $-O-CH_2-$, $-CH_2O-$, $-CH=CH-$, $-OCO-CH=CH-$, $-CH=N-$, $-C(CH_3)=N-$, $-O-CO-O-$, $-N=N-$, 或 1-6 个碳原子, 优选 1-3 个碳原子的短烷基间隔基。

[0060] 更优选 Z^1 , Z^2 各自独立地为单键, $-O-$, $-CH_2(CO)-$, $-COO-$, $-OCO-$, $-CH_2-CH_2-$, $-OCO-CH=CH-$, $-N=N-$, 或 1-3 个碳原子的短烷基间隔基。

[0061] 式 (I) 的优选化合物是那些, 其中:

[0062] Ar^1 是式 (II) 的环系:

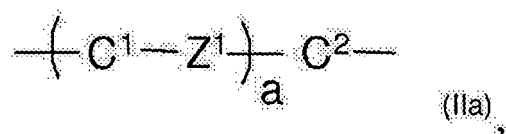
[0063]



[0064] 和

[0065] Ar^2 是式 (IIa) 的环系：

[0066]



[0067] 其中：

[0068] C^1, C^2 各自独立地为 5-14 个原子的非芳族或芳族的、任选取代的碳环或杂环基团，其优选借助桥连基团 Z^1 和 Z^2 在相对位置处彼此连接，

[0069] Z^1, Z^2 各自独立地为单键或优选选自下述中的桥连基团： $-\text{CH}(\text{OH})-$ ， $-\text{O}-$ ， $-\text{CH}_2(\text{CO})-$ ， $-\text{SO}-$ ， $-\text{CH}_2(\text{SO})-$ ， $-\text{SO}_2-$ ， $-\text{CH}_2(\text{SO}_2)-$ ， $-\text{COO}-$ ， $-\text{OCO}-$ ， $-\text{COF}_2-$ ， $-\text{CF}_2\text{CO}-$ ， $-\text{S-CO}-$ ， $-\text{CO-S}-$ ， $-\text{SOO}-$ ， $-\text{OSO}-$ ， $-\text{CH}_2-\text{CH}_2-$ ， $-\text{O-CH}_2-$ ， $-\text{CH}_2\text{O}-$ ， $-\text{CH}=\text{CH}-$ ， $-\text{C}\equiv\text{S}-$ ， $-\text{SH}=\text{CH-COO}-$ ， $-\text{OCO-CH}=\text{CH}-$ ， $-\text{CH}=\text{N}-$ ， $-\text{C}(\text{CH}_3)=\text{N}-$ ， $-\text{O-CO-O}-$ ， $-\text{N}=\text{N}-$ ，或 1-6 个碳原子，优选 1-3 个碳原子的短烷基间隔基，

[0070] a 是 0, 1, 2 或 3, 优选 a 是 0 或 1, 更优选是 0,

[0071] 条件是与双键直接相连的 C^2 是不饱和的且共轭到它之上；

[0072] 或更优选的是式 (Ia) 的化合物，其中：

[0073] 和其中：

[0074] 若 X 是氢和 Y 是 CN ，

[0075] 则 R^1, R^2 或 R^3 彼此独立地为氢，卤素或 $-\text{CF}_3$ ，条件是 R^1, R^2 或 R^3 不同时为氢；

[0076] 或优选地，若 X 是氢和 Y 是 CN ，

[0077] 则 R^1 是氟，氯，溴或 $-\text{CF}_3$ ，以及 R^2 和 R^3 是氢；或

[0078] R^1 和 R^2 彼此独立地为氟，氯，溴或 $-\text{CF}_3$ ，和

[0079] R^3 是氢；或 R^1, R^2 或 R^3 同时为氟，氯或溴；或

[0080] 若 X 是 CN 和 Y 是氢；

[0081] 则 R^1 是氟，氯，溴或 $-\text{CF}_3$ ，以及 R^2 和 R^3 是氢；或

[0082] R^1 和 R^2 彼此独立地为氟，氯，溴或 $-\text{CF}_3$ ，和

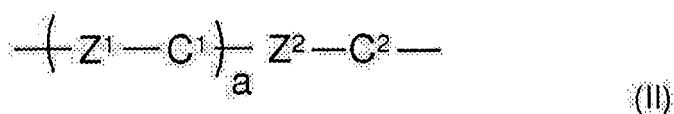
[0083] R^3 是氢；或 R^1, R^2 或 R^3 同时为氢，氟，氯或溴；

[0084] M 是单键，或者具有 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 或 24, 优选 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 或 16, 更优选 6, 7, 8, 9, 10, 11 或 12 个碳原子，最优选 8, 9, 10 或 11 个碳原子的直链或支链的亚烷基残基，其中一个或多个 $-\text{CH}_2-$ 基团独立地可以被选自下述中的基团取代： $-\text{O}-$ ， $-\text{CO}-$ ， $-\text{COO}-$ ， $-\text{OCO}-$ ， $-\text{C}=\text{C}-$ ， $-\text{C}\equiv\text{C}-$ ；

[0085] P 是氢原子，任选取代的烷基或可聚合基团。

[0086] 因此，更优选地化合物是式 (I) 的化合物，其中 Ar^1 是式 (II) 的环系：

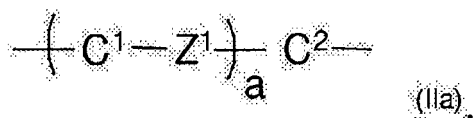
[0087]



[0088] 和

[0089] Ar^2 是式 (IIa) 的环系：

[0090]



[0091] 其中：

[0092] C^1, C^2 各自独立地为苯基或亚苯基；

[0093] Z^1, Z^2 各自独立地为单键或 $-\text{O}-$, $-\text{CH}_2(\text{CO})-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{OCO}-\text{CH}=\text{CH}-$, $-\text{N}=\text{N}-$, 或 1-3 个碳原子的短烷基间隔基；

[0094] a 是 0 或 1, 优选 0；

[0095] 或最优选的是式 (Ia) 化合物；

[0096] 和其中：

[0097] 若 X 是氢和 Y 是 CN ,

[0098] 则 R^1, R^2 或 R^3 彼此独立地为氢, 卤素或 $-\text{CF}_3$, 条件是 R^1, R^2 或 R^3 不同时为氢；

[0099] 或优选地, 若 X 是氢和 Y 是 CN ,

[0100] 则 R^1 是氟, 氯, 溴或 $-\text{CF}_3$, 以及 R^2 和 R^3 是氢；或者 R^1 和 R^2 彼此独立地为氟, 氯, 溴或 $-\text{CF}_3$, 和

[0101] R^3 是氢；或者 R^1, R^2 或 R^3 同时为氟, 氯或溴；或者

[0102] 若 X 是 CN 和 Y 是氢；

[0103] 则 R^1 是氟, 氯, 溴或 $-\text{CF}_3$, 以及 R^2 和 R^3 是氢；或

[0104] R^1 和 R^2 彼此独立地为氟, 氯, 溴或 $-\text{CF}_3$, 和

[0105] R^3 是氢；或者 R^1, R^2 或 R^3 同时为氢, 氟, 氯或溴；

[0106] M 是单键, 或者具有 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 或 24, 优选 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 或 16, 更优选 6, 7, 8, 9, 10, 11 或 12 个碳原子, 最优选 8, 9, 10 或 11 个碳原子的直链或支链的亚烷基残基, 其中一个或多个 $-\text{CH}_2-$ 基团独立地可以被选自下述中的基团取代： $-\text{O}-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{C}=\text{C}-$ ；

[0107] P 是氢原子, 任选取代的烷基, 或选自下述中的可聚合基团：丙烯酸酯, 甲基丙烯酸酯, 乙烯基醚和酯, 环氧基, 硅氧烷, 硅烷, 二胺类, 酰亚胺单体, 酰胺酸单体及其酯, 及其混合物, 或者它们的相应均聚物和共聚物。

[0108] 除非上下文中另外要求, 术语“烷基”包括直链和支链烷基, 以及饱和与不饱和基团。

[0109] 正如本发明上下文中单独或者结合使用的术语“低级烷基”, 例如“低级烷氧基”等优选表示具有 1-6, 优选 1-3 个碳原子的直链和支链饱和烃基。特别优选甲基, 乙基, 丙基和异丙基。在“低级烷氧基”情况下, 特别优选甲氧基, 乙氧基, 丙氧基和异丙氧基。

[0110] 除非上下文中另外要求, 术语“脂族”包括直链和支链烷基, 以及饱和与不饱和基团。可能的取代基包括烷基, 芳基 (进而得到芳脂族基团) 和环烷基, 以及氨基, 氰基, 环氧基, 卤素, 羟基, 硝基, 氧代等。可取代碳原子的可能的杂原子包括氮, 氧和硫。在氮的情况下, 用诸如烷基, 芳基和环烷基之类的基团进一步取代是可能的。

[0111] 正如本发明上下文中所使用的术语“脂环族”优选表示具有 3-30 个碳原子的任选取代的非芳族碳环或杂环的环系,例如环丙烷,环丁烷,环戊烷,环戊烯,环己烷,环己烯,环己二烯,萘烷,四氢呋喃,二噁烷,吡咯烷,哌啶或甾体骨架,例如胆甾醇。

[0112] 正如本发明上下文中所使用的术语“芳族”优选表示引入了 5,6,10 或 14 个环原子的任选取代的碳环和杂环的芳族基团,例如呋喃,苯,吡啶,嘧啶,蔡,菲,亚联苯基,或四氢化蔡单元。

[0113] 正如本发明上下文中所使用的术语“亚苯基”优选表示任选取代的 1,2-,1,3- 或 1,4- 亚苯基。优选的是亚苯基是或者 1,3- 或者 1,4- 亚苯基。特别优选 1,4- 亚苯基。

[0114] 术语“卤素”表示氯,氟,溴,或碘取代基,优选氯或氟取代基。

[0115] 正如本发明上下文中所使用的术语“极性基团”主要表示诸如羟基,硝基,腈, $-\text{CF}_3$ 或羧基之类的基团。

[0116] 正如本发明上下文中所使用的术语“杂原子”主要表示氧,硫和氮,优选氧和氮,在下一情况下,优选为 $-\text{NH}-$ 形式。

[0117] 正如本发明上下文中所使用的术语“任选取代”主要表示被低级烷基,低级烷氧基,羟基,卤素或被以上定义的极性基团取代。

[0118] 关于直链或支链烷基,亚烷基,烷氧基,烷氧基羰基,烷基羰基,烷基羰基氧基,重复指出的是一些或若干个 $-\text{CH}_2-$ 基团可以例如被杂原子,但也可以被其他基团取代。在这种情况下,通常优选这种取代基团并不直接彼此连接。或者优选杂原子,和尤其氧原子并不直接彼此连接。

[0119] 正如本发明上下文中所使用的术语“可聚合基团”是指可(任选地与其他共聚单体)进行聚合得到本发明的低聚物,枝状体或聚合物的官能团。对于本领域的技术人员来说,显而易见的是所述官能团拟用于任何特定的聚合物。因此,例如在所指的聚合物骨架中的“酰亚胺单体”情况下,对于本领域技术人员来说显而易见的是聚合得到聚酰亚胺的实际的单体单元例如是二胺和二酐。类似地,关于“聚氨酯单体”,实际的单体单元是二醇和二异氰酸酯。

[0120] 可使用本领域技术人员公知的方法,容易地制备预整理 (prefinished) 单体形式的本发明化合物。合适的方法可例如发现于 Houben-Weyl, Methoden der Organischen Chemie, Thieme-Verlag, Stuttgart。

[0121] 随后这些预整理的单体典型地进行直接聚合,获得低聚物,枝状体或聚合物。因此,本发明的化合物也可以是低聚物,枝状体或聚合物的一部分,所述聚合物可以是均聚物或共聚物。

[0122] 在具体的实施方案中,可与任何其他单体,官能部分和添加剂一起配制式 (I) 的化合物。

[0123] 对于直接聚合来说,首先由单独的组分独立地制备单体和(任选地)共聚单体。随后根据任何给定聚合物本身已知的方式,例如在 UV 辐照或热的影响下或者在自由基或离子催化剂的作用下,进行聚合物的形成。过二硫酸钾,过氧化二苯甲酰,偶氮二异丁腈或二叔丁基过氧化物是自由基引发剂的实例。离子催化剂是碱金属-有机化合物,例如苯基锂或蔡基锂或路易斯酸,例如 BF_3 , AlCl_3 , SnCl_4 或 TiCl_4 。可在溶液,悬浮液,乳液或物质内聚合单体。

[0124] 若与其他共聚单体共聚合,则所得共聚物由在任何前述含义内定义的式(I)衍生的单体单元和可商购或者不可商购的任何其他已知的单体单元组成。

[0125] 经聚合,则可进一步有利的是在达到合适的链长之后,通过使用本领域公知的具体试剂,使在链端处存在的可聚合基团封端,终止生长的聚合物链。

[0126] 合适的聚合物包括聚丙烯酸酯,聚甲基丙烯酸酯,聚丙烯酰胺,聚甲基丙烯酰胺,聚乙烯基醚和聚乙烯基酯,聚烯丙基醚和酯,聚苯乙烯类,聚硅氧烷类,聚酰亚胺类,聚酰胺酸类和它们的酯,聚酰胺酰亚胺,马来酸类,富马酸类,聚氨酯或其衍生物或其混合物。

[0127] 这些聚合物全部可根据本领域公知的方法来制备。因此,例如本文描述的聚(甲基)丙烯酸酯可根据例如在 Polymer Synthesis Characterization: A Laboratory Manual (Stanley R. Sandler, Wolf Karo, JoAnne Bonesteel, Eli M. Pearce) 和 Principles of Polymerization (George Odian) 中描述的方法来制备。

[0128] 因此,在当单体单元带有丙烯酸或甲基丙烯酸端基时的情况下,该共聚单体单元可用以下列出的化合物表示。它们中的大多数商购于诸如 Aldrich, ABCR, ACROS, Fluka 之类的化学品供应商。

