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RAN 6220/109

Polymers

9605598-3

The invention is concerned with novel linear and cyclic polymers or oligomers having a photoreactive ethene group for use as orientating layers for liquid crystals.

The alignment of liquid crystal phases in cells can be brought about in various ways and is usually effected by rubbing a glass plate coated with a polymer layer or by the inclined vapour deposition of a SiO_x layer on a glass plate. Mainly uniformly aligned layers can be produced in this manner.

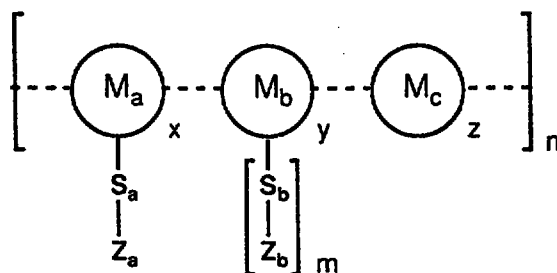
It is, however, also possible to obtain a structured orientation of the liquid crystal phase. This can be achieved, for example, by coating a glass plate with a polymer with which are admixed, for example, photochemically orientatable dyestuff molecules or photochemically dimerizable molecules, as described, for example, in EP-A-0445629. These methods are, however, not optimal, since on the one hand the solubility of such orientatable molecules in the polymer is limited and on the other hand the stability with time can not be guaranteed to a sufficient extent. A further possibility for the production of photochemically orientatable polymer layers is described, for example, in Jpn. J. Appl. Phys. Vol. 31 (1992), 2155 and comprises esterifying the free hydroxy groups on the polymer with dimerizable units. A disadvantage of this method is, however, the fact that the esterification of the free hydroxy groups on the polymer with photochemically dimerizable units usually leads to a non-reproducible and, above all, to an incomplete conversion. The free hydroxy groups still present in the orientating layer lead to an undesired ion solubility.

There is therefore a need to find an orientating layer which no longer has the aforementioned disadvantages.

The invention is accordingly concerned with polymers having isomerization/dimerization units of the general formula:

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wherein

M_a, M_b, M_c signify monomer units for homo- or copolymers;

x, y, z indicate mole fractions of the copolymers,
whereby in each case
 $0 < x \leq 1; 0 \leq y \leq 1$ and $0 \leq z < 1$;

S_a, S_b represent spacer units;

Z_a, Z_b represent molecule units which can undergo
photochemical isomerization/dimerization;

n is a magnitude of 4-100 000 and

m is 0 or 1.

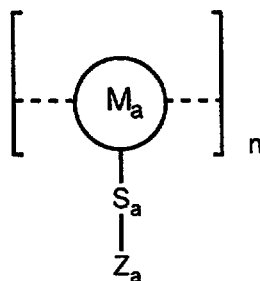
The monomer units M_a, M_b and M_c set forth in general formula 1 are units for the formation of homopolymers or copolymers and have, in the scope of the present invention, the structures which are usual in polymer chemistry. Such monomer units are, for example, acrylate, methacrylate, 2-chloroacrylate, 2-phenylacrylate, acryloylphenylene, acrylamide, methacrylamide, 2-chloroacrylamide, 2-phenylacrylamide, vinyl ether, styrene derivatives, vinyl ester, maleic acid derivatives, fumaric acid derivatives, siloxanes, epoxides and the like. Acrylate, methacrylate, 2-chloroacrylate, acrylamide, methacrylamide, 2-chloroacrylamide, styrene derivatives, siloxanes and the like are preferred monomer units.

Under the term "copolymers" there are to be understood not only statistical copolymers but also alternating copolymers, for example alternating copolymers from maleic acid derivatives with styrene. Statistical copolymers are preferably used. Homopolymers embrace linear and cyclic polymers such as, for example, cyclic polysiloxane.

Polymers in which $z = 0$, but especially homopolymers of general formula 1-A:

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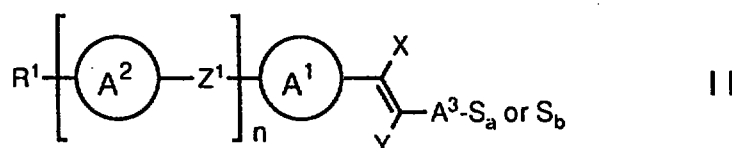
I-A,

are especially preferred.

The spacer units S_a and, respectively, S_b join the isomerization/dimerization unit (Z_a and, respectively, Z_b) with the monomer unit (M_a and, respectively, M_b). Such spacer units are known per se. In the present instance the term "spacer units" S_a and S_b signifies, for example, independently of one another, a n-alkylene chain with 1 to 10, preferably with 1 to 4, carbon atoms, a cycloalkylene group with 3 to 8 carbon atoms, preferably with 5 or 6 carbon atoms, or phenylene, which can be substituted with lower alkyl or lower alkoxy, -CN, -NO₂, but especially with halogen, or carbonate, an ester group, an ether group and the like or a combination of the said groups.

Methylene, 1,2-ethylene, 1,3-propylene, 1,4-butylene, cyclopentane-1,2-diyl, cyclopentane-1,3-diyl, cyclohexane-1,3-diyl, cyclohexane-1,4-diyl, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, ethyleneoxy, ethyleneoxycarbonyl, ethylenecarboxyl and the like are examples of preferred spacer units (S_a and S_b).

