

HOMEOTROPICALLY-ALIGNED LIQUID CRYSTAL FILM AND METHOD FOR MANUFACTURING THE SAME

TECHNICAL FIELD

5 [0001] The present invention relates to a homeotropically-aligned liquid crystal film and a method for manufacturing the same.

BACKGROUND ART

10 [0002] A liquid crystal film in which a liquid crystal compound is aligned in a predetermined direction is used as an optical film having functions such as optical compensation of a liquid crystal display and prevention of external light reflection of an organic EL device. A liquid crystal compound alignment film is advantageous for reduction in thickness or weight because its birefringence is larger than that of a stretched polymer film. For example, a homeotropically-aligned liquid crystal film
15 in which liquid crystal molecules having positive refractive index anisotropy are aligned in the normal direction (thickness direction) of a substrate surface has a thickness-direction refractive index (extraordinary refractive index) n_z , which is a refractive index in an alignment direction of liquid crystal molecules, higher than in-plane refractive indices (ordinary refractive indices) n_x and n_y , and therefore can
20 be used as a positive C plate having a refractive index anisotropy of $n_z > n_x = n_y$.

[0003] Substances that spontaneously align in a homeotropic manner are very limited. In general, a homeotropically-aligned liquid crystal film is formed by applying a liquid crystal compound onto a substrate having a vertical alignment film. Patent Document 1 discloses that a composition containing a specific side
25 chain-type liquid crystal polymer and a photopolymerizable liquid crystal monomer is homeotropically aligned on a substrate having no vertical alignment film. More specifically, the liquid crystalline composition is applied onto a substrate, heated to convert the liquid crystal polymer to a liquid crystal state, and then cooled to fix the alignment of the liquid crystal polymer, and the liquid crystal monomer is
30 polymerized or crosslinked by photoirradiation. In this way, a homeotropically-aligned liquid crystal film is obtained.

[0004] Patent Document 1 discloses a method in which a liquid crystalline

composition is applied onto a film having a small optical anisotropy, such as a norbornene-based film, to form a homeotropically-aligned liquid crystal film, and a method in which a liquid crystal alignment film formed on a plastic film having optical anisotropy or a metal film is transferred onto a plastic film having a small
5 optical anisotropy. Patent Document 1 discloses an example in which a liquid crystalline composition is applied onto a norbornene-based polymer film or a glass substrate, heated to 130°C to align liquid crystal, and then irradiated with ultraviolet ray to form a homeotropically-aligned liquid crystal film.

10 PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005] Patent Document 1: Japanese Patent No. 4174192

SUMMARY OF THE INVENTION

15 PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] There has been demand for higher-definition and higher-luminance displays, and therefore optical films for displays are required to have higher in-plane uniformity. As for liquid crystal alignment