[0129] 丙烯酸 2, 2, 2- 三氟乙酯, 丙烯酸 2- 羟乙酯, 丙烯酸, 丙烯酸缩水甘油酯, 丙烯酸甲酯, 丙烯酸叔丁酯, 丙烯酸乙酯, 丙烯酸丁酯, 丙烯酸 2- 乙基己酯, 丙烯酸 3- 磺基丙酯, 钾盐, 丙烯酸 4- 羟丁酯, 丙烯酸 2- 溴乙酯, 丙烯酸 2- 氰基乙酯, 丙烯酸四氢糠酯, 丙烯酸烯丙酯, 丙烯酸硬脂基酯, 丙烯酸 2-(2- 乙氧基乙氧基) 乙酯, 丙烯酸 2- 羟丙酯, 丙烯酸异十六烷酯, 丙烯酸 2- 四氢呋喃酯, 丙烯酸 n, n- 二甲基氨基乙酯, 丙烯酸 1h, 1h- 全氟辛酯, 丙烯酸 1h, 1h- 七氟丁酯, 丙烯酸 2, 2, 3, 3, 3- 五氟丙酯, 丙烯酸 1h, 1h, 5h- 八氟戊酯, 丙烯酸 1, 1, 1, 3, 3, 3- 六氟异丙酯, 丙烯酸 d, 1- 薄荷酯, 丙烯酸 β - 羧乙酯, 丙烯酸 1h, 1h, 11h- 二十氟十一烷酯, 丙烯酸 2- 氟乙酯, 丙烯酸 1h, 1h, 2h, 2h- 全氟癸酯, 丙烯酸五氟苄酯, 丙烯酸五氟苯酯, 丙烯酸 1h, 1h, 2h, 2h- 全氟辛酯, 丙烯酸 2, 2, 3, 3- 四氟丙酯, 丙烯酸异丁酯, 丙烯酸月桂酯, 丙烯酸 n, n- 二乙基氨基乙酯, 丙烯酸 2- 乙氧基乙酯, (r)-(+) - α - 丙烯酰氧基 - β , β - 二甲基 - γ - 丁内酯, 丙烯酸 2, 2, 3, 4, 4, 4- 六氟丁酯, 丙烯酸 2- 氯乙酯, 丙烯酸环己酯, 丙烯酸甲基烯丙酯, 丙烯酸苯酯, 丙烯酸酐, 丙烯酸苄酯, 丙烯酸 2- 甲氧基乙酯, 丙烯酸肉桂酯, 丙烯酸 3- 甲氧基丁酯, 丙烯酸异丙酯, 丙烯酸正癸酯, 丙烯酸十一烷酯, 丙烯酸十三烷酯, 丙烯酸 2- 乙基丁酯, 丙烯酸正丙酯, 丙烯酰氧基三 - 正丁基锡, 丙烯酸 2- 正丁氧基乙酯, 丙烯酸正戊酯, 丙烯酸正己酯, 丙烯酸正庚酯, 丙烯酸正辛酯, 丙烯酸 2- 羟基 - 3- 氯丙酯, 丙烯酸 2- 苯氧基乙酯, 丙烯酸异戊酯, 丙烯酸仲丁酯, n-(3- 丙烯酰氧基 - 2- 羟丙基) - 3- 氨基丙基三乙氧基硅烷, (3- 丙烯酰氧基丙基) 甲基双(三甲基甲硅烷氧基) 硅烷, (3- 丙烯酰氧基丙基) 二甲基甲氧基 - 硅烷, 3- 丙烯酰氧基丙基三(三甲基甲硅烷氧基) 硅烷, (3- 丙烯酰氧基丙基) 三甲氧基硅烷, (3- 丙烯酰氧基丙基) 甲基二氯硅烷, (3- 丙烯酰氧基丙基) 三氯硅烷, 丙烯酸乙烯酯, 丙烯酸 2, 3- 二溴丙酯, 邻苯二甲酸单-(丙烯酰氧基乙酯), 3- 丙烯酰氧基丙基 - 2-n- 苯基氨基甲酸酯, 丙烯酸 2- 羟基 - 3- 苯氧基丙酯, 丙烯酸钾, 丙烯酸钠, [2-(丙烯酰氧基) 乙基] (4- 苯甲酰基苄基) 二甲基溴化铵, n- 丙烯酰氧基琥珀酰亚胺, 丙烯酸 1h, 1h, 9h- 十六氟壬酯, 丙烯酸 3, 3, 5- 三甲基环己酯, 丙烯酸正壬酯, 丙烯酸环戊酯, 丙烯酸全氟辛酯, 丙烯酸 2- 烯丙基氧基乙氧基乙酯, 丙烯酸巴豆酯, 丙烯酸 4- 枯基苯酯, 丙烯酸 2, 4, 6- 三溴苯酯, 丙烯酸十六烷酯, 丙烯酸炔丙酯, 丙烯酸

铵, 丙烯酸铈, 丙烯酸锂, 丙烯酸铷, n-(丙烯酰氧基乙基)邻苯二甲酰亚胺, n-(丙烯酰氧基乙基)琥珀酰亚胺, 马来酸单-2-丙烯酰氧基乙酯, 丙烯酸 2-烯丙基氧基乙酯, 丙烯酸烯丙基氧基丙酯, 丙烯酸二十二烷酯, 丙烯酸 1, 3-双(4-苯甲酰基-3-羟基苯氧基)-2-丙酯, 丙烯酸异冰片酯, 丙烯酸 2-(溴-1-萘基氧基)-乙酯, 丙烯酸 2-(1-溴-2-萘基氧基)-乙酯, 丙烯酸对氯苯氧基乙酯, 丙烯酸 4-氯苯酯, 丙烯酸 2-氰基乙氧基乙酯, 环醇丙烯酸酯, 丙烯酸异癸酯, 丙烯酸二丁锡, 丙烯酸 n, n-二乙基氨基乙酯 q-盐, 甲磺酸盐, [2-(丙烯酰氧基)乙基]三甲基氯化铵, 丙烯酸 3, 6-二氧杂庚酯, 丙烯酸糠酯, 丙烯酸 2, 3-二羟丙酯, 丙烯酸己氧基乙酯, 丙烯酸 3-碘苄酯, 丙烯酸 d-薄荷酯, 丙烯酸 1-薄荷酯, 丙烯酸 2-甲基丁酯, 丙烯酸 2-n-吗啉基乙酯, 丙烯酸 α -萘酯, 丙烯酸 β -萘酯, 丙烯酸 2-(1-萘基氧基)-乙酯, 丙烯酸 2-(2-萘基氧基)-乙酯, 丙烯酸 2-硝基乙酯, 丙烯酸对硝基苯酯, 丙烯酸壬基苯酯, 丙烯酸降冰片酯, 丙烯酸 2-辛酯, 丙烯酸异辛酯, 丙烯酸五溴苯酯, 丙烯酸五氯苯酯, 丙烯酸新戊酯, 丙烯酸(全氟环己基)甲酯, 丙烯酸 2-苯基乙酯, 丙烯酸苯基丙酯, 邻苯二甲酸单-2-丙烯酰氧基乙酯, 丙烯酸 1-哌啶乙酯, 丙烯酸银, 丙烯酸山梨醇酯, 丙烯酸三氯乙酯, [2-(丙烯酰氧基)乙基]三甲基铵甲硫酸盐, 丙烯酸 3, 5, 5-三甲基己酯, 丙烯酸乙烯基苄酯, 丙烯酸 2-(正丁基全氟辛磺酰胺基)乙酯, 丙烯酸 2-(正乙基全氟辛磺酰胺基)乙酯, 丙烯酸 3-(三氟甲基)苄酯, 丙烯酸 1h, 1h, 7h-十二氟庚酯, 丙烯酸 3-二甲氨基新戊酯, 丙烯酸 1h, 1h, 3h-六氟丁酯, 丙烯酸 2-(4-苯甲酰基-3-羟基苯氧基)乙酯, 磷酸单丙烯酰氧基乙酯, 丙烯酸 2, 2-二硝基丙酯, 丙烯酸氢化松香醇酯, 丙烯酸钾半水合物, 2-(丙烯酰氧基乙氧基)三甲基硅烷, (3-丙烯酰氧基丙基)甲基二甲氧基硅烷, 丙烯酰氧基三甲基硅烷, 丙烯酰氧基三苯基锡, 丙烯酸钠半水合物, 丙烯酸二环戊烯酯, 二己内酯 2-(丙烯酰氧基)乙酯, 二(乙二醇)2-乙基己基醚丙烯酸酯, 二环戊烯基氧基乙基丙烯酸酯, 丙烯酸 3-(二甲氨基)丙酯, 4, 4-二甲基-2-氧代四氢呋喃-3-基丙烯酸酯, 丙烯酸 2-(全氟丁基)乙酯, 丙烯酸 3-(全氟丁基)-2-羟丙酯, 丙烯酸 3-(全氟己基)-2-羟丙酯, 丙烯酸 3-(全氟辛基)-2-羟丙酯, 丙烯酸 2-(全氟癸基)乙酯, 丙烯酸 2-(全氟-3-甲基丁基)乙酯, 丙烯酸 3-(全氟-3-甲基丁基)-2-羟丙酯, 丙烯酸 2-(全氟-5-甲基己基)乙酯, 丙烯酸 2-(全氟-9-甲基辛基)乙酯, 丙烯酸 2-(全氟-9-甲基癸基)乙酯, 氨基甲酸酯丙烯酸酯, 琥珀酸单-2-(丙烯酰氧基)乙酯, 丙烯酸七氟-2-丙酯, (3-(脲酰基氧基(allanoyloxy))-5-[4-(苯甲酰基氨基)-2-氧代噻啉-1(2h)-基]四氢呋喃-2-基, 二氢二环戊二烯基丙烯酸酯, 乙酰乙酸 2-(丙烯酰氧基)乙酯, 丙烯酸 3-(1-氧代-1, 3-二氢-异吡啶-2-基)-苯酯, 丙烯酸 4-叔丁基环己酯, 丙烯酸 3-(3, 5-二氧代-4-氮杂-三环(5.2.1.0(2,6))癸-8-烯-4-基)-ph 酯, 丙烯酸 3-(4-硝基-1, 3-二氧代-1, 3-二氢-异吡啶-2-基)-苯酯, 丙烯酸 3-(4, 5, 6, 7-四氯-1, 3-二氧代-1, 3-2h-异吡啶-2-基)-苯酯, 丙烯酸甲基糠酯, rcl r35,845-2, 丙烯酸 3-(2, 5-二氧代-吡咯烷-1-基)-苯酯, 丙烯酸 3-(1, 3-二氧代-1, 3-二氢-异吡啶-2-基)-苯酯, 丙烯酸钴, 丙烯酸锰, 3-丙烯酰氧基丙基-2-n-苯基氨基甲酸酯, 丙烯酸酯化的双酚“a”缩水甘油基醚, 丙烯酸 3-(全氟-5-甲基己基)-2-羟丙酯, 丙烯酸 3-(全氟-7-甲基辛基)-2-羟丙酯, 新戊二醇丙烯酸苯甲酸酯, 丙烯酸 2'-肉桂酰基氧基乙酯, 丙烯酸三异丙基甲硅烷酯, uvecryl p 36, 丙烯酸 2-[[[(丁基氨基)羰基]氧基]乙酯, 丙烯酸 1h, 1h-全氟-正癸酯, 甲基丙烯酸, 甲基丙烯酸 2-羟乙酯, 甲基丙烯酸 2-羟丙酯, 甲基丙烯酸缩水甘油酯, 甲基丙烯酸酐, 甲基丙烯酸甲酯, 甲基丙烯

酸 2-(二甲基氨基)乙酯, 甲基丙烯酸烯丙酯, 3-甲基丙烯酰氧基丙基三甲氧基硅烷, 甲基丙烯酸异丁酯, 甲基丙烯酸月桂酯, 甲基丙烯酸乙酯, 甲基丙烯酸 2-乙氧基乙酯, 甲基丙烯酸正丁酯, 甲基丙烯酸 2-乙基己酯, 磺基丙基甲基丙烯酸钾, 甲基丙烯酸 2, 2, 2-三氟乙酯, 甲基丙烯酸环己酯, 甲基丙烯酸四氢糠酯, 甲基丙烯酸 2-(叔丁基氨基)乙酯, 甲基丙烯酸正己酯, 二甲基丙烯酸 1, 6-己二醇酯, 3-甲基-2-苯并噻唑啉酮, 具有 4'-(2-(甲基-丙烯酰基-o)乙氧基)二苯甲酮的吡嗪, 甲基丙烯酸 2-(对硝基苯氧基)乙酯, 甲基丙烯酸硬脂基酯, 2-羟基-3-甲基丙烯酰氧基丙基三甲基氯化铵, 甲基丙烯酸 2-苯基乙酯, 甲基丙烯酸 2-(二乙基氨基)乙酯, 甲基丙烯酸 1h, 1h-全氟辛酯, 甲基丙烯酸 1h, 1h-七氟丁酯, 甲基丙烯酸 2, 2, 3, 3, 3-五氟丙酯, 甲基丙烯酸 1h, 1h, 5h-八氟戊酯, 甲基丙烯酸 1, 1, 1, 3, 3, 3-六氟异丙酯, n-(3-磺丙基)-n-甲基丙烯酰氧基乙基-n, n-二甲基铵甜菜碱, 甲基丙烯酸 3-氯-2-羟丙酯, 甲基丙烯酸 d, l-薄荷酯, 甲基丙烯酸 1h, 1h, 11h-全氟十一烷酯, 甲基丙烯酸 2-氟乙酯, 甲基丙烯酸 1h, 1h, 2h, 2h-全氟癸酯, 甲基丙烯酸 2, 2, 3, 4, 4, 4-六氟丁酯, 甲基丙烯酸五氟苄酯, 甲基丙烯酸五氟苯酯, 甲基丙烯酸 2, 2, 3, 3-四氟丙酯, 甲基丙烯酸 2-溴乙酯, 甲基丙烯酸氯化铬, 甲基丙烯酸 2-氯乙酯, 甲基丙烯酸环戊酯, 1, 4-环己烷二甲基 1, 4-二甲基丙烯酸酯, 甲基丙烯酸 2-氰基乙酯, 甲基丙烯酸钡, 甲基丙烯酸钾, 甲基丙烯酸镁, 甲基丙烯酸钠, 甲基丙烯酸锌, 甲基丙烯酸糠酯, 甲基丙烯酸苯酯, 二甲基丙烯酸新戊二醇酯, 甲基丙烯酸甲基烯丙酯, 甲基丙烯酸 2-甲氧基乙酯, 甲基丙烯酸炔丙酯, 甲基丙烯酸 3-甲氧基丁酯, 甲基丙烯酸叔丁酯, 甲基丙烯酸异丙酯, 甲基丙烯酸异戊酯, 甲基丙烯酸正癸酯, 甲基丙烯酸仲丁酯, 甲基丙烯酸 2-乙基丁酯, 甲基丙烯酸正丙酯, 甲基丙烯酸 2-正丁氧基乙酯, 甲基丙烯酸羟丙酯, 甲基丙烯酰氧基丙基甲基二氯硅烷, 甲基丙烯酸苄酯, 甲基丙烯酸 2-苯氧基乙酯, 甲基丙烯酰氧基丙基三(甲氧基乙氧基)硅烷, 3-甲基丙烯酰氧基丙基五甲基二硅氧烷, 甲基丙烯酸异癸酯, 甲基丙烯酰氧基三正丁基锡, 甲基丙烯酸正戊酯, 甲基丙烯酸正辛酯, 甲基丙烯酸三甲基甲硅烷酯, 甲基丙烯酸 2-(三甲基甲硅烷氧基)乙酯, 甲基丙烯酰氧基丙基双(三甲基甲硅烷氧基)甲基硅烷, 甲基丙烯酰氧基丙基三(三甲基甲硅烷氧基)硅烷, 甲基丙烯酰氧基丙基二甲基乙氧基硅烷, 3-甲基丙烯酰氧基丙基甲基二乙氧基硅烷, 3-甲基丙烯酰氧基丙基二甲基氯硅烷, 2-甲基丙烯酰氧基乙基二甲基(3-三甲氧基甲硅烷基丙基)氯化铵, 甲基丙烯酸乙酰乙酰氧基乙酯, 甲基丙烯酰氧基丙基三氯硅烷, 3-甲基丙烯酰氧基丙基三(乙氧基二甲基甲硅烷氧基)硅烷, 甲基丙烯酸三甲基甲硅烷基甲酯, (甲基丙烯酰氧基甲基)苯基二甲基硅烷, 甲基丙烯酰氧基丙基三甲氧基硅烷, 甲基丙烯酸钙, 甲基丙烯酸十三烷酯, 甲基丙烯酸乙烯酯, 甲基丙烯酸甲氧基乙氧基乙酯, [2-(甲基丙烯酰氧基)乙基]三甲基氯化铵, 邻苯二甲酸单-(2-(甲基丙烯酰氧基)-乙酯), 甲基丙烯酸 2-羟基-3-苯氧基丙酯, 甲基丙烯酰氧基丙基三乙氧基硅烷, 甲基丙烯酸 2-二异丙基氨基乙酯, 甲基丙烯酸 1h, 1h, 2h, 2h-全氟辛酯, 甲基丙烯酸 2-氨基乙酯盐酸盐, 2-三甲基铵乙基甲基丙烯酸酯甲磺酸盐, 甲基丙烯酸三甲苯酯, 甲基丙烯酸全氟辛酯, 甲基丙烯酸 2, 4, 6-三溴苯酯, 甲基丙烯酸 4-羟丁酯, 甲基丙烯酸十六烷酯, 甲基丙烯酸十一烷酯, 甲基丙烯酸正壬酯, 甲基丙烯酸 2-烯丙基氧基乙氧基乙酯, 甲基丙烯酸 3, 3, 5-三甲基环己酯, 甲基丙烯酸 2, 3-二溴丙酯, 甲基丙烯酸肉桂酯, 甲基丙烯酸巴豆酯, 甲基丙烯酸 1h, 1h, 9h-十六氟壬酯, 甲基丙烯酸正庚酯, 甲基丙烯酸 2-烯丙基氧基乙酯, 甲基丙烯酸烯丙基氧基丙酯, 甲基丙烯酸新戊酯, 甲基丙烯酸 2-(1-