The isomerization/dimerization units Z_a and Z_b are molecule units which can undergo either photochemical cis/trans-isomerization and photochemical [2 + 2] cycloaddition and thus lead to a cross-linking of the polymer or oligomer. The isomerization/dimerization units Z_a and Z_b are, as already mentioned, linked via the spacer S_a to the monomer unit M_a , or via a spacer S_b to the monomer unit M_b and each independently have the general formula



In formula II,

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- ring A¹ signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- ring A² signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-piperidyl;
- A³ signifies -COO-, -CO-E-, 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- E signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- Z¹ signifies a single covalent bond, -CH₂CH₂-, -COO-, -OCH₂-, -C≡C-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O- or the trans form of -OCH₂CH=CH-, -CH=CHCH₂O-, -(CH₂)₂CH=CH- or -CH=CH(CH₂)₂-;
- R¹ signifies hydrogen, halogen, cyano, alkyl with 1 to 12 carbon atoms, which is optionally substituted with fluorine and in which optionally 1 or 2 non-adjacent -CH₂- groups can be replaced by oxygen, -COO-, -OOC-, -CO- and/or a -CH₂CH₂- group can be replaced by -CH=CH-;
- n signifies 0, 1 or 2;
- X, Y each independently signify hydrogen, halogen, cyano, alkyl with 1 to 12 carbon atoms which is optionally substituted with fluorine and in which optionally

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1 or 2 non-adjacent $-CH_2-$ groups can be replaced by oxygen, $-COO-$, $-OOC-$, $-CO-$ and/or $-CH=CH-$; and

S_a, S_b , signify spacer units;

with the proviso that simultaneously A^3 does not signify $-COO-$, n does not signify 0, A^1 does not signify phenyl, R^1 does not signify hydrogen or methoxy and S_a and, respectively, S_b do not signify a single bond.

The isomerization/dimerization units of general formula II, the ethene groups of which are not or only to a small extent incorporated into the polymer under the polymerization conditions, can be selectively aligned, after the application of the polymer layer to a carrier, by irradiation with linear polarized light. This takes place either by isomerization of the ethene group, by dimerization of the ethene group or by simultaneous isomerization and dimerization of these ethene groups. Very specific surface regions can now be aligned by the selective irradiation of the molecule units of formula II and these regions are also simultaneously stabilized by the dimerization.

The term "1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen" embraces in the scope of the present application 1,4-phenylene, 2-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2,6-difluoro-1,4-phenylene, 2-chloro-1,4-phenylene, 2,3-dichloro-1,4-phenylene, 2,6-dichloro-1,4-phenylene, 2-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2-bromo-1,4-phenylene, 2-methyl-1,4-phenylene, as well as pyridine-2,5-diyl, pyrimidine-2,5-diyl and the like. 1,4-Phenylene, 2-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2,6-difluoro-1,4-phenylene, pyridine-2,5-diyl or pyrimidin-2,5-diyl are especially preferred.

The term "1,4-or 2,6-naphthylene, in which a CH group can be replaced by nitrogen" embraces in the scope of the present invention 1,4-naphthylene, 2,6-naphthylene, 1-benzazine-2,6-diyl and 2-benzazine-1,4-diyl.

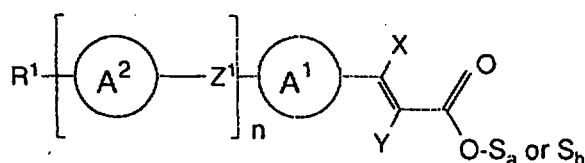
The term "alkyl with 1 to 12 carbon atoms, which is optionally substituted with fluorine and in which optionally 1 or 2 non-adjacent $-CH_2-$ groups can be replaced by oxygen, $-COO-$, $-OOC-$, $-CO-$ and/or a $-CH_2CH_2-$ group can be replaced by $-CH=CH-$ " embraces in the scope of the present invention straight-chain and branched (optionally chiral) residues such as alkyl, alkenyl,



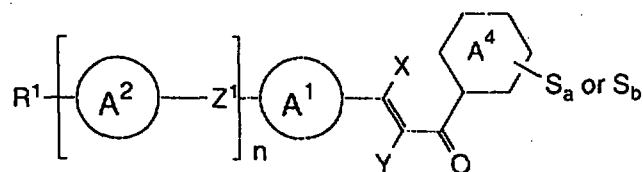
alkoxy, alkenyloxy alkoxyalkyl, alkenyloxyalkyl, alkoxyalkenyl, 1-fluoroalkyl, 1,1-difluoroalkyl, 2-fluoroalkyl, 2-fluoroalkoxy, terminal fluoroalkyl, terminal difluoromethylalkyl, terminal trifluoromethylalkyl, terminal trifluoromethylalkoxy, and the like with 1 or, respectively, 2 to 12 carbon atoms. Examples of preferred residues are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 1-methylpropyl, 1-methylheptyl, 2-methylbutyl, 3-methylpentyl, vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 4-pentenyl, 4Z-hexenyl, 5-hexenyl, 6-heptenyl, 7-octenyl, methoxy, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, 1-methylpropyloxy, 1-methylheptyloxy, 2-methylbutyloxy, allyloxy, 2E-butenyloxy, 2E-pentenlyoxy, 3-butenyloxy, 3Z-pentenlyoxy, 4-pentenlyoxy, 5-hexenyloxy, 6-heptenyloxy, 7-octenyloxy, 2-methoxyethyl, 3-methoxypropyl, 3-methoxy-1E-propenyl, 1-fluoropropyl, 1-fluoropentyl, 2-fluoropropyl, 2,2-difluoropropyl, 3-fluoropropyl, 3,3-difluoropropyl, 3,3,3-trifluoropropyl, 2-fluoropropyloxy, 3-fluoropropyloxy, 2,2-difluorovinyl, 2-(3,3-difluoro)propenyl and the like. Especially preferred residues have 1 or, respectively, 2 to 6 carbon atoms.

The term "halogen" denotes in the scope of the present invention fluorine, chlorine, bromine and iodine, but especially fluorine and chlorine.

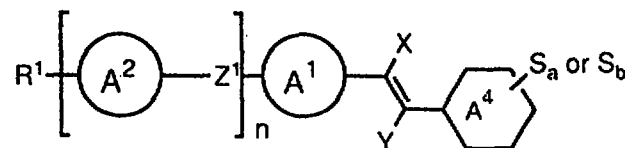
Preferred isomerization/dimerization units of general formula II are



II-A



II-B



II-C

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in which formulae II-A, II-B and II-C

ring A¹ signifies 1,4-phenylene, which is unsubstituted or substituted with halogen, or pyrimidine-2,5-diyl, pyridine-2,5-diyl, 2,5-thiophenylene, 2,5-furanylene, 1,4-naphthylene or 2,6-naphthylene;

ring A² signifies 1,4-phenylene, which is unsubstituted or substituted with halogen, or pyrimidine-2,5-diyl, pyridine-2,5-diyl, 2,5-thiophenylene, 2,5-furanylene, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-piperidyl;

ring A⁴ signifies 1,4-phenylene, which is unsubstituted or substituted with halogen;