吡啶基)-乙酯,甲基丙烯酸二十二烷酯,5-降冰片烯-2-甲醇甲基丙烯酸酯,甲基丙烯酸1,3-双(4-苯甲酰基-3-羟基苯氧基)-2-丙酯,甲基丙烯酸乙氧基乙氧基乙酯,甲基丙烯酸对氯苯氧基乙酯,甲基丙烯酸4-枯烯苯酯,甲基丙烯酸二丁锡,甲基丙烯酸n,n-二乙基氨基乙酯q-盐,甲磺酸盐,二乙二醇单-甲基丙烯酸酯,甲基丙烯酸2,3-二羟丙酯,甲基丙烯酸3,3-二甲基丁醇-2-酯,甲基丙烯酸乙基三甘醇酯,二甲基丙烯酸乙叉酯(ethylidene dimethacrylate),甲基丙烯酸乙基硫代乙酯,甲基丙烯酸己氧基乙酯,甲基丙烯酸2-(1-咪唑酰基)乙酯,甲基丙烯酸3-碘代苄酯,甲基丙烯酸异氰酸根乙酯,甲基丙烯酸d-薄荷酯,甲基丙烯酸1-薄荷酯,甲基丙烯酸铝,n-(甲基丙烯酰氧基乙基)邻苯二甲酰亚胺,n-(甲基丙烯酰氧基乙基)琥珀酰亚胺,4-甲基丙烯酰氧基乙基偏苯三酸酐,4-甲基丙烯酰氧基-2-羟基二苯甲酮,单-(2-(甲基丙烯酰氧基)-乙基)马来酸酯,2-甲基丙烯酰氧基甲基-2,3-二氢-4h-吡喃,甲基丙烯酸甲氧基丙酯,甲基丙烯酸3-甲基丁醇-2-酯,甲基丙烯酸3-甲基丁烯-2-基酯,甲基丙烯酸2-甲基丁酯,甲基丙烯酸3-(4-甲基苯氧基)-2-羟丙酯,甲基丙烯酸2-n-吗啉基乙酯,甲基丙烯酸 α -萘酯,甲基丙烯酸2-萘酯,甲基丙烯酸2-(1-萘基氧基)-乙酯,甲基丙烯酸2-(2-萘基氧基)-乙酯,甲基丙烯酸2-硝基乙酯,甲基丙烯酸对硝基苯酯,甲基丙烯酸壬基苯酯,甲基丙烯酸降冰片酯,甲基丙烯酸异辛酯,甲基丙烯酸五溴苯酯,甲基丙烯酸五氯苯酯,甲基丙烯酸全氟环己基甲酯,甲基丙烯酸苯基丙酯,甲基丙烯酸1-哌啶乙酯,甲基丙烯酸山梨醇酯,甲基丙烯酸2-磺基乙酯,甲基丙烯酸三溴新戊酯,甲基丙烯酸三氯乙酯,甲基丙烯酸1h,1h,7h-十二氟庚酯,甲基丙烯酸3,5,5-三甲基己酯,甲基丙烯酰氧基乙氧基三(三甲基甲硅烷氧基)硅烷,甲基丙烯酸乙烯基苄酯,甲基丙烯酸2-(n-乙基全氟辛烷磺酰胺基)乙酯,甲基丙烯酸3-(三氟甲基)苄酯,甲基丙烯酸异冰片酯,聚(乙二醇)甲基丙烯酸酯,甲基丙烯酸羟丙酯,甲基丙烯酸2-乙基己酸铅,2-甲基丙烯酰氧基乙基糖苷,磷酸双-(2,3-二溴丙基)2-(甲基丙烯酰氧基)-乙酯,3-甲基-2-苯并噻唑啉酮,具有4-(2-(甲基-丙烯酰基-o)eto)-m-茴香醛的吡嗪,2-(甲基丙烯酰氧基)乙基n-(3-溴苯基)氨基甲酸酯,2-(甲基丙烯酰氧基)乙基n-(n-(3,5-二氯苯基)氨基甲酰基)氨基甲酸酯,2-(甲基丙烯酰氧基)乙基n-(4-异丙基苯基)氨基甲酸酯,乙二醇甲基丙烯酸酯磷酸酯,三羟甲基丙烷二烯丙基醚单-甲基丙烯酸酯,甲基丙烯酸氢化松香醇酯,异氰酸根合乙基甲基丙烯酸酯丁基氨基甲酸酯,异氰酸根合乙基甲基丙烯酸酯辛基氨基甲酸酯,异氰酸根合乙基甲基丙烯酸酯己内酰胺加合物,异氰酸根合乙基甲基丙烯酸酯吡咯烷酮加合物,甲基丙烯酸羟丙酯,甲基丙烯酸钙水合物,2-羟基-4-[2-羟基-3-(甲基丙烯酰氧基)-丙氧基]二苯甲酮,甲基丙烯酰氧基二苯基锑,(2-甲基丙烯酰氧基乙氧基)三异丙氧基锑酸酯,(甲基丙烯酰氧基甲基)双(三甲基甲硅烷氧基)甲基硅烷,(甲基丙烯酰氧基甲基)二甲基乙氧基硅烷,甲基丙烯酰氧基甲基三乙氧基硅烷,甲基丙烯酰氧基甲基三甲氧基硅烷,甲基丙烯酰氧基甲基三甲基锗烷,甲基丙烯酰氧基甲基三(三甲基甲硅烷氧基)硅烷,甲基丙烯酰氧基丙基二甲基甲氧基硅烷,甲基丙烯酰氧基丙基甲基二甲氧基硅烷,甲基丙烯酰氧基丙基氧氮杂硅二环十一烷(silatrane),甲基丙烯酰氧基三乙基锗烷,甲基丙烯酸三异丙醇钛,甲基丙烯酸二环戊烯酯,甲基丙烯酸四氢吡喃酯,己内酯2-(甲基丙烯酰氧基)乙酯,甲基丙烯酸2-甲基-2-硝基丙酯,甲基丙烯酸2-(2-氧代-1-咪唑烷基)乙酯,四(2-甲基丙烯酰氧基乙氧基)硅烷,甲基丙烯酸2-(甲硫基)乙酯,甲基丙烯酸2-[3-(2h-苯并三唑-2-基)-4-羟基苯基]乙酯,甲基丙

烯酸二环戊烯基氧基乙酯, 2-甲基-丙烯酸 4-羟基-苯酯甲基丙烯酸 2-(全氟丁基)乙酯, 甲基丙烯酸 2-(全氟癸基)乙酯, 甲基丙烯酸 2-(全氟-3-甲基丁基)乙酯, 甲基丙烯酸 3-(全氟-3-甲基丁基)-2-羟丙酯, 甲基丙烯酸 2-(全氟-5-甲基己基)乙酯, 甲基丙烯酸 3-(全氟-5-甲基己基)-2-羟丙酯, 甲基丙烯酸 2-(全氟-7-甲基辛基)乙酯, 甲基丙烯酸 3-(全氟-7-甲基辛基)-2-羟丙酯, 甲基丙烯酸 2-(全氟-9-甲基癸基)乙酯, 甲基丙烯酸 3-(全氟-8-甲基癸基)-2-羟丙酯, 甲基丙烯酸 (9-蒎基)酯, 甲基丙烯酸 (9-菲基)甲酯, n-(3-甲基丙烯酰氧基-2-羟丙基)-3-氨基丙基三乙氧基硅烷, 4-(甲基丙烯酰氧基)查耳酮, 琥珀酸单-2-(甲基丙烯酰氧基)乙酯, 甲基丙烯酸 2-(磺基氧基)乙酯, 铵盐, 乙二醇甲基丙烯酸磷酸酯, 2-甲基丙烯酸 2-(4-(1,3-二氧化-1,3-二氢-异吡啶-2-基)-苯基)-乙酯, 2-(2'-甲基丙烯酰氧基-5'-甲基苯基)苯并三唑, 2-甲基-丙烯酸 3(3,5-二氧化-4-氮杂-三环(5.2.1.0(2,6))癸-8-烯-4-基)苯酯, 2-甲基丙烯酸 4-(4-硝基-1,3-二氧化-1,3-二氢-异吡啶-2-基)-苯酯, rcl r35,715-4, 甲基丙烯酸 9-蒎基甲酯, 甲基丙烯酸 1-苾基甲酯, 2-甲基-丙烯酸 3-(1-氧代-1,3-二氢-异吡啶-2-基)-苯酯, 2-甲基-丙烯酸 3-(4-硝基-1,3-二氧化-1,3-二氢-异吡啶-2-基)-苯酯, 2-甲基-丙烯酸 3-(2,5-二氧化-吡咯烷-1-基)-苯酯, 2-甲基-丙烯酸 4-(2,5-二氧化-吡咯烷-1-基)-苯酯, rcl r35,836-3, 2-甲基-丙烯酸 4-乙酰基氨基-苯酯, 甲基丙烯酸 (1-苾)甲酯, 邻苯二甲酸 2-羟丙基 2-(甲基丙烯酰氧基)乙酯, peg 单甲基丙烯酸酯, 3-甲基丁烯-2-基-1-甲基丙烯酸酯, (甲基丙烯酰氧基甲基)双(三甲基甲硅烷氧基)-(甲基甲硅烷氧基)甲基硅烷, (r)-2-羟基-2'-甲基丙烯酰氧基-1,1'-双-2-萘醇, 4-[[6-(甲基丙烯酰氧基)己基]氧基]苯羧酸, 甲基丙烯酸异氰酸根合乙酯的六氟异丙基氨基甲酸酯, 二环戊烯基-2-甲基丙烯酸酯, 甲基丙烯酸 (r)-(-)-异冰片酯, 甲基丙烯酸 3-全氟己基-2-羟丙酯, 甲基丙烯酸 3-全氟辛基-2-羟丙酯, 甲基丙烯酸 (1-萘基)乙酯, 甲基丙烯酸 (1-萘基)甲酯, o-甲基丙烯酰基 hoechst 33258, o-(甲基丙烯酰氧基乙基)-n-(三乙氧基甲硅烷基丙基)氨基甲酸酯, 4-[3-(甲基丙烯酰氧基)丙基]苯羧酸, 4-[4-(甲基丙烯酰氧基)丁氧基]苯羧酸, 六氟异丙基氨基甲酸酯-n-乙基甲基丙烯酸酯, 2-甲基-丙烯酸 2-(4-(4,5-二氢-噁唑-2-基)-苯氧基)-乙酯, 3-甲基丙烯酰氧基丙基三(五甲基二甲硅烷氧基)硅烷, 二(丙二醇)烯丙基醚甲基丙烯酸酯, 三丙酮氨酰基 (triacetoneaminoyl) 甲基丙烯酸酯, 甲基丙烯酸 1h, 1h-全氟-正癸酯, 甲基丙烯酸 3-(全氟丁基)-2-羟丙酯, 2-甲基-丙烯酸 4-(3-苯基-丙烯酰基)-苯酯, 2-甲基丙烯酸 3-(5-硝基-1,3-二氧化-1,3-二氢-2h-异吡啶-2-基)苯酯, n-(2-羟基-3((2-甲基-1-氧代-2-丙烯基)氧基)丙基)-n-(4-甲基苯基)-甘氨酸或其混合物。

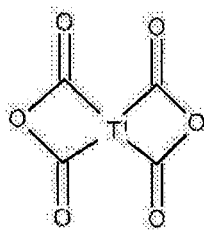
[0130] 可根据已知的方法, 例如在 Plast. Eng. 36(1996), (Polyimides, fundamentals and applications), Marcel Dekker Inc 中描述的那些制备本发明的聚酰胺酸, 聚酰胺酸酯和聚酰亚胺。例如, 在溶液内在极性非质子有机溶剂, 例如 γ -丁内酯, N,N-二甲基乙酰胺, N-甲基吡咯烷酮或 N,N-二甲基甲酰胺中进行制备聚酰胺酸的缩聚反应。在大多数情况下, 使用等摩尔量的二酸酐和二胺, 也就是说每一酸酐基一个氨基。若期望稳定聚合物的分子量, 则对于该目的来说, 可添加过量或小于化学计量量的这两种组分之一, 或者添加二羧酸单酸酐形式或者单胺形式的单官能化合物。这种单官能化合物的实例是马来酸酐, 邻苯二甲酸酐, 苯胺, 如此等等。优选在小于 100°C 的温度下进行该反应。

[0131] 可通过加热,也就是说,通过在除去水的情况下缩合,或者通过与试剂的其他酰亚胺化反应,进行形成聚酰亚胺的聚酰胺酸的环化。当纯粹在热下进行,聚酰胺酸的酰亚胺化并不总是完全,也就是说,所得聚酰亚胺仍然可能含有一定比例的聚酰胺酸。通常在 60-250℃ 的温度下,但优选在小于 200℃ 下进行酰亚胺化反应。为了在相当较低的温度下实现酰亚胺化,可在该反应混合物内另外地混合有助于除去水的试剂。这种试剂例如是由酸酐,例如乙酸酐,丙酸酐,邻苯二甲酸酐,三氟乙酸酐,和叔胺,例如三乙胺,三甲胺,三丁胺,吡啶, N, N- 二甲基苯胺,二甲基吡啶,三甲基吡啶等组成的混合物。在该情况下所使用的试剂量优选为至少 2 当量胺和 4 当量酸酐 / 当量待缩合的聚酰胺酸。

[0132] 可在施加到载体上之前或者仅仅在其后进行酰亚胺化反应。后一变体是优选的,特别是当所讨论的聚酰亚胺在常规溶剂内具有差的溶解度时。

[0133] 因此,可以通过使至少一种用通式 (I) 表示的化合物与一种或多种通式 (IV) 的四羧酸酐反应,来获得或者可获得来自聚酰胺酸,聚酰胺酸酯或聚酰亚胺(和它们的任何混合物)组中的聚合物材料或低聚物材料,其中 G 代表二胺基和任选地一种或多种另外的其他二胺(如以上给出的):

[0134]



(IV)

[0135] 其中:

[0136] T¹代表四价有机基。

[0137] 四价有机基 T¹优选衍生于脂族,脂环族或芳族四羧酸二酐。

[0138] 脂族或脂环族四羧酸二酐的优选实例是:

[0139] 1, 1, 4, 4- 丁烷四羧酸二酐, 亚乙基马来酸二酐,

[0140] 1, 2, 3, 4- 环丁烷四羧酸二酐,

[0141] 1, 2, 3, 4- 环戊烷四羧酸二酐,

[0142] 2, 3, 5- 三羧基环戊基乙酸二酐,

[0143] 3, 5, 6- 三羧基降冰片基乙酸二酐,

[0144] 2, 3, 4, 5- 四氢呋喃四羧酸二酐,

[0145] rel-[1S, 5R, 6R]-3- 氧杂双环 [3.2.1] 辛烷 -2, 4- 二酮 -6- 螺 -3'- (四氢呋喃 -2', 5'- 二酮), 4- (2, 5- 二氧化四氢呋喃 -3- 基) 四氢萘 -1, 2- 二羧酸二酐, 5- (2, 5- 二氧化四氢呋喃 -3- 基) -3- 甲基 -3- 环己烯 -1, 2- 二羧酸二酐, 双环 [2.2.2] 辛 -7- 烯 -2, 3, 5, 6- 四羧酸二酐, 双环 [2.2.2] 辛烷 -2, 3, 5, 6- 四羧酸二酐,

[0146] 1, 8- 二甲基双环 [2.2.2] 辛 -7- 烯 -2, 3, 5, 6- 四羧酸二酐和类似物。

[0147] 芳族四羧酸二酐的优选的实例是

[0148] 均苯四酸二酐,

[0149] 3, 3', 4, 4'- 二苯甲酮四羧酸二酐,

- [0150] 4,4'-氧基二邻苯二甲酸二酐,
- [0151] 3,3',4,4'-二苯砜四羧酸二酐,
- [0152] 1,4,5,8-萘四羧酸二酐,
- [0153] 2,3,6,7-萘四羧酸二酐,
- [0154] 3,3',4,4'-二甲基二苯基硅烷四羧酸二酐,
- [0155] 3,3',4,4'-四联苯基硅烷四羧酸二酐,
- [0156] 1,2,3,4-呋喃四羧酸二酐,
- [0157] 4,4'-双(3,4-二羧基苯氧基)二苯硫醚二酐,
- [0158] 4,4'-双(3,4-二羧基苯氧基)二苯砜二酐,
- [0159] 4,4'-双(3,4-二羧基苯氧基)二苯基丙烷二酐,
- [0160] 3,3',4,4'-联苯四羧酸二酐,
- [0161] 乙二醇双(均苯四酸)二酐,
- [0162] 4,4'-(1,4-亚苯基)双(邻苯二甲酸)二酐,
- [0163] 4,4'-(1,3-亚苯基)双(邻苯二甲酸)二酐,
- [0164] 4,4'-(六氟亚异丙基)二苯二甲酸二酐,
- [0165] 4,4'-氧基二(1,4-亚苯基)双(苯二甲酸)二酐,
- [0166] 4,4'-亚甲基二(1,4-亚苯基)双(苯二甲酸)二酐,
- [0167] 和类似物。
- [0168] 更优选,形成四价有机基 T¹所使用的四羧酸二酐选自:
- [0169] 1,2,3,4-环丁烷四羧酸二酐,
- [0170] 1,2,3,4-环戊烷四羧酸二酐,
- [0171] 2,3,5-三羧基环戊基乙酸二酐,
- [0172] 5-(2,5-二氧代四氢呋喃-3-基)-3-甲基-3-环己烯-1,2-二羧酸二酐,
- [0173] 4-(2,5-二氧代四氢呋喃-3-基)四氢萘-1,2-二羧酸二酐,
- [0174] 4,4'-(六氟亚异丙基)二苯二甲酸二酐和
- [0175] 双环[2.2.2]辛-7-烯-2,3,5,6-四羧酸二酐。
- [0176] 术语“二胺”或“二胺化合物”要理解为表示具有至少两个氨基,即也可具有3个或更多个氨基的化学结构。
- [0177] 二胺表示具有1-40个碳原子且优选由下述结构组制成或者选自下述结构组的任选取代的脂族,芳族或脂环族二氨基:苯胺,对苯二胺,间苯二胺,联苯胺,二氨基苄或它们的衍生物,条件是所列出的没有携带两个氨基的化合物被视为具有至少一个额外氨基的衍生物且更优选由也可用作共聚单体的下述可商购的氨基化合物制成或者选自其中(供应商的实例:Aldrich, ABCR, ACROS, Fluka):
- [0178] 4-氨基-2,3,5,6-四氟苯甲酸
- [0179] 4-氨基-3,5-二碘苯甲酸,3,4-二氨基苯甲酸
- [0180] 4-氨基-3-甲基苯甲酸,
- [0181] 4-氨基-2-氯苯甲酸
- [0182] 4-氨基水杨酸
- [0183] 4-氨基苯甲酸

- [0184] 4-氨基邻苯二甲酸
- [0185] 1-(4-氨基苯基)乙醇
- [0186] 4-氨基苄醇
- [0187] 4-氨基-3-甲氧基苯甲酸
- [0188] 4-氨基苯基乙基甲醇
- [0189] 4-氨基-3-硝基苯甲酸
- [0190] 4-氨基-3,5-二硝基苯甲酸
- [0191] 4-氨基-3,5-二氯苯甲酸
- [0192] 4-氨基-3-羟基苯甲酸
- [0193] 4-氨基苄醇盐酸盐
- [0194] 4-氨基苯甲酸盐酸盐
- [0195] 对苯胺碱
- [0196] 4-氨基-5-氯-2-甲氧基苯甲酸
- [0197] 4-(六氟-2-羟基异丙基)苯胺
- [0198] 哌嗪-p-氨基苯甲酸酯
- [0199] 4-氨基-3,5-二溴苯甲酸
- [0200] 异烟酸酰肼对氨基水杨酸盐
- [0201] 4-氨基-3,5-二碘水杨酸
- [0202] 4-氨基-2-甲氧基苯甲酸
- [0203] 2-[2-(4-氨基苯基)-2-羟基-1-(羟甲基)乙基]异二氢吡啶-1,3-二酮
- [0204] 4-氨基-2-硝基苯甲酸
- [0205] 2,4-二氨基苯甲酸
- [0206] p-氨基苯甲酸,
- [0207] [3,5-3h]-4-氨基-2-甲氧基苯甲酸
- [0208] L-(+)-苏式-2-氨基-1-(4-氨基苯基)-1,3-丙二醇
- [0209] L-(+)-苏式-2-(N,N-二甲基氨基)-1-(4-氨基苯基)-1,3-丙二醇
- [0210] 2-(4-氨基苯基)-3,3,3-三氟-2-羟基丙酸乙酯
- [0211] 2-(4-氨基-3-甲基苯基)-3,3,3-三氟-2-羟基丙酸乙酯
- [0212] 2-(4-氨基-3-甲氧基苯基)-3,3,3-三氟-2-羟基丙酸乙酯
- [0213] 3,4-二氨基苄醇二盐酸盐
- [0214] 4-氨基萘-1,8-二羧酸
- [0215] 4-氨基-3-氯-5-甲基苯甲酸
- [0216] 4-氨基-2,6-二甲基苯甲酸
- [0217] 4-氨基-3-氟苯甲酸
- [0218] 4-氨基-5-溴-2-甲氧基苯甲酸
- [0219] 2,7-二氨基苄
- [0220] 4,4'-二氨基八氟联苯
- [0221] 3,3'-二氨基对二氨基联苯
- [0222] 3,3',5,5'-四甲基对二氨基联苯

- [0223] 3,3'-二甲氧基对二氨基联苯
[0224] o-联甲苯胺
[0225] 3,3'-二硝基对二氨基联苯
[0226] 2-硝基对二氨基联苯
[0227] 3,3'-二羟基对二氨基联苯
[0228] o-联甲苯胺砒
[0229] 对二氨基联苯,
[0230] 3,3'-二氯对二氨基联苯
[0231] 2,2',5,5'-四氯对二氨基联苯,
[0232] 对二氨基联苯-3,3'-二羧酸
[0233] 4,4'-二氨基-1,1'-联萘
[0234] 4,4'-二氨基二苯基-3,3'-二羟基乙酸
[0235] 二氢乙锭
[0236] o-联茴香胺
[0237] 2,2'-二氯-5,5'-二甲氧基对二氨基联苯
[0238] 3-甲氧基对二氨基联苯
[0239] 3,3'-二氯对二氨基联苯(二苯基-d6),
[0240] 2,7-二氨基-9-芴酮
[0241] 3,5,3',5'-四溴-联苯-4,4'-二胺
[0242] 2,2'-双(三氟甲基)对二氨基联苯
[0243] 2,2'-二氯[1,1'-联苯基]-4,4'-二胺
[0244] 3,9-二氨基-1,11-二甲基-5,7-二氢-二苯并(a,c)环庚烯-6-酮
[0245] 3,3'-双(三氟甲基)对二氨基联苯
[0246] 二苯并(1,2)噻烯(dithiine)-3,8-二胺
[0247] 3,3'-联甲苯胺-5-磺酸
[0248] 3,3'-二氯对二氨基联苯-d6
[0249] 四甲基对二氨基联苯
[0250] 3,3'-二氨基二苯甲酮,
[0251] 3,3'-二氨基二苯甲烷,
[0252] 4,4-双-(3-氨基-4-羟基苯基)-戊酸
[0253] 2,2-双(3-氨基-4-羟基苯基)六氟丙烷
[0254] 2,2-双(3-氨基-4-甲基苯基)六氟丙烷
[0255] 四溴亚甲基二苯胺
[0256] 2,7-二氨基-9-芴酮
[0257] 2,2-双(3-氨基苯基)六氟丙烷
[0258] 双-(3-氨基-4-氯-苯基)-甲酮
[0259] 双-(3-氨基-4-二甲基氨基-苯基)-甲酮
[0260] 3-[3-氨基-5-(三氟甲基)苄基]-5-(三氟甲基)苯胺
[0261] 1,5-二氨基萘

[0262] 或它们的衍生物,再次条件是所列的没有携带两个氨基的化合物被视为具有至少一个额外氨基的衍生物。

[0263] 额外的其他二胺的优选实例是:

[0264] 乙二胺,1,3-丙二胺,1,4-丁二胺,1,5-戊二胺,1,6-己二胺,1,7-庚二胺,1,8-辛二胺,1,9-壬二胺,1,10-亚十烷基二胺,1,11-亚十一烷基二胺,1,12-亚十二烷基二胺, α , α' -二氨基-m-二甲苯, α , α' -二氨基-p-二甲苯,(5-氨基-2,2,4-三甲基环戊基)甲胺,1,2-二氨基环己烷,4,4'-二氨基二环己基甲烷,1,3-双(甲基氨基)环己烷,4,9-二氧杂十二烷-1,12-二胺,3,5-二氨基苯甲酸甲酯,3,5-二氨基苯甲酸己酯,3,5-二氨基苯甲酸十二烷酯,3,5-二氨基苯甲酸异丙酯,4,4'-亚甲基二苯胺,4,4'-亚乙基二苯胺,4,4'-二氨基-3,3'-二甲基二苯甲烷,3,3',5,5'-四甲基对二氨基联苯,4,4'-二氨基二苯砜,4,4'-二氨基二苯醚,1,5-二氨基萘,3,3'-二甲基-4,4'-二氨基联苯,3,4'-二氨基二苯醚,3,3'-二氨基二苯甲酮,4,4'-二氨基二苯甲酮,4,4'-二氨基-2,2'-二甲基联苯,双[4-(4-氨基苯氧基)苯基]砜,1,4-双(4-氨基苯氧基)苯,1,3-双(4-氨基苯氧基)苯,1,3-双(3-氨基苯氧基)苯,2,7-二氨基苄,9,9-双(4-氨基苯基)苄,4,4'-亚甲基-双(2-氯苯胺),4,4'-双(4-氨基苯氧基)联苯,2,2',5,5'-四氯-4,4'-二氨基联苯,2,2'-二氯-4,4'-二氨基-5,5'-二甲氧基联苯,3,3'-二甲氧基-4,4'-二氨基联苯,4,4'-(1,4-亚苯基亚异丙基)联苯胺,4,4'-(1,3-亚苯基亚异丙基)联苯胺,2,2-双[4-(4-氨基苯氧基)苯基]丙烷,2,2-双[3-(4-氨基苯氧基)苯基]六氟丙烷,2,2-双[3-氨基-4-甲基苯基]六氟丙烷,2,2-双(4-氨基苯基)六氟丙烷,2,2'-双[4-(4-氨基-2-三氟甲基苯氧基)苯基]六氟丙烷,4,4'-二氨基-2,2'-双(三氟甲基)联苯,和4,4'-双[(4-氨基-2-三氟甲基)苯氧基]-2,3,5,6,2',3',5',6'-八氟联苯。