Z¹ signifies a single covalent bond, -CH₂CH₂-, -COO-, -OCH₂-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

R¹ signifies halogen, cyano, alkyl with 1 to 12 carbon atoms, which is optionally substituted with fluorine and in which optionally 1 or 2 non-adjacent -CH₂- groups can be replaced by oxygen or -COO- and/or a -CH₂CH₂- group can be replaced by -CH=CH-;

n signifies 0, 1 or 2;

X signifies hydrogen or alkyl with 1 to 6 carbon atoms, which is optionally substituted with halogen;

Y signifies hydrogen, cyano, -COO-alkyl, alkyl with 1 to 6 carbon atoms, which is optionally substituted with fluorine; and

S_aS_b signify spacer units;

with the proviso that in formula II-A simultaneously n does not signify 0, A¹ does not signify phenyl, R¹ does not signify hydrogen or methoxy, X and Y do not signify hydrogen and S_a or S_b does not signify a single bond.

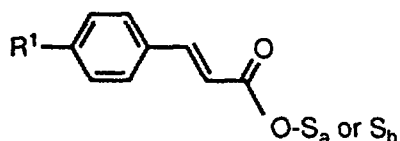
Preferred compounds of general formula I-A to I-C are those in which X signifies hydrogen and Y signifies hydrogen,

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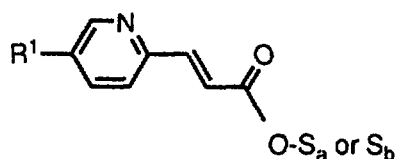


cyano or alkyl with 1 to 6 carbon atoms, which is optionally substituted with fluorine; those in which X and Y represent hydrogen are, however, especially preferred.

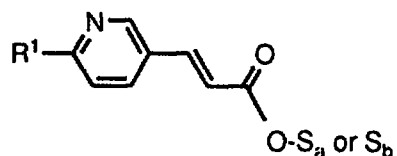
Particularly preferred isomerization/dimerization units are those of general formula II-A such as, for example,



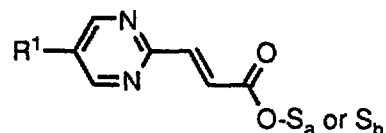
IIa



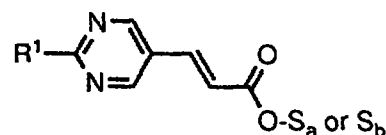
IIb



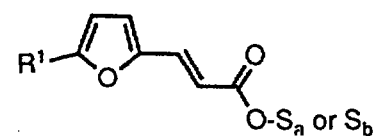
IIc



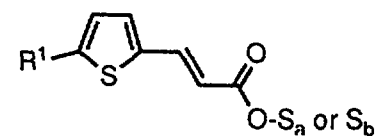
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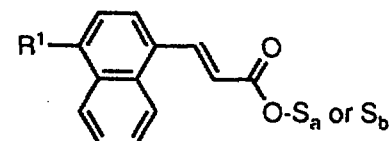
IIe



IIIf



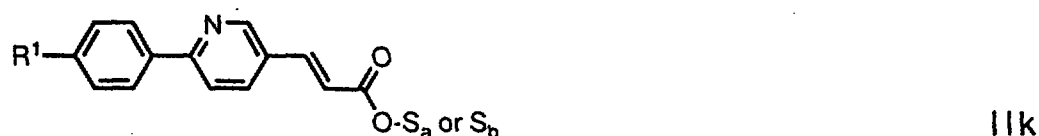
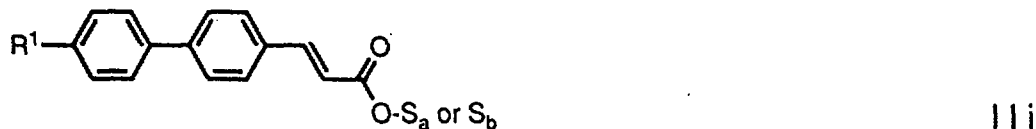
IIg



IIh

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wherein R^1 signifies halogen, cyano, alkyl or alkoxy with 1 to 6 carbon atoms, with the proviso that in formula IIa simultaneously R^1 does not signify hydrogen or methoxy and S_a or S_b does not signify a single bond.

The polymers of formula I are distinguished by the fact that they are readily accessible. The monomers are firstly synthesized from the individual components, i.e. from the isomerization/dimerization unit of formula II, the spacers (S_a , S_b) and the polymerizable parts (M_a , M_b or M_c). The formation of the polymer is subsequently effected in a manner known per se. The polymerization can be effected, for example, in the melt or in solution with the exclusion of oxygen and in the presence of a radical initiator which can generate radicals thermally, photochemically or by a Redox reaction. The reaction can be effected in a temperature range of -10°C to 120°C , preferably in a range of 20°C to 100°C .

For the production of polymer layers in regions selectively limited by area, a solution of the polymer material obtained can, for example, firstly be prepared and then spread out in a spin-coating apparatus on a carrier (e.g. a glass plate coated with indium-tin oxide) (ITO) coated with an electrode such that homogeneous layers of $0.05\text{-}50\text{ }\mu\text{m}$ thickness result. Simultaneously, irradiation can be applied to the region to be isomerized and dimerized (to be cross-linked), e.g. with a mercury high-pressure lamp, a xenon lamp or a pulsed UV laser using a polarizer and optionally a mask for the formation of structures. The duration of irradiation depends on the capacity of the individual lamps and can vary from a few minutes to several hours. The cross-linkage can, however, also be effected by



irradiating the homogeneous layer using filters which e.g. let through only radiation suitable for the cross-linkage reaction.

The polymers in accordance with the invention are illustrated in more detail by the following Examples. In the following Examples T_g signifies the glass temperature, Δc_p signifies the change in the specific heat capacity at constant pressure, ΔH signifies the transition enthalpy, $\log I_0/I$ signifies the extinction, C signifies a crystalline phase, S signifies a smectic phase, N signifies a nematic phase and I signifies the isotropic phase.

Example 1

1 g of methacryloyloxyethyl 3-(E)-[4-pentyl-4'-biphenyl]acrylate and 0.002 g of azobisisobutyronitrile were dissolved in 4 ml of tetrahydrofuran. The solution was flushed for 10 min. with a weak nitrogen stream and the reaction vessel was subsequently closed air-tight. The solution was heated to 60°C for 24 hours. Thereafter, the reaction vessel was opened and the solution was diluted with 5 ml of tetrahydrofuran while stirring. Subsequently, the diluted solution was added dropwise to 450 ml of diethyl ether while stirring at room temperature. The separated polymer was filtered off, dried, dissolved in 30 ml of dichloromethane and this solution was added dropwise to 450 ml of diethyl ether. This procedure was repeated twice. After filtration and drying at 50°C in a vacuum this gave 0.4 g of poly-(methacryloyloxyethyl 3-(E)-[4-pentyl-4'-biphenyl]acrylate), T_g 123°C, cl.p. (S-I) 160°C;

The methacryloyloxyethyl 3-(E)-[4-pentyl-4'-biphenyl]acrylate used as the starting material was prepared as follows:

(a). A solution of 10 g of 4-pentyl-4'-cyanobiphenyl in 150 ml of toluene was treated dropwise at 0°C with 65 ml of a 1M solution of diisobutylaluminium hydride in toluene while gassing with nitrogen. The reaction mixture was stirred at room temperature overnight, then treated dropwise with 340 ml of 1N sulphuric acid, stirred at room temperature for 1 hour, poured into 1,000 ml of water and then extracted three times with 100 ml of ethyl acetate each time. The combined organic phases were washed twice with 50 ml of saturated sodium chloride solution each time, dried over magnesium sulphate, filtered and subsequently

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concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 9:1) gave 10.1 g of 4-pentyl-4'-biphenylcarboxaldehyde.

(b). A mixture of 11.9 g of phosphonoacetic acid P,P-diethyl-trimethyl-silyl ester in 370 ml of absolute tetrahydrofuran was placed at 0°C while gassing with nitrogen and then treated dropwise with 27.7 ml of a 1.6M solution of butyllithium in hexane. The reaction mixture was stirred at room temperature for 2 hours, then treated with a solution of 10.1 g of 4-pentyl-4'-biphenylcarboxaldehyde and 15 ml of absolute tetrahydrofuran, stirred at room temperature for a further 1.5 hours, poured into 100 ml of water and then extracted three times with 50 ml of ethyl acetate each time. The combined organic phases were washed twice with 50 ml of saturated sodium chloride solution each time, dried over magnesium sulphate, filtered and subsequently concentrated. Two-fold recrystallization of the crude product from ethyl alcohol gave 17.0 g of 3-(E)-[4-pentyl-4'-biphenyl]acrylic acid, m.p. (C-N) 209°C and cl.p. (N-I) 284°C (decompositon).

(c). 9.4 g of N,N'-dicyclohexylcarbodiimide were added at 0°C within 15 minutes while stirring to a solution of 2-hydroxyethyl methacrylate, 11.6 g of 3-(E)-[4-pentyl-4'-biphenyl]acrylic acid and 1.21 g of 4-(dimethylamino)pyridine in 300 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature overnight, then filtered, the filtrate was poured into water and extracted three times with 50 ml of ethyl acetate each time. The combined organic phases were washed twice with 50 ml of saturated sodium chloride solution each time, dried over magnesium sulphate, filtered and subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 9:1) and two-fold recrystallization from ethyl alcohol of the fractions which were pure according to thin-layer chromatography gave 4.5 g of methacryloyloxyethyl 3-(E)-[4-pentyl-4'-biphenyl]acrylate, m.p. 72°C.

The following compounds can be prepared in an analogous manner:

Poly(methacryloyloxyethyl 3-(E)-[4-methyl-4'-biphenyl]acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-ethyl-4'-biphenyl]acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-propyl-4'-biphenyl]acrylate);



poly(methacryloyloxyethyl 3-(E)-[4-butyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-hexyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-heptyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-octyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxypropyl 3-(E)-[4-pentyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxybutyl 3-(E)-[4-pentyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxypropyl 3-(E)-[4-pentyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxyhexyl 3-(E)-[4-pentyl-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-methyloxy-4'-
biphenyl]acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-ethoxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-propyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-butyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-hexyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-heptyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-octyloxy-4'-biphenyl]-
acrylate), Tg. 106°C, (S-I) 170°C;

poly(methacryloyloxypropyl 3-(E)-[4-octyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxybutyl 3-(E)-[4-octyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxypropyl 3-(E)-[4-octyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyhexyl 3-(E)-[4-octyloxy-4'-biphenyl]-
acrylate);

poly(methacryloyloxyethyl 3-(E)-[4-cyano-4'-biphenyl]-
acrylate), Tg. 134°C;

poly(methacryloyloxypropyl 3-(E)-[4-cyano-4'-biphenyl]-
acrylate);

poly(methacryloyloxybutyl 3-(E)-[4-cyano-4'-biphenyl]-
acrylate);

poly(acryloyloxybutyl 3-(E)-[4-[(R)-2-octyloxy]-4'-
biphenyl]acrylate);

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poly(methacryloyloxypropyl acrylate);	3-(E)-[4-cyano-4'-biphenyl]-
poly(methacryloyloxyhexyl acrylate);	3-(E)-[4-cyano-4'-biphenyl]-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-methylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-ethylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-propylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-butylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate), Tg. 88°C;	3-(E)-[4-(trans-4-pentylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-hexylcyclo-
poly(methacryloyloxyethyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-heptylcyclo-
poly(methacryloyloxypropyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-pentylcyclo-
poly(methacryloyloxybutyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-pentylcyclo-
poly(methacryloyloxypropyl hexyl)phenyl]acrylate);	3-(E)-[4-(trans-4-pentylcyclo-
poly(methacryloyloxyhexyl hexyl)phenyl]acrylate).	3-(E)-[4-(trans-4-pentylcyclo-