[0265] 本发明聚合物的分子量 M_w 为 1 000 至 5 000 000,然而优选 5 000 至 2 000 000,特别有利地 10 000 至 1 000 000。

[0266] 根据本发明的聚合物链由其合成的单体结构嵌段的数量可以在宽范围内变化。它通常为 2-2000,但特别地 3-200。

[0267] 根据本发明的聚合物可进一步含有添加剂,例如含硅烷的化合物和含环氧基的交联剂以供进一步改进聚合物对基底的粘合。硅烷粘合促进剂的实例描述于文献,例如 *Plast. Eng.* 36(1996) (*Polyimides, fundamentals and applications*) 中。上述含环氧基的交联剂优选包括 4,4'-亚甲基双(N,N-二缩水甘油基苯胺),三羟甲基丙烷三缩水甘油基醚,苯-1,2,4,5-四羧酸 1,2:4,5-N,N'-二缩水甘油基二酰亚胺,聚乙二醇二缩水甘油基醚,N,N-二缩水甘油基环己基胺和类似物。

[0268] 根据本发明的聚合物可含有添加剂,例如光敏剂,光自由基生成剂和/或阳离子光引发剂。这种添加剂的实例是 2,2-二甲氧基苯基乙酮,二苯基甲酮和 N,N-二甲基苯胺或 4-(二甲基氨基)苯甲酸乙酯的混合物,咕吨酮,噻吨酮,IRGACURE™184,369,500,651 和 907(Ciba),Michler's 酮,三芳基铈盐和类似物。

[0269] 本发明的聚合物可作为单一聚合物或者作为与其他聚合物、低聚物、单体、光活性聚合物、光活性低聚物和/或光活性单体的混合物形式使用。因此可改性该层的性能,得到所寻求的性能。例如,可获得诱导的预倾斜角,良好的表面润湿,高的电压保持比,比锚定能等。

[0270] 然后可将本发明的聚合物施加到载体上,和在可能需要的任何酰亚胺化步骤之后,通过用校准光,优选用线性偏振光辐照而交联,也就是说通过环加成含有光反应性基团的它们的侧链而获得,这取决于在取向的优选方向上辐照的光的偏振方向和与校准层接触的液晶的倾斜角。通过空间选择辐照本发明的分子单元,因此可能的情形是,需校准表面的非常特定的区域并提供有确定的倾斜角。与此同时,如此生产的校准层还通过环加成稳定化。

[0271] 可例如通过在旋涂装置内首先制备施加到载体(所述载体任选地用电极涂布,例如是用氧化锡铟(ITO)涂布的玻璃板)上的所得聚合物材料的溶液,以便生产厚度为5纳米到2微米的均匀层,从而生产这种校准层。然后,或者任选地在在先的酰亚胺化之后,可使用偏振器和任选地用于生成结构图像的掩模,例如用高压汞蒸汽灯,氙灯或脉冲UV激光器辐照待取向的区域。辐照时间取决于单独的灯的输出且可从数秒变化到数小时。然而也可使用滤光器辐照均匀层,进行光反应,所述滤光器例如仅仅允许适合于交联反应的辐射线透过。

[0272] 可在生产具有至少一层取向层以及未结构化和结构化的光学元件和多层系统的光学或光电器件中使用本发明的这种校准层。因此,本发明进一步涉及光学或光电器件,它包括一种或多种本发明的低聚物,枝状体或聚合物;优选交联形式。

[0273] 本发明新的化合物的技术优点是在用于取向可聚合和可移动液晶的若干应用中它们具有高的对比度。另外,高速取向可以是途径(accesses)和良好的方位角稳定性。后一性能对于提供结构化延迟器,例如用于3D的光学薄膜,安全器件,功能性箔,例如阻隔层来说是重要的。

[0274] 随后的实施例进一步阐述本发明。它们通过阐述而绝不是限制给出。落在本发明范围内的在这些实施例上的变化对于本领域技术人员来说是显而易见的。

实施例

[0275] 在实施例中所使用的定义:

[0276] LC/MS: 液相色谱法/质谱法

[0277] $[M+Na]$ = 分子量加钠

[0278] $[M+H]$ = 分子量加质子

[0279] $[M+NH_4]$ = 分子量加铵

[0280] ^1H NMR = ^1H 核磁共振光谱法

[0281] DMSO- d_6 = 氘化二甲亚砜

[0282] THF- d_8 = 氘化四氢呋喃

[0283] 300MHz = 300 兆赫

[0284] m = 多重态

[0285] d = 双重态

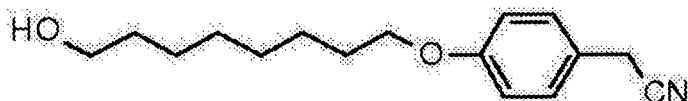
[0286] dd = 双重线双重线

[0287] t = 三重线

[0288] s = 单重线(singulet)

[0289] q = 五重线(quintet)

- [0290] br = 宽
 [0291] δ = 化学位移
 [0292] HCl = 氯化氢
 [0293] MeOH: 甲醇
 [0294] EtOAc: 乙酸乙酯
 [0295] NMP: N-甲基-2-吡咯烷酮
 [0296] THF: 四氢呋喃
 [0297] TBME: 叔丁基甲醚
 [0298] DMF: N,N-二甲基甲酰胺
 [0299] RT: 室温, 通常范围为 18-28°C
 [0300] $[\eta]$: 粘度
 [0301] v. t. %: 体积百分比
 [0302] MLC7067: 是电介质各向异性为 10.3, 光学各向异性为 0.1025 和旋转粘度为 81mPa.s 的获自 Merck KGA 的液晶的混合物。
 [0303] 实施例 1: 制备 4-[(8-羟基辛基)氧基]苯基}乙腈 1A
 [0304]



[0305] 将 20.0g (150mmol) (4-羟基苯基)乙腈和 29.5g (179mmol) 8-氯辛-1-醇溶解在 400ml N,N-二甲基甲酰胺中。添加 41.5g (300mmol) 碳酸钾和 5.0g (30mmol) 碘化钾, 并加热该悬浮液到 80°C。在 48h 之后, 将过量碳酸钾过滤掉, 并将所得滤液倾倒在冰水中。用乙酸乙酯萃取水层 2 次。用盐水洗涤合并的有机层并蒸发至干。在 SiO₂ 柱色谱法上用庚烷/乙酸乙酯: 7/3 作为洗脱剂纯化粗产物 2 次, 并在 40°C 下干燥过夜。获得 24.5g 黄色固体形式的 4-[(8-羟基辛基)氧基]苯基}乙腈 (62% 产率)。

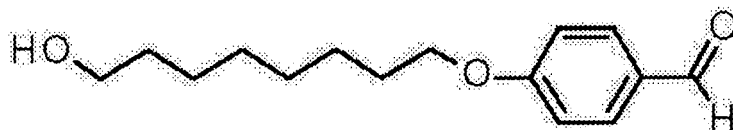
[0306] 根据实施例 1 针对化合物 1A 描述的方法制备化合物 1B, 1C, 条件是 8-氯辛-1-醇分别被 6-溴己-1-醇, 11-溴十一烷-1-醇替代。

[0307] 根据实施例 1 针对化合物 1C 描述的方法制备化合物 1D, 条件是 (4-羟基苯基)乙腈被 [4-羟基-3-甲氧基-苯基]乙腈替代。

[0308] 根据实施例 1 针对化合物 1D 描述的方法制备化合物 1E, 条件是 11-溴十一烷-1-醇被 8-氯辛-1-醇替代。

[0309] 实施例 2: 制备 4-[(8-羟基辛基)氧基]苯醛

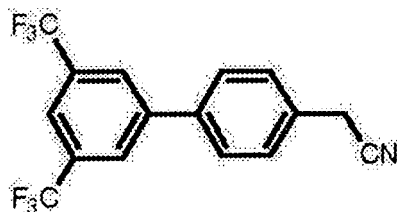
[0310]



[0311] 根据实施例 1 中描述的工序, 由 4-羟基苯醛和 8-氯辛-1-醇为起始, 制备 4-[(8-羟基辛基)氧基]苯醛。62% 产率。

[0312] 实施例 4: 制备 [3', 5'-双(三氟甲基)-1, 1'-联苯-4-基]乙腈

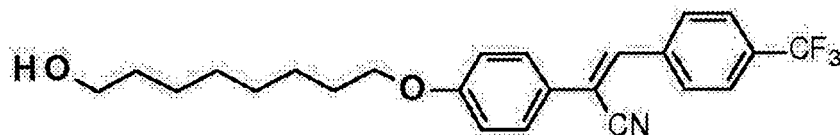
[0313]



[0314] 将 0.664g (3.4mmol) (4-溴苯基)乙腈, 0.645g (3.4mmol) [3,5-双(三氟甲基)苯基]硼酸和 937mg (6.8mmol) 碳酸钾溶解在 20ml 四氢呋喃和 5ml 水中。用氩气吹扫该溶液, 并添加 78mg 四(三苯基膦)钯(0)。用氩气吹扫该溶液并加热到 80℃。在 80℃下 12 小时之后, 冷却该反应混合物到室温, 并用乙酸乙酯萃取水层 2 次。用盐水洗涤合并的有机层, 并蒸发至干。在 SiO₂柱色谱法上用庚烷/乙酸乙酯 3/2 作为洗脱剂纯化粗产物 2 次, 并在 30℃下干燥过夜。获得实施例 4 的 527mg 白色固体。

[0315] 实施例 6: 制备 (2Z)-2-{4-[(8-羟基辛基)氧基]苯基}-3-[4-(三氟甲基)苯基]丙-2-烯腈 6A

[0316]



[0317] 将来自实施例 1A 5.0g (19.1mmol), 3.5g (19.1mmol) 4-(三氟甲基)苯醛溶解在 50ml 丙-2-醇中。加热该溶液到 60℃, 并逐滴添加 1.9ml (1.9mmol) 1M 四丁基氢氧化铵在甲醇内的溶液。在 60℃下 2 小时之后, 冷却该反应混合物到 0℃。过滤掉沉淀, 用冷丙-2-醇洗涤并在丙-2-醇内重结晶。获得实施例 6A 4.7g 白色固体 (59% 产率)。

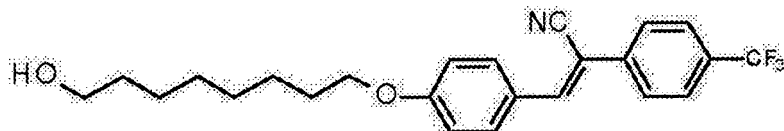
[0318] 根据实施例 6 中针对化合物 6A 描述的方法, 制备化合物 6B, 6E, 6H, 6X, 6U, 6V, 6AA, 6AB, 条件是 4-(三氟甲基)苯醛分别被 3,5-(三氟甲基)苯醛, 3-(三氟甲基)苯醛, 4-氟苯醛, 苯醛, 4-氯苯醛, 4-溴苯醛, 3,4,5-三氟苯醛, 4,6-二氟苯醛替代。

[0319] 根据实施例 6 中针对化合物 6A 描述的方法, 制备化合物 6J, 6K, 6L, 条件是实施例 1A 分别被实施例 1E, 实施例 1B, 实施例 1D 替代。

[0320] 根据实施例 6 中针对化合物 6B 描述的方法, 制备化合物 6N, 条件是实施例 1A 被实施例 1C 替代。

[0321] 实施例 7: 制备 (2Z)-3-{4-[(8-羟基辛基)氧基]苯基}-2-[4-(三氟甲基)苯基]丙-2-烯腈 7A

[0322]



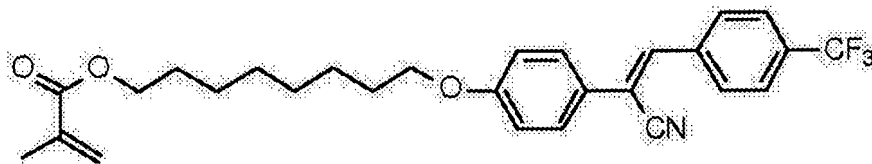
[0323] 根据实施例 6 中描述的工序, 由实施例 2 和 [(4-三氟甲基)苯基]乙腈为起始, 制备实施例 7A。76% 产率。

[0324] 根据实施例 7 中针对化合物 7A 描述的方法, 制备化合物 7B, 7D, 7E, 7W, 7Y, 条件是 [(4-三氟甲基)苯基]乙腈分别被 [(3,5-双(三氟甲基))苯基]乙腈, 实施例 4, [(4-氟)苯基]乙腈, [(4-氯)苯基]乙腈, [(4-溴)苯基]乙腈, [(3,4,5-三氟)苯基]

乙腈, [(4,6-二氟)苯基]乙腈替代。

[0325] 实施例 10: 制备 2-甲基丙烯酸 8-(4-{(Z)-1-氰基-2-[4-(三氟甲基)苯基]乙烯基}苯氧基)辛酯 10A

[0326]