Example 2

1.5 g of 4-methacryloyloxybutyl (E)-3-[4-(4-methoxyphenyl carbonyloxy)phenyl]acrylate and 0.003 g of azobisisobutyronitrile were dissolved in 6.8 ml of tetrahydrofuran. The solution was flushed for 10 min. with a weak argon stream and subsequently the reaction vessel was closed air-tight. The solution was heated to 60°C for 20 hours. Thereafter, the reaction vessel was opened and the solution was diluted with 3.5 ml of tetrahydrofuran while stirring. Subsequently, the diluted solution was added dropwise to 300 ml of diethyl ether at room temperature while stirring. The separated polymer was filtered off, dried, dissolved in 10 ml of dichloromethane and this solution was added dropwise to 300 ml of diethyl ether. This procedure was repeated twice. After filtration and drying at 50°C in a vacuum this gave 1.15 g of poly(4-methacryloyloxybutyl (E)-3-[4-(4-methoxyphenylcarbonyloxy)phenyl]acrylate). The polymer has a glass stage at $T_g = 38^\circ\text{C}$ ($\Delta c_p = 0.17 \text{ J/gK}$) and a clearing point (S_A -I) at 202°C ($\Delta H = 6.9 \text{ J/g}$).

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The 4-methacryloyloxybutyl (E)-3-[4-(4-methoxyphenyl-carbonyloxy)phenyl]acrylate used as the starting material was prepared as follows:

a) 5 g of (E)-4-hydroxycinnamic acid were dissolved in a solution of 2.8 g of potassium hydroxide in 25 ml of water. Four 1 g portions of ethyl chloroformate were added to the ice-cooled solution and the mixture was stirred intensively for 10 minutes after each addition. The reaction mixture was stirred at 0°C for a further 30 minutes and subsequently neutralized with 2N hydrochloric acid. The crude product was filtered off and recrystallised twice from ethanol/water (vol. 8:2). This gave 5.7 g of 4-(E)-ethyloxycarbonyloxycinnamic acid, m.p. 173-176°C.

b) A solution of 5.2 g of 4-(E)-ethyloxycarbonyloxycinnamic acid in 20 ml of thionyl chloride and 0.05 ml of N,N-dimethylformamide was heated under reflux for 3 hours. Subsequently, excess thionyl chloride was distilled off. 3.3 g of 4-hydroxybutyl methacrylate were added dropwise to a solution of the resulting 4-(E)-ethyloxycarbonyloxycinnamic acid chloride in 15 ml of pyridine while stirring at 0°C within 15 minutes. The reaction mixture was stirred at room temperature for a further 12 hours, then poured into water and extracted three times with 50 ml of ethyl acetate each time. The combined organic phases were dried over magnesium sulphate, filtered and subsequently concentrated. Chromatographic purification on silica gel with hexane/ethyl acetate (vol. 7:3) gave 3 g of 4-methacryloyloxybutyl (E)-3-(4-ethoxycarbonyloxyphenyl)acrylate, m.p. 54-56°C.

c) 5 g of 4-methacryloyloxybutyl (E)-3-(4-ethoxycarbonyloxyphenyl)acrylate were dissolved in 40 ml of pyridine and treated at room temperature with a mixture of 60 ml of acetone and 7 ml of 25% aqueous ammonia solution. The reaction mixture was stirred at room temperature for 12 hours. After distillation of the acetone the mixture was neutralized with 2N hydrochloric acid, diluted with 100 ml of water and subsequently extracted 3 times with 100 ml of diethyl ether each time. The combined organic phases were dried over sodium sulphate, filtered and concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 7:3) gave 4-methacryloyloxybutyl (E)-3-(4-hydroxyphenyl)acrylate.

d) 2.0 g of 4-methoxybenzoyl chloride in 25 ml of dichloromethane were added dropwise at 0°C while stirring within 30 min. to a



solution of 3.5 g of 4-methacryloyloxybutyl (E)-3-(4-hydroxyphenyl)acrylate and 1.2 g of triethylamine in 40 ml of dichloromethane. The reaction mixture was stirred at room temperature overnight, then filtered and subsequently concentrated. Chromatographic purification of the residue on silica gel with hexane/ethyl acetate (vol. 7:3) and two-fold recrystallization from ethanol gave 4.5 g of 4-methacryloyloxybutyl (E)-3-[4-(4-methoxyphenylcarbonyloxy)phenyl]acrylate, m.p. 89-90°C.

The following compounds can be prepared in analogous manner:

poly(methacryloyloxyethyl 3-(E)-[4-(4-methoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-ethoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-propoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-butyloxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-pentyloxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-hexyloxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-heptyloxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-octyloxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxypropyl 3-(E)-[4-(4-methoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxypropyl 3-(E)-[4-(4-methoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyhexyl 3-(E)-[4-(4-methoxybenzoyloxy)phenyl]acrylate);
 poly(methacryloyloxyethyl 3-(E)-[4-(4-[(S)-2-methylbutyloxy]benzoyloxy)phenyl]acrylate);
 poly(acryloyloxybutyl 3-(E)-[4-(4-methoxybenzoyloxy)phenyl]acrylate).

Example 3

2.5 g of methacryloyloxyethyl (E)-3-4(4-methoxyphenyl)-acrylate) and 2.5 g of 2-methacryloyloxyethyl (E)-3-(4-chlorophenyl)acrylate as well as 0.014 g of azobisisobutyronitrile were dissolved in 35 ml of tetrahydrofuran. The



solution was flushed for 10 minutes with a weak argon stream and the reaction vessel was subsequently closed air-tight. The solution was heated to 60°C for 24 hours. Thereafter, the reaction vessel was opened and the solution was diluted with 7.5 ml of tetrahydrofuran while stirring. Subsequently, the diluted solution was added dropwise to 500 ml of diethyl ether while stirring at room temperature. The separated polymer was filtered off, dried, dissolved in 40 ml of dichloromethane and this solution was added dropwise to 500 ml of diethyl ether. This procedure was repeated twice. After filtration and drying at 50°C in a vacuum this gave 3.0 g of poly(2-methacryloyl-oxyethyl (E)-3-(4-methoxyphenyl)acrylate-co-2-methacryloyloxyethyl (E)-3-(4-chlorophenyl)acrylate). The polymer has a glass stage at $T_g = 74^\circ\text{C}$. λ_{max} . (0.586 mg/100 ml CH_2Cl_2): 227 nm, ($\log I_0/I$) = 0.213), 287.8nm, ($\log I_0/I$ = 0.367).

The monomers used as the starting materials were prepared as follows:

50 g of 4-(E)-chlorocinnamic acid, 33.9 g of 2-hydroxyethyl methacrylate and 0.3 g of 4-dimethylaminopyridine were placed in 200 ml of tetrahydrofuran. A solution of 57.2 g of dicyclohexylcarbodiimide in 100 ml of tetrahydrofuran was added dropwise at room temperature within 120 minutes. The mixture was stirred at room temperature for a further 28 hours. Subsequently, the precipitated N,N'-dicyclohexylurea was filtered off and washed with 100 ml of tetrahydrofuran. After distillation of the tetrahydrofuran the residue was dissolved in 300 ml of dichloromethane. The dichloromethane solution was washed with 200 ml of 5% acetic acid and subsequently three times with 250 ml of water each time and dried over sodium sulphate. After removing the solvent the residue was recrystallized from ethanol at -50°C . This gave 20.4 g of 2-methacryloyloxyethyl (E)-3-(4-chlorophenyl)acrylate as white crystals with a melting point of $58-60^\circ\text{C}$.

2-Methacryloyloxyethyl (E)-3-(4-methoxyphenyl)-acrylate with a melting point of $35-36^\circ\text{C}$ was prepared analogously thereto.

The following polymers can be prepared in an analogous manner:

poly(2-methacryloyloxyethyl (E)-3-(4-cyanophenyl)-acrylate-co-2-methacryloyloxyethyl (E)-3-(4-methoxyphenyl)-acrylate);

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poly(2-methacryloyloxypropyl (E)-3-(4-cyanophenyl)-acrylate-co-2-methacryloyloxyhexyl (E)-3-(4-cyanophenyl)-acrylate);

poly(acryloyloxybutyl (E)-3-(4-cyanophenyl)acrylate-co-2-methacryloyloxyethyl (E)-3-(4-methoxyphenyl)-(Z)-3-methylacrylate);

poly(acryloyloxybutyl (E)-3-(4-methoxyphenyl)-2-carboxyethyl-acrylate-co-acryloyloxybutyl (Z)-3-(4-methoxyphenyl)-2-carboxyethyl-acrylate);

poly(styryl-4-carbonyloxyhexyl (E)-3-(4-cyanophenyl)acrylate-co-styryl-4-carbonyloxyhexyl (E)-3-(4-methoxyphenyl)acrylate);

poly(2-methacryloyloxyethyl (E)-3-(4-cyanophenyl)acrylate co-2-methacryloyloxyethyl (E)-3-(4-methoxyphenyl)acrylate);

poly(2-chloroacryloyloxyethyl (E)-3-(4-chlorophenyl)acrylate-co-2-chloroacryloyloxyethyl (E)-3-(4-methoxyphenyl)acrylate);

poly(2-methacrylamidoethyl (E)-3-(4-cyanophenyl)-acrylate-co-2-methacrylamidobutyl 3- (E)-[4-propyloxy-4'-biphenyl]acrylate));

poly(2-chloroacrylamidoethyl (E)-3-(4-cyano-4'-biphenyl)acrylate-co-2-chloroacrylamidoethyl 3-(E)-[4-methyloxyphenyl]acrylate));

poly(acrylamidomethyl (E)-3-(4-butyloxyphenyl)acrylate-co-acrylamidobutyl 3-(E)-[4-butyloxy-4'-biphenyl]acrylate));

poly(2-methacrylamidoethyl (E)-3-(4-octyloxy-4'-biphenyl)acrylate-co-2-acrylamidobutyl 3-(E)-[4-[(R)-2-octyloxy]-4'-biphenyl]acrylate));

poly(2-methacryloyloxybutyl (E)-3-(4-ethyloxyphenyl)(Z)-3-methyl-acrylate-co-2-methacryloyloxyethyl (E)-3-(4-methoxy-4'-biphenyl)-2-cyanoacrylate);

poly(methacryloyloxybutyl 3-(E)-[4-(trans-4-butylcyclohexyl)phenyl]-3-(Z)-methylacrylate-co-styrene);

poly(acryloyloxyethyl-3-(E)-[4-octyloxy-4'-biphenyl]-acrylate-co-methylacrylate);

poly(ethyl methacrylate-co-methacryloyloxyethyl 3-(E)-[4-(4-propoxybenzoyloxy)phenyl]acrylate);

poly(methacrylamidoethyl (E)-3-(4-propyloxyphenyl)-acrylate-co-methyl methacrylamide);

poly(2-chloroacryloyloxyhexyl 3-(E)-[4-(trans-4-methylcyclohexyl)phenyl]acrylate-co-methyl 2-chloroacrylate);

poly(2-chloroacryloyloxypentyl (E)-3-(4-methoxy-4'-biphenyl)-2-carboxyethyl-acrylate-co-2-chloroacryloyloxybutyl (Z)-3-(4-methoxy-4'-biphenyl)-2-carboxyethyl-acrylate-co-methyl 2-chloroacrylate);

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poly(ethyl 2-methacrylate-co-2-methacryloyloxypropyl (E)-3-(4-pentyloxyphenyl)acrylate-co-2-methacryloyloxybutyl (E)-3-(4-[(S)-2-methylbutyloxy]-4'-biphenyl)-2-carboxyethyl-acrylate);

poly(methacryloyloxypropyl 3-(E)-[4-(trans-4-butylcyclohexyl)phenyl]-3-(Z)-methylacrylate-co-2-methacryloyloxypropyl (E)-3-(4-[(R)-2-octyloxy]phenyl)-3-(Z)-methylacrylate-co-styrene).

Example 4

2.4 g of but-3-ene 3-phenylacrylate and 0.6 g of poly(methyl-hydrogen-siloxane) were dissolved in 8 ml of toluene (thiophene-free). The solution was flushed through a septum on the reaction vessel for 10 minutes with a weak argon stream. Subsequently, 20 μ l of a platinum-divinyltetramethyldisiloxane solution (mfr. PETRARCH SYSTEMS, PC075) were sprayed into the reaction mixture at room temperature while stirring. The reaction mixture was stirred at room temperature for 30 minutes and at 60°C for 18 hours. Subsequently, the reaction mixture was added dropwise to 200 ml of n-hexane while stirring. The precipitated polymer was separated, dissolved in 10 ml of toluene and again precipitated in 200 ml of n-hexane. This procedure was repeated twice. After drying in a high vacuum this gave 1.8 g of poly[(butyl-3-phenylacrylate)-methyl siloxane] with a glass stage $T_g = -25^\circ\text{C}$, $\Delta c_p = 0.31 \text{ J/gK}$.