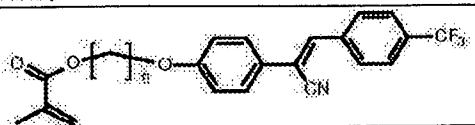
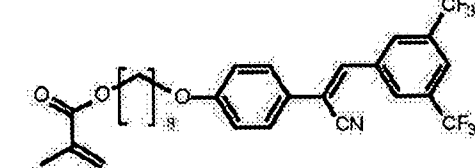
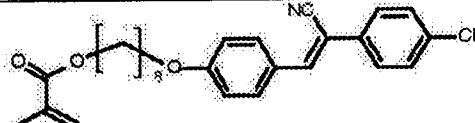
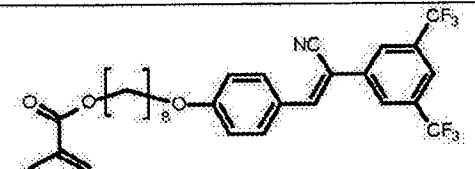
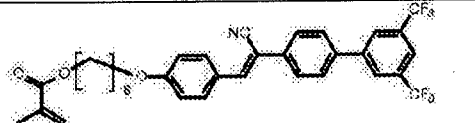
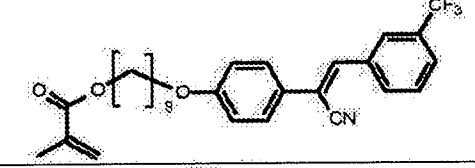
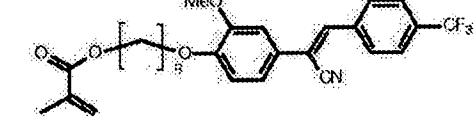
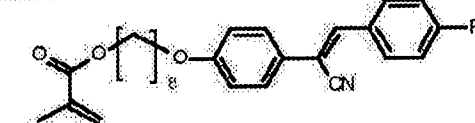
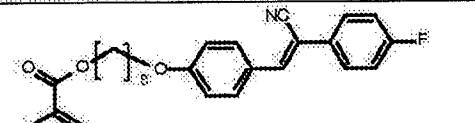
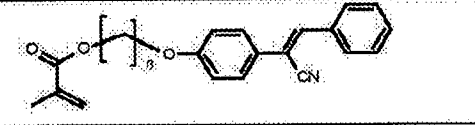
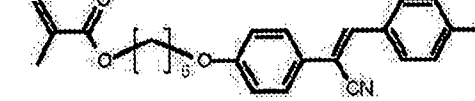


[0327] 将来自实施例 6A 2.03g(4.9mmol), 59mg(0.49mmol) 4-二甲基氨基吡啶和 1.48g(14.69mmol) 三乙胺溶解在 40ml 四氢呋喃中。冷却该溶液到 0℃, 并在 0℃下在 1 小时内逐滴添加 0.9g(5.8mmol) 甲基丙烯酸酐在 10mL 四氢呋喃内的溶液。在 0℃下 2 小时之后, 然后允许加热该反应混合物到室温。在 15 小时之后, 将该反应混合物倾倒在冰水上。过滤掉沉淀, 在 30℃下干燥, 并在甲醇内用小量 2,6-二叔丁基-4-甲基苯酚重结晶。获得实施例 10A 1.4g 白色固体 (61% 产率)。

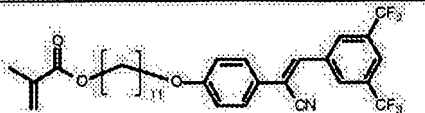
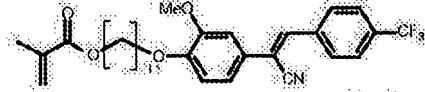
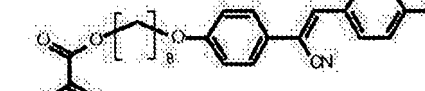
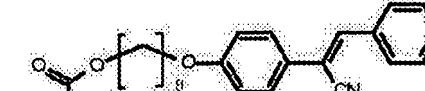
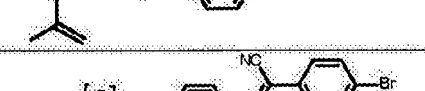
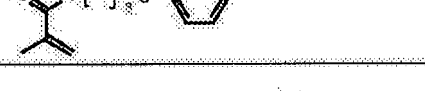
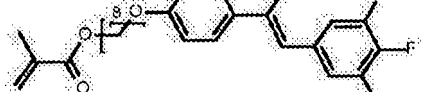
[0328] 根据实施例 10 中针对化合物 10A 描述的方法, 制备化合物 10B, 10E, 10F, 10H, 10I, 10L, 10M, 10N, 10O, 10P, 10R, 10S, 10U, 10V, 10W, 10Y, 10AA, 10AB, 条件是实施例 6A 分别被实施例 6B, 实施例 7A, 实施例 7B, 实施例 7D, 实施例 6E, 实施例 6J, 实施例 6H, 实施例 7E, 实施例 6X, 实施例 6K, 实施例 6N, 实施例 6L, 实施例 6U, 实施例 6V, 实施例 7W, 实施例 7Y, 6AA, 6AB 替代。

[0329] 在下表中给出了化合物的分析数据:

[0330]

	结构	分析数据
10A		LC/MS: $[M+H]^+ = 486.2$
10B		LC/MS: $[M+Na]^+ = 576.7$
10E		LC/MS: $[M+Na]^+ = 508.2$
10F		LC/MS: $[M+Na]^+ = 576.1$
10H		LC/MS: $[M+NH_4]^+ = 647.2$
10I		LC/MS: $[M+Na]^+ = 508.2$
10L		LC/MS: $[M+Na]^+ = 538.1$
10M		LC/MS: $[M+Na]^+ = 458.1$
10N		LC/MS: $[M+H]^+ = 436.2$
10O		LC/MS: $[M+Na]^+ = 440.5$
10P		LC/MS: $[M+Na]^+ = 480.1$

[0331]

10R		LC/MS: $[M+Na]^+ = 618.1$
10S		LC/MS: $[M+Na]^+ = 580.2$
10U		LC/MS: $[M+Na]^+ = 474.1$
10V		LC/MS: $[M+Na]^+ = 518.1$
10W		LC/MS: $[M+Na]^+ = 474.1$
10Y		LC/MS: $[M+Na]^+ = 518.1$
10AA		^1H NMR DMSO- d_6 (300MHz): 7.89 (s, 1H), 7.81 (m, 2H), 7.67 (d, 2H), 7.08 (d, 2H), 6.01 (s, 1H), 5.66 (s, 1H), 4.09 (dd, 2H), 4.02 (dd, 2H), 1.87 (s, 3H), 1.73 (m, 2H), 1.62 (m, 2H), 1.33 (m, 8H).
10AB		^1H NMR DMSO- d_6 (300MHz): 8.04 (dd, 1H), 7.82 (s, 1H), 7.69 (dd, 2H), 7.45 (dd, 1H), 7.29 (dd, 1H), 7.06 (d, 2H), 6.01 (s, 1H), 5.66 (s, 1H), 4.09 (m, 2H), 4.02 (m, 2H), 1.87 (s, 3H), 1.72 (m, 2H), 1.61 (m, 2H), 1.33 (m, 8H).

[0332] 实施例 11: 制备 8-(4-((Z)-1-氰基-2-[4-(三氟甲基)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯 11A

[0333] 将来自实施例 10A 2.00g (4.1mmol) 溶解在 10mL 脱气的环己酮中。用氩气吹扫该溶液并加热到 60℃。逐滴添加 20.0mg (0.14mmol) 2,2'-偶氮双(2-甲基丙腈)在 2mL 环己酮内的溶液。在 60℃下 36 小时之后, 冷却该反应混合物到室温, 用 5mL 四氢呋喃稀释, 并在 200mL 冷甲醇内沉淀。过滤掉沉淀, 用甲醇洗涤并在 30℃下干燥过夜。获得实施例 11A 1.50g 白色固体 (75%产率)。

[0334] 根据实施例 11 中针对化合物 11A 描述的方法, 制备化合物 11B, 11E, 11F, 11H, 11I, 11L, 11M, 11N, 11O, 11P, 11R, 11S, 11U, 11V, 11W, 11Y, 11AA, 11AB, 条件是实施例 10A 分别被实施例 10B, 实施例 10E, 实施例 10F, 实施例 10H, 实施例 10I, 实施例 10L, 实施例 10M, 实施例 10N, 实施例 10O, 实施例 10P, 实施例 10R, 实施例 10S, 实施例 10U, 实施例 10V, 实施例

10W, 实施例 10Y, 实施例 10AA, 实施例 10AB 替代。

[0335]

	名称	¹ H NMR(300MHz)在 THF-d ₈ 内	M _w GPC-PS- 等价物
11A	8-(4-((Z)-1- 氧基 -2-[4-(三氟甲基)苯 基]乙烯基}苯氧基) 辛基聚-2-甲基丙烯 酸酯	7.98 (d, 2H), 7.70 (d, 2H), 7.64 (m, 3H), 6.94 (d, 2H), 3.96 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56- 1.20 (m, 10H), 1.15-0.79 (m, 3H)	166 000
11B	8-(4-((Z)-2[3,5- 双 (三氟甲基)苯基]-1- 氧基乙烯基}苯氧基) 辛基聚-2-甲基丙 烯酸酯	8.43 (s, 2H), 8.04 (s, 1H), 7.78 (s, 1H), 7.67 (d, 2H), 6.97 (d, 2H), 4.00 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	101 900
11E	8-(4-((Z)-2- 氧基 -2-[4-(三氟甲基)苯 基]乙烯基}苯氧基) 辛基聚-2-甲基丙烯 酸酯	7.92 (d, 2H), 7.81 (d, 2H), 7.74 (s, 1H), 7.68 (d, 2H), 6.96 (d, 2H), 3.98 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	79 000
11F	8-(4-((Z)-2[3,5- 双 (三氟甲基)苯基]-2- 氧基乙烯基}苯氧基) 辛基聚-2-甲基丙 烯酸酯	8.19 (m, 2H), 7.97 (m, 2H), 7.93 (m, 2H), 6.98 (dd, 2H), 4.00 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 10H), 1.15-0.79 (m, 3H)	66 300

[0336]

11H	8-(4-((Z)-2[3',5'-双(三氟甲基)-1,1'-联苯-4-基]-2-氟基乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	8.17 (m, 2H), 7.92 (m, 3H), 7.77 (m, 5H), 6.94 (d, 2H), 3.97 (m, 4H), 3.82 (s, 3H), 1.84-1.61 (m, 2H), 1.64 (m, 2H), 1.56-1.20 (m, 16H), 1.15-0.79 (m, 3H)	66 000
11I	8-(4-((Z)-1-氟基-2-[3-(三氟甲基)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	8.15 (d, 2H), 8.09 (s, 1H), 7.80-7.50 (m, 5H), 6.94 (d, 2H), 3.96 (m, 4H), 1.86-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.20-0.80 (m, 3H)	62 000
11L	8-(4-((Z)-1-氟基-2-[4-(三氟甲基)苯基]乙烯基)-2-甲氧基苯氧基)辛基聚-2-甲基丙烯酸酯	7.98 (d, 2H), 7.70 (d, 2H), 7.66 (s, 1H), 7.23 (m, 2H), 6.90 (d, 1H), 3.96 (m, 4H), 3.83 (s, 3H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	24 200
11M	8-{4-[(Z)-1-氟基-2-(4-氟苯基)乙烯基]苯氧基}辛基聚-2-甲基丙烯酸酯	7.91 (d, 2H), 7.59 (d, 2H), 7.54 (s, 1H), 7.15 (m, 2H), 6.92 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	89 000
11N	8-(4-((Z)-2-氟基-2-[4-(氟)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.86 (d, 2H), 7.66 (dd, 2H), 7.54 (s, 1H), 7.12 (dd, 2H), 6.94 (d, 2H), 3.97 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	121 000
11O	8-{4-[(Z)-1-氟基-2-苯基乙烯基]苯氧基}辛基聚-2-甲基丙烯酸酯	7.86 (d, 2H), 7.51 (d, 2H), 7.56 (s, 1H), 7.38 (m, 3H), 6.93 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 10H), 1.25-0.80 (m, 3H)	349 000

[0337]

11P	6-(4-((Z)-1- 氟基-2-[4-(三氟甲基)苯基]乙烯基)苯氧基)己基聚-2-甲基丙烯酸酯	7.97 (d, 2H), 7.69 (d, 2H), 7.63 (m, 1+2H), 6.93 (d, 2H), 3.96 (m, 4H), 1.90-1.55 (m, 4H), 1.55-1.25 (m, 6H), 1.25-0.80 (m, 3H)	66 000
11R	11-(4-((Z)-2-[3,5-双(三氟甲基)苯基]-1-氟基乙烯基)苯氧基)十一烷基聚-2-甲基丙烯酸酯	8.43 (s, 2H), 8.04 (s, 1H), 7.78 (s, 1H), 7.67 (d, 2H), 6.97 (d, 2H), 3.99 (m, 4H), 2.00-1.55 (m, 4H), 1.55-1.25 (m, 16H), 1.25-0.80 (m, 3H)	111 700
11S	11-(4-((Z)-1- 氟基-2-[4-(三氟甲基)苯基]乙烯基)-聚-2-甲氧基苯氧基)十一烷基-聚-2-甲基丙烯酸酯	7.99 (d, 2H), 7.73 (s, 1H), 7.69 (d, 2H), 7.26 (m, 2H), 6.91 (d, 1H), 3.96 (m, 4H), 3.83 (s, 3H), 2.00-1.55 (m, 4H), 1.55-1.25 (m, 16H), 1.25-0.80 (m, 3H)	63 700
11U	8-(4-((Z)-1- 氟基-2-[4-(氯)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.90 (d, 2H), 7.65 (m, 3H), 7.45 (d, 2H), 7.05 (m, 2H), 4.01 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.30 (m, 9H), 1.25-0.80 (m, 3H)	58700
11V	8-(4-((Z)-1- 氟基-2-[4-(溴)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.95 (d, 2H), 7.65 (m, 5H), 6.95 (d, 2H), 3.94 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	62200
11W	8-(4-((Z)-2- 氟基-2-[4-(氯)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.95 (d, 2H), 7.66 (m, 3H), 7.44 (d, 2H), 7.05 (d, 2H), 4.05 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	64600

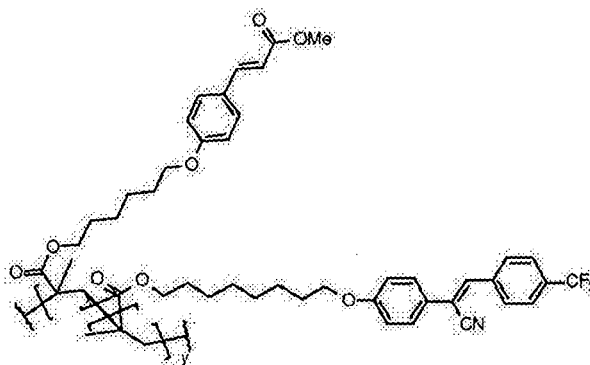
[0338]

11Y	8-(4-((Z)-2- 氰基-2-[4-(溴)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.95 (d, 2H), 7.66 (m, 5H), 7.05 (m, 2H), 4.05 (m, 4H), 1.90-1.55 (m, 5H), 1.55-1.25 (m, 9H), 1.25-0.80 (m, 3H)	44800
11AA	8-(4-((Z)-2- 氰基-2-[3,4,5-(三氟)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	7.49 (m, 4H), 7.20 (s, 1H), 6.87 (m, 2H), 3.93 (m, 4H), 2.10-1.20 (m, 12H), 1.20-0.70 (m, 3H)*	58000
11AB	8-(4-((Z)-1- 氰基-2-[4-(4,6-二氟)苯基]乙烯基)苯氧基)辛基聚-2-甲基丙烯酸酯	20 (dd, 1H), 7.53 (d, 1H), 7.48 (s, 1H), 6.89 (m, 4H), 3.93 (m, 4H), 2.10-1.20 (m, 12H), 1.20-0.70 (m, 3H)*	53000

[0339] *:在 CDCl_3 内进行的 NMR

[0340] 实施例 12: 制备聚-2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯-共-聚-2-甲基丙烯酸 8-{4-[(Z)-1-氰基-2-苯基乙烯基]苯氧基}辛酯 (98:2 之比)

[0341]

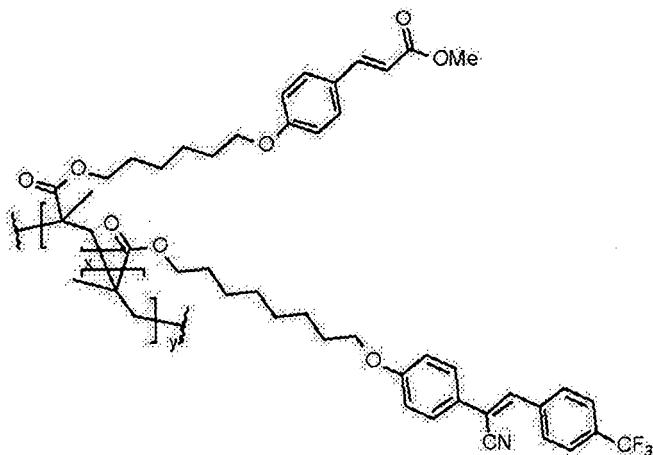


[0342] 将 990mg (2.858mmol) 2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯 (US 6,107,427 的实施例 4) 和来自实施例 10A 28.6mg (0.059mmol) 溶解在 5.0mL 脱气的环己酮中。用氩气吹扫该溶液并加热到 60℃。逐滴添加 9.0mg (0.055mmol) 2,2'-偶氮双(2-甲基丙腈)在 1mL 环己酮内的溶液。在 60℃ 下 17 小时之后,冷却该反应混合物到室温,用 5mL 四氢呋喃稀释,并在 150mL 冷甲醇内沉淀。过滤掉沉淀,用甲醇洗涤并在 30℃ 下干燥过夜。获得实施例 12 的 864mg 白色固体 (85% 产率)。

尺寸-排阻色谱法 (PS- 等价物): M_w 62,700。

[0343] 实施例 13: 制备聚-2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯-共-聚-2-甲基丙烯酸 8-{4-[(Z)-1-氰基-2-苯基乙烯基]苯氧基}辛酯 (95:5 之比)

[0344]

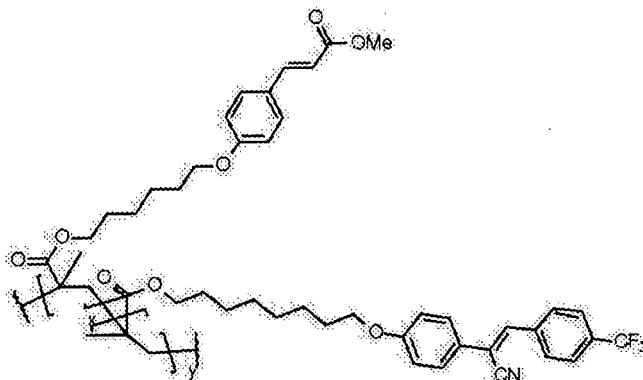


[0345] 根据针对实施例 12 描述的工序, 由 987mg (2.849mmol) 2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯 (US 6,107,427 的实施例 4) 和来自实施例 10A 73.8mg (0.152mmol) 为起始, 制备实施例 13。

[0346] 尺寸-排阻色谱法 (PS- 等价物): M_w 60,800。

[0347] 实施例 14: 制备聚-2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯-共-聚-2-甲基丙烯酸 8-{4-[(Z)-1-氰基-2-苯基乙烯基]苯氧基}辛酯 (90:10 之比)

[0348]

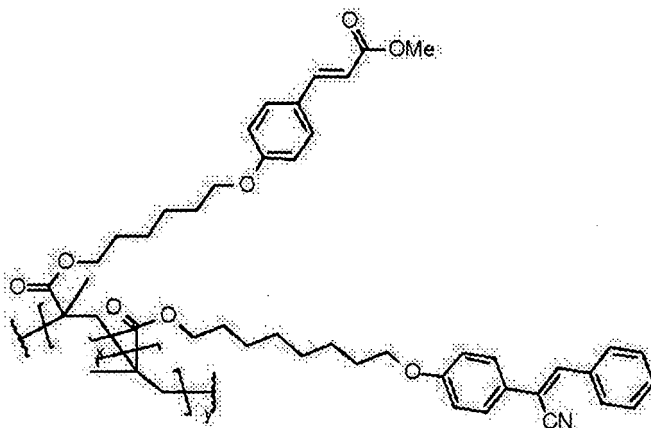


[0349] 根据针对实施例 12 描述的工序, 由 1000mg (2.887mmol) US 6,107,427 的实施例 4 和来自实施例 10A 156mg (0.321mmol) 为起始, 制备实施例 14。

[0350] 尺寸-排阻色谱法 (PS- 等价物), M_w 53,100。

[0351] 实施例 15: 制备聚-2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯-共-聚-2-甲基丙烯酸 8-{4-[(Z)-1-氰基-2-苯基乙烯基]苯氧基}辛酯 (90:10 之比)

[0352]

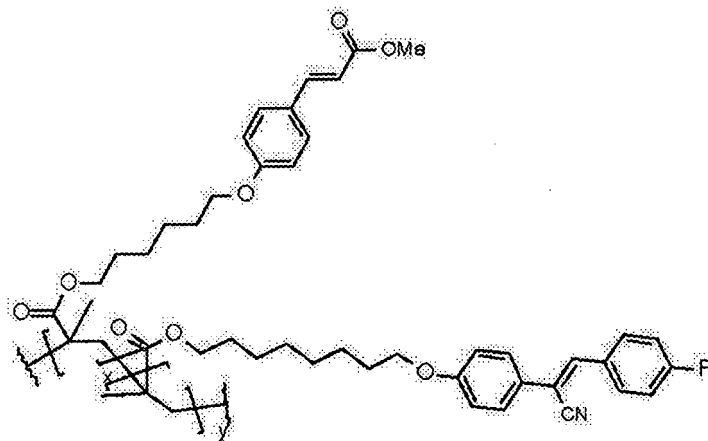


[0353] 根据针对实施例 12 描述的工序, 由来自 US 6,107,427 的实施例 41000mg (2.887mmol) 和来自实施例 100 134mg (0.321mmol) 为起始, 制备实施例 15。

[0354] 尺寸-排阻色谱法 (PS- 等价物) M_w 75,400。

[0355] 实施例 16: 制备聚-2-甲基丙烯酸 6-{4-[(1E)-3-甲氧基-3-氧代丙-1-烯基]苯氧基}己酯-共-聚-2-甲基丙烯酸 8-{4-[(Z)-1-氰基-2-(4-氟苯基)乙烯基]苯氧基}辛酯 (90:10 之比)

[0356]

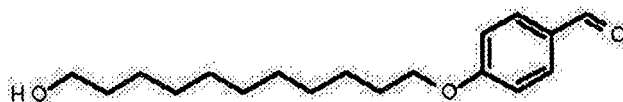


[0357] 根据针对实施例 12 描述的工序, 由来自 US 6,107,427) 的实施例 41000mg (2.887mmol) 和来自实施例 10M 140mg (0.321mmol) 为起始, 制备实施例 16。

[0358] 尺寸-排阻色谱法 (PS- 等价物) M_w 78,900。

[0359] 实施例 17: 制备 4-[(11-羟基十一烷基)氧基]苯醛 17A

[0360]



[0361] 根据针对实施例 2 描述的工序, 由 4-羟基苯醛和 11-溴十一烷-1-醇为起始, 制备实施例 17A, 57% 产率。根据针对实施例 2 描述的工序, 由 4-羟基-3-甲氧基苯醛和 11-溴十一烷-1-醇为起始, 制备实施例 17B, 97% 产率。

[0362] 实施例 18: 制备 (Z)-2-(4-氟苯基)-3-[4-(11-羟基十一烷氧基)苯基]丙-2-烯腈

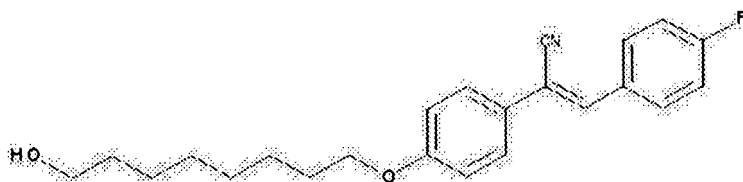
[0363]



[0364] 根据针对实施例 7 描述的工序,由实施例 17A 和 [(4- 氟) 苯基] 乙腈为起始,制备实施例 18A。

[0365] 实施例 20: (Z)-2-(4- 氟苯基)-3-[4-(11- 羟基十一烷氧基) 苯基] 丙-1- 烯腈

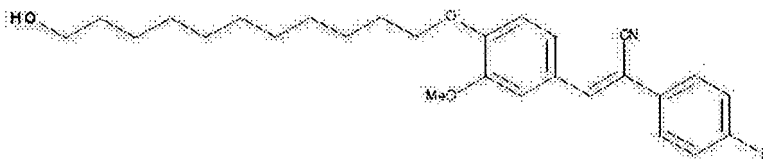
[0366]



[0367] 根据针对实施例 7 描述的工序,由实施例 1A 和 4- 氟苯醛为起始,制备实施例 20。

[0368] 实施例 21: 制备 (Z)-2-(4- 氟苯基)-3-[4-(11- 羟基十一烷氧基)-3- 甲氧基- 苯基] 丙-2- 烯腈

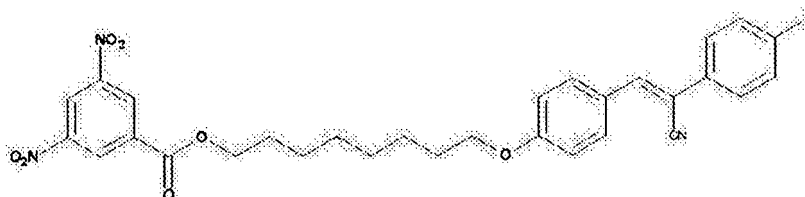
[0369]



[0370] 根据针对实施例 6 描述的工序,由实施例 17B 和 [(4- 氟) 苯基] 乙腈为起始,制备实施例 21。

[0371] 实施例 22: 制备 3, 5- 二硝基苯甲酸 8-[4-[(Z)-2- 氰基-2-(4- 氟苯基) 乙烯基] 苯氧基] 辛酯 22A

[0372]



[0373] 将 3290mg (14.2mmol) 3, 5- 二硝基苯甲酰氯溶解在 30mL 甲苯和 2 滴 DMF 中。缓慢地添加来自实施例 19B 5000mg (13.6mmol), 160mg (1.3mmol) 4- 二甲基氨基吡啶和 3240mg (41.0mmol) 吡啶在 10mL 甲苯内的溶液。在室温下搅拌该混合物 96 小时。然后加热该溶液到 80℃ 并添加 10mL MeOH。在室温下搅拌该悬浮液 1 小时并在 0℃ 下搅拌 1 小时。过滤掉沉淀。将该固体分散在 40mL MeOH 和 10mL HCl 1N 的混合物内并在室温下搅拌 1 小时。过滤掉该悬浮液,用冷 MeOH 洗涤若干次,并在高真空下干燥 12 小时,得到 9600mg (71%) 实施例 22A。

[0374] 根据针对实施例 22A 描述的工序,由实施例 20 为起始,制备实施例 22B。

[0375] 根据针对实施例 22A 描述的工序,由实施例 18A 为起始,制备实施例 22C。

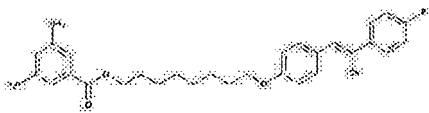
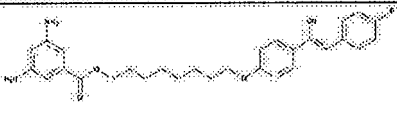
[0376] 根据针对实施例 22A 描述的工序,由实施例 21 为起始,制备实施例 22F。

[0377] 实施例 23: 制备 3,5-二氨基苯甲酸 8-[4-[(Z)-2-氰基-2-(4-氟苯基)乙烯基]苯氧基]辛酯 23A

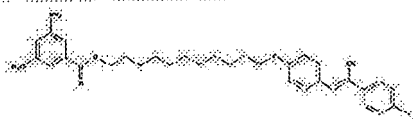
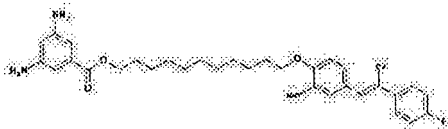
[0378] 将 4.8g(5.55mmol) 实施例 22A 溶解在 63ml DMF 和 7ml 水的混合物中。添加 13.8g(51.3mmol) 六水合氯化铁。在 30 分钟内分步添加 5.58g(85.5mmol) 锌粉。允许该混合物反应 2 小时。然后在乙酸乙酯和水之间分配该反应混合物并过滤。用水反复洗涤有机相,在硫酸钠上干燥,过滤并通过旋转蒸发浓缩。使用甲苯:乙酸乙酯(1:3)作为洗脱剂在硅胶上过滤滤液,和产率为实施例 23A 3.56g(99%) 白色粉末。