The but-3-ene 3-phenylacrylate used as the starting material was prepared as follows:

22.2 g of cinnamic acid, 12.5 g of but-3-en-1-al and 0.2 g of 4-N,N-dimethylaminopyridine were placed in 80 ml of dichloromethane. A solution of 33.05 g of dicyclohexylcarbodiimide in 80 ml of dichloromethane was added dropwise at 5-10°C within 120 minutes. The mixture was stirred at room temperature for a further 18 hours. Subsequently, the precipitated N,N'-dicyclohexylurea was filtered off and washed with 150 ml of dichloromethane. The dichloromethane solution was washed with 200 ml of 5% acetic acid and subsequently three times with 250 ml of water each time, filtered and dried over sodium sulphate. After concentrating the solution the residue was chromatographed on silica gel with dichloromethane. After drying in a high vacuum this gave 22.1 g of but-3-ene 3-phenylacrylate as a colourless liquid.

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The following compounds can be prepared in an analogous manner:

Poly(methyl-[propyl-3-(E)-(4-methyloxy-4'-biphenyl)-acrylate siloxane);

poly(methyl-{pentyl-3-(E)-[4-(trans-4-propylcyclohexyl)phenyl]acrylate} siloxane);

poly(methyl-{hexyl-3-(E)-[4-(4-methoxybenzoyl)phenyl]acrylate} siloxane);

1,3,5,7-tetra[butyl-3-(E)-(4-methoxy-4'-biphenyl)acrylate]-1,3,5,7-tetramethyl-cyclotetrasiloxane;

poly(methyl-[butyl-3-(E)-(4-methoxyphenyl)acrylate] siloxane);

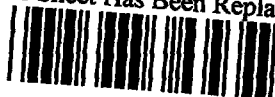
poly(methyl-[butyl-(E)-3-(4-methoxyphenyl)acrylate] siloxane-co-methyl-[propyl-3-(E)-[4-ethyloxy-4'-biphenyl]acrylate] siloxane);

poly(dimethylsiloxane-co-methyl-[butyl-3-(E)-[4-methyloxy-4'-biphenyl]acrylate] siloxane);

poly(dimethylsiloxane-co-methyl-[propyl-(E)-3-(4-methoxyphenyl)-2-carboxyethyl-acrylate] siloxane-co-methyl-[propyl-3-(Z)-[4-methoxyphenyl)-2-carboxyethyl-acrylate] siloxane);

poly(dimethylsiloxane-co-methyl-[octyl-3-(E)-(4-methyloxy-4'-biphenyl)acrylate] siloxane-co-[pentyl-(E)-3-(4-methoxyphenyl)acrylate] siloxane).

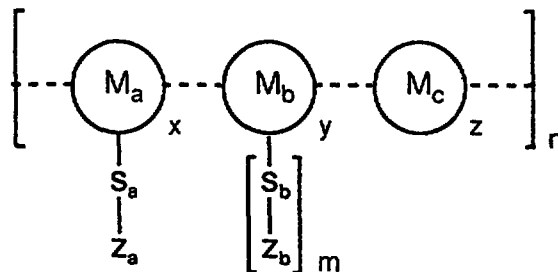
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Patent Claims

1. Polymers of general formula I



wherein

M_a, M_b, M_c signify monomer units for homo- or copolymers;

x, y, z indicated mole fractions of the copolymers,
whereby in each case

$0 < x \leq 1; 0 \leq y \leq 1$ and $0 \leq z < 1$;

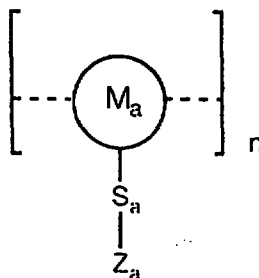
S_a, S_b represent spacer units;

Z_a, Z_b represent molecule units which can undergo
photochemical isomerization/dimerization;

n is a magnitude of 4-100 000 and

m is 0 or 1.

2. Polymers according to claim 1 of general formula I-A:



I - A

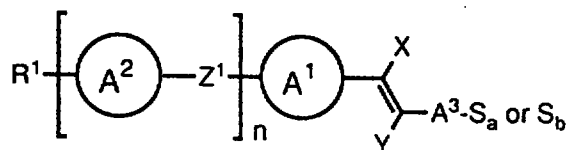
wherein M_a, S_a, Z_a and n have the significances given in claim 1.

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3. Polymers according to claim 1 or 2, characterized in that the isomerization/dimerization units Z_a or Z_b each independently have general formula II



II

wherein

- ring A^1 signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- ring A^2 signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-piperidyl;
- A^3 signifies -COO-, -CO-E-, 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- E signifies 1,4-phenylene, which is unsubstituted or substituted with halogen and in which 1 or 2 CH groups can be replaced by nitrogen, or 2,5-thiophenylene, 2,5-furanylene, 1,4- or 2,6-naphthylene, in which a CH group can be replaced by nitrogen;
- Z^1 signifies a single covalent bond, -CH₂CH₂-, -COO-, -OCH₂-, -C≡C-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O- or the trans form of -OCH₂CH=CH-, -CH=CHCH₂O-, -(CH₂)₂CH=CH- or -CH=CH(CH₂)₂-;

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R¹ signifies hydrogen, halogen, cyano, alkyl with 1 to 12 carbon atoms, which is optionally substituted with flourine and in which optionally 1 or 2 non-adjacent -CH₂- groups can be replaced by oxygen, -COO-, -OOC-, -CO- and/or a -CH₂CH₂- group can be replaced by -CH=CH-;

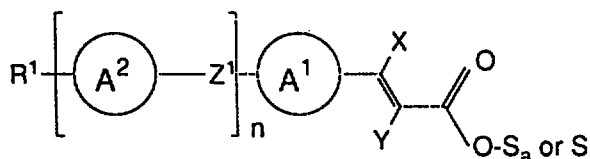
n signifies 0, 1 or 2;