[0379] 根据实施例 23 针对化合物 23A 描述的方法,制备化合物 23B,23C,23F,条件是实施例 22A 分别被实施例 22B,实施例 22C,实施例 22F 替代。

[0380]

	名称	结构	¹ H NMR(300MHz) 在 DMSO-d ₆ 内
23A	3,5-二氨基苯甲酸 8-[4-[(Z)-2-氰基-2-(4-氟苯基)乙烯基]苯氧基]辛酯		7.92 (d, 2H), 7.91 (s, 1H), 7.80-7.73 (m, 2H), 7.35 (dd, 2H), 7.09 (d, 2H), 6.43 (d, 2H), 6.02 (dd, 1H), 4.98 (s, broad, 4H), 4.16 (t, 2H), 4.05 (t, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.36 (m, 8H)
23B	3,5-二氨基苯甲酸 8-[4-[(Z)-1-氰基-2-(4-氟苯基)乙烯基]苯氧基]辛酯		7.96 (m, 2H), 7.91 (s, 1H), 7.65 (d, 2H), 7.38 (dd, 2H), 7.04 (d, 2H), 6.43 (d, 2H), 6.03 (dd, 1H), 4.99 (s, 4H), 4.16 (t, 2H), 4.02 (t, 2H), 1.70 (m, 4H), 1.36 (m, 8H)

[0381]

	基)乙烯基] 苯氧基]辛酯		
23 C	3,5-二氨基 苯甲酸 11-[4- [(Z)-2-氨基 -2-(4-氟苯 基)乙烯基] 苯氧基]十一 烷酯		7.92 (d, 2H), 7.91 (s, 1H), 7.80-7.73 (m, 2H), 7.35 (dd, 2H), 7.09 (d, 2H), 6.43 (d, 2H), 6.02 (dd, 1H), 4.99 (s broad, 4H), 4.16 (t, 2H), 4.05 (t, 2H), 1.74 (m, 2H), 1.66 (m, 2H), 1.36 (m, 14H)
23F	3,5-二氨基 苯甲酸 11-[4- [(Z)-2-氨基 -2-(4-氟苯 基)乙烯基] 基]-2-甲氧 基-苯氧基] 十一烷酯		7.91 (s, 1H), 7.79 (m, 2H), 7.66 (d, 1H), 7.55 (dd, 1H), 7.38 (m, 2H), 7.13 (d, 1H), 6.42 (d, 2H), 6.02 (t, 1H), 4.98 (s, 4H), 4.14 (t, 2H), 4.03 (t, 2H), 3.81 (s, 3H), 1.73 (m, 2H), 1.64 (m, 2H), 1.29 (m, 14H)

[0382] 实施例 24: 制备 PAA1

[0383] 将 469mg (2.4mmol) 1, 2, 3, 4- 环丁烷四羧酸加入到 1200mg (2.4mmol) 实施例 23A 产物在 6.6g NMP 内的溶液中。然后在 0℃ 下进行搅拌 2 小时。随后允许该混合物在室温下反应 21 小时。用 4.4mL NMP 稀释该聚合物混合物并在 150mL 水中沉淀, 在 40℃ 下真空干燥之后, 得到 1700mg 白色粉末形式的 PAA-1, $\eta = 0.38\text{dL/g}$ 。

[0384] 实施例 25: 制备 PAA-2 至 PAA-7

[0385] 类似于制备 PAA-1 (实施例 24), 由二胺 (参见下表) 与 2, 3, 5- 三羧基环戊基乙酸-1, 2:3, 4- 二酐制备 PAA-2 至 PAA-7。在下表中给出了分析数据。

[0386]

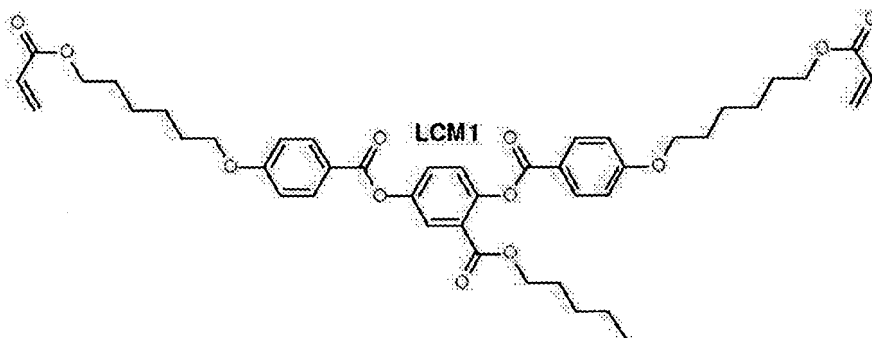
二胺	聚酰胺酸	粘度 (dL/g)
实施例 23A	PAA-4	0.52
实施例 23B	PAA-2	0.38

实施例 23C	PAA-3	0.37
实施例 23F	PAA-7	0.42

[0387] 实施例 26: 制备液晶可光聚合的单体配方 S2

[0388] 使用茴香醚作为溶剂, 制备 29.1wt% LCM1, 0.3wt% 光引发剂, 获自 Ciba SC 的 IRGACURE™369, 0.3wt% Tinuvine 123 和 0.3wt% BHT 的溶液。在室温下搅拌该溶液 30 分钟并在 0.20 μm PTFE hi-cap 上过滤。

[0389]



[0390] 实施例 27: 作为光校准材料施加

[0391] 在环戊酮中制备 2wt% 光反应性聚合物材料的溶液 S1。在室温下搅拌该溶液 30 分钟, 并在 0.20 μm PTFE hi-cap 上过滤。在玻璃基底上在 2000rpm 下旋涂该溶液, 然后在 180°C 下干燥 5 分钟。随后用来自汞高压灯的偏振 UVA 光辐照基底, 辐照方向垂直于基底表面。对于偏振来说, 使用 Moxtec 偏振器。使用 Moxtec 偏振器, 偏振的 UVA 的曝光能从 0.2 变化到 250mJ. cm⁻²。在用线性偏振光曝光的基底上, 在 800rpm 下旋涂配方 S2 (实施例 26), 然后在 50°C 下干燥 30 秒。随后用氮气氛围吹扫所得基底 30 秒, 然后在氮气氛围下, 用 1J. cm⁻² 的各向同性 UV 光曝光。将所制备的器件置于具有交叉偏振器的莱茨显微镜下, 并通过与该显微镜相连的光电倍增管, 在透明 (clear) 和暗态下独立地测量光强度, 并输送该结果到数字电压计上。根据下述方程式计算对比度比值:

[0392] 对比度 = $[I_{45} - I_{\text{offset}}] / [I_0 - I_{\text{offset}}]$, 其中:

[0393] I_0 (V) 是最小光强度, 即暗态

[0394] I_{45} (V) 是最大光强度, 即透明状态

[0395] I_{offset} (V) 是在没有涂布 S2 溶液的情况下测量的光强度

[0396] 针对每一化合物, 测量获得良好校准 (对比度 >800) 所需的最小能量。测量在该特定能量下的对比度。下表概述了来自实施例 11A, 实施例 11B, 实施例 11F, 实施例 11M, 实施例 11N, 实施例 11O, 实施例 11P, 实施例 11U, 实施例 11V, 实施例 11W, 实施例 11Y, 实施例 11I, 实施例 11S 的光反应性聚合物获得的结果。

[0397]

来自实施例	用于取向的 E_{min} (mJ. cm ²)	采用 E_{min} 的对比度
110	1.6	1800

11N	1.6	2600
11U	<0.6	4310
11V	<0.6	1190
11W	1	3400
11Y	1	900
11F	12	1100
11B	8	2220
11A	1.3	3200
11R	8	2300
11I	4	1200
11M	0.6	1600
11S	8	1400
11P	1.6	1300
11AA	1	1480
11AB	1.6	1470

[0398] 实施例 28:

[0399] 对于 $150\text{mJ} \cdot \text{cm}^{-2}$ 的偏振 UVA 的曝光能量来说, 测量来自实施例 110, 实施例 11N, 实施例 11F, 实施例 11E, 实施例 11M 的在实施例 27 中制备的器件的高对比度, 并列于下表中。

[0400]

来自实施例	对比度
110	5500
11N	8600
11F	7800
11E	6000
11M	5000

[0401] 实施例 29:

[0402] 方位角稳定性说明了在光校准材料上用线性偏振的 UV 光施加的第一曝光 E1 和随后根据第一辐照方向在 45° 下旋转样品之后,用具有 $E2 = E1$ 的这一相同光曝光的稳定性。在 0 和 45° 下的两次曝光的方法确定了通过施加变化的能量,LPP 取向的稳定性,若在另一平面角下进行补充曝光的话。使用环戊酮作为溶剂,制备 2wt% 由光反应性聚合物配方制造的溶液。在室温下搅拌该溶液 30 分钟,并在 $0.20\ \mu\text{m}$ PTFE hi-cap 上过滤。在玻璃基底上在 2000rpm 下旋涂该溶液,然后在 180°C 下干燥 5 分钟。随后用来自汞高压灯的偏振 UVA 光辐照该基底,辐照方向垂直于基底表面。对于偏振来说,使用 Moxtec 偏振器。使用 Moxtec 偏振器,偏振的 UVA 光的曝光能为 $128\text{mJ}\cdot\text{cm}^{-2}$ 。然后在移动段辅助下,由起始位置旋转样品 45° 。掩蔽第一曝光区,保持在 0° 下进行的参考曝光结果。用能量为 $128\text{mJ}\cdot\text{cm}^{-2}$ 的这一相同的偏振 UVA 光辐照其余基底。在用线性偏振光曝光的基底上在 800rpm 下旋涂配方 S2(实施例 26),然后在 50°C 下干燥 30 秒。随后用氮气氛围吹扫所得基底 30 秒,然后在氮气氛围下用 $1\text{J}\cdot\text{cm}^{-2}$ 各向同性的 UV 光曝光。在旋转段上,将所制备的器件置于偏振显微镜下,并将用 E1 曝光的第一区的暗态定义为参考 (0°) 位置。接下来将样品移动到用 $E1(0^\circ)+E2(45^\circ)$ 曝光的区,当 $E2 = E1$ 时。在旋转段辅助下发现暗态位置。测量参考位置和第二位置之间的角度差,即方位角的偏差,并在下表中针对下述光反应性聚合物报道。

[0403] 若方位角的偏差低于 6° ,则方位角的稳定性定义为非常好。若方位角的偏差介于 7° 至 15° ,则方位角的稳定性定义为好。若方位角的偏差介于 16° 至 20° ,则方位角的稳定性定义为中等。若方位角的偏差高于 21° ,则方位角的稳定性定义为差。在下表中概述了结果。

[0404]

来自实施例	方位角稳定性
110	非常好
11B	非常好
11A	非常好
11E	中等
11R	非常好
11I	非常好
11M	非常好
11N	好
11L	非常好
11S	非常好

11W	好
11Y	好
11AA	非常好
11AB	非常好

[0405] 实施例 30 :对于 IPS 模型来说,采用 PAA-1 (实施例 24) 作为光校准材料

[0406] 制备液晶单元 1,其中通过光反应性聚酰胺酸 PAA-1,校准该液晶,并在两个平面电极之间在单元间隙的每一侧上施加电场。

[0407] 通过在 NMP 内混合固体聚酰胺酸 PAA-1,并彻底搅拌,直到固体聚酰胺酸 PAA-1 溶解,制备 4.0% 聚酰胺酸 PAA-1 溶液,并添加第二溶剂丁基纤维素 (BC),和彻底搅拌整个组合,获得最终溶液。NMP 和丁基纤维素之间的溶剂比为 1:1。在两个 ITO 涂布的玻璃基底上,在 1700rpm 的旋转速度下旋涂上述聚合物溶液 30 秒。在旋涂之后,对基底进行烘烤工序,上述烘烤工序由在 130℃ 下预烘烤 1.5 分钟和在 200℃ 的温度下后烘烤 40 分钟组成。所得层厚为约 70nm。曝光这一基底,以便在线性偏振的 UV 光 (LPUV) 的方向和电极条的方向之间的角度为 78°。相对于基底表面的法向,LPUV 的入射角为 0°。偏振面在由基底法向和光的传播方向跨越 (span) 的平面内。所施加的曝光剂量为 500mJ/cm²。在 LPUV 曝光之后,用 2 个基底组装单元,曝光的聚合物层面向该单元的内侧。相对于彼此调节基底,使得诱导的校准方向彼此平行 (对应于反平行,即 180°,在通过擦拭工序校准的情况下擦拭的构造)。用液晶 MLC7067 (Merck KGA) 毛细填充该单元。之后,在约 92℃ 下任选地退火该单元 10 分钟,并缓慢地冷却到室温。在该单元热退火之后,在该单元内的液晶显示出非常确定和均匀的平面取向。

[0408] 实施例 31 :与实施例 30 一样,采用 PAA-1, PAA-2, PAA-3, PAA-4, PAA-7 制备单元。通过将该单元置于两个交叉的偏振器之间,检测在该单元内的液晶校准质量,并调节以获得暗态。若暗态没有显示出缺陷和液晶非常好地取向,则校准质量定义为非常好。若因该单元的一些区域内液晶轻微的不均匀取向导致暗态具有光泄露,则校准质量定义为中等。若液晶没有取向且不存在暗态,则校准质量定义为差。在 NB 模式 (交叉偏振器) 下,使用白光光源测量该单元的对比度。旋转偏振器,直到测量到最小透射 T_{min},然后在平行偏振器之间测定最大透射 T_{max}。

[0409] 对比度比值 = T_{max}/T_{min}

[0410] 该结果显示出对于根据本发明制造的单元来说的高对比度值。在下表中概述了结果。

[0411]

化合物	校准质量	对比度比值
PAA-1	非常好	1750-1850
PAA-2	非常好	1750-1850

PAA-3	非常好	1650-1750
PAA-4	非常好	1750-1850
PAA-7	非常好	1600-1700

[0412] 实施例 32 :作为光校准材料施加

[0413] 与实施例 27 一样制备校准层,所不同的是使用来自实施例 12- 实施例 17 的材料,和随后用偏振 UVB 和 UVA 辐照基底。针对每一化合物,测定在 LCP 薄膜内没有缺陷的情况下,获得良好校准质量所需的最小能量。还与实施例 29 一样,测量方位稳定性。在下表中给出了结果。

[0414]

来自实施 例	采用 UVA, 用于取向的 $E_{\min}$ (mJ.cm ²)	采用 UVB, 用于取向的 $E_{\min}$ (mJ.cm ²)	方位稳定性
12	32	4	好
13	12	4	好
14	12	4	好
15	16	4	中等
16	8	4	好