X, Y each independently signify hydrogen, halogen, cyano, alkyl with 1 to 12 carbon atoms, which is optionally substituted with fluorine and in which optionally 1 or 2 non-adjacent -CH₂- groups can be replaced by oxygen, -COO-, -OOC-, -CO- and/or -CH=CH-; and

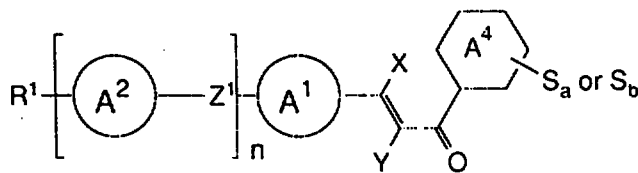
S_a, S_b , signify spacer units;

with the proviso that simultaneously A³ does not signify -COO-, n does not signify 0, A¹ does not signify phenyl, R¹ does not signify hydrogen or methoxy and S_a and, respectively, S_b do not signify a single bond.

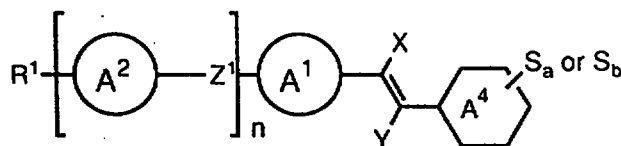
4. Polymers according to any one of claims 1-3, characterized in that the isomerization/dimerization units Z_a , Z_b each independently have the general formula



11-A



11-B



11-C

wherein

ring A¹ signifies 1,4-phenylene, which is unsubstituted or substituted with halogen, or pyrimidine-2,5-diyl,





pyridine-2,5-diyl, 2,5-thiophenylene, 2,5-furanylene, 1,4-naphthylene or 2,6-naphthylene;

ring A² signifies 1,4-phenylene, which is unsubstituted or substituted with halogen, or pyrimidine-2,5-diyl, pyridine-2,5-diyl, 2,5-thiophenylene, 2,5-furanylene, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or 1,4-piperidyl;

ring A⁴ signifies 1,4-phenylene, which is unsubstituted or substituted with halogen;

Z¹ signifies a single covalent bond, -CH₂CH₂-, -COO-, -OCH₂-, -(CH₂)₄-, -O(CH₂)₃- or -(CH₂)₃O-;

R¹ signifies halogen, cyano, alkyl with 1 to 12 carbon atoms, which is optionally substituted with fluorine and in which optionally 1 or 2 non-adjacent -CH₂- groups can be replaced by oxygen or -COO- and/or a -CH₂CH₂- group can be replaced by -CH=CH-;

n signifies 0, 1 or 2;

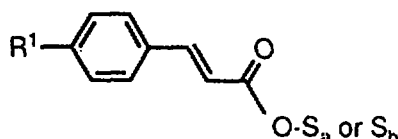
X signifies hydrogen or alkyl with 1 to 6 carbon atoms, which is optionally substituted with halogen;

Y signifies hydrogen, cyano, -COO-alkyl, alkyl with 1 to 6 carbon atoms, which is optionally substituted with fluorine; and

S_aS_b signify spacer units;

with the proviso that in formula II-A simultaneously n does not signify 0, A¹ does not signify phenyl, R¹ does not signify hydrogen or methoxy, X and Y do not signify hydrogen and S_a or S_b does not signify a single bond.

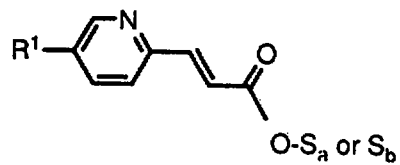
5. Polymers according to any one of claims 1-4, characterized in that the isomerization/dimerization units Z_a or Z_b each independently have the general formula



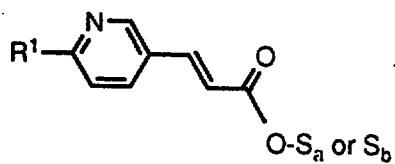
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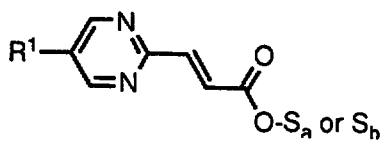
IIa



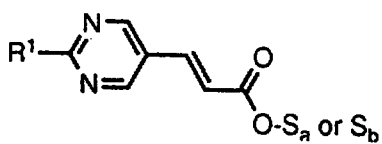
IIb



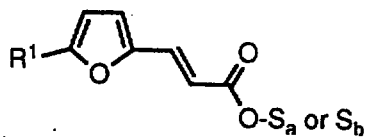
IIc



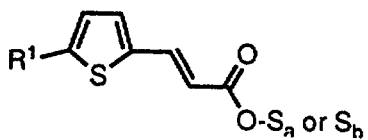
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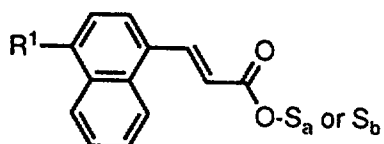
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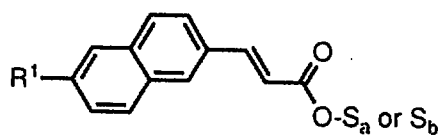
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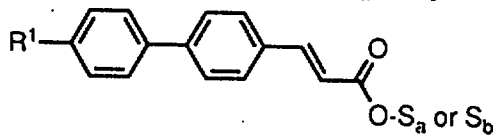
IIg



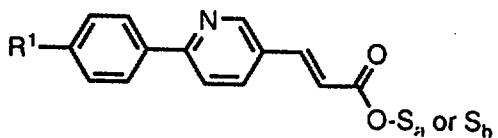
IIh



IIi



IIj



IIk

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wherein R^1 signifies halogen, cyano, alkyl or alkoxy with 1 to 6 carbon atoms, with the proviso that in formula IIa simultaneously R^1 does not signify hydrogen or methoxy and S_a or S_b does not signify a single bond.

6. The use of linear and cyclic polymers or oligomers having a photoreactive ethene group in accordance with any one of claims 1-5 as an orientating layer for liquid crystals.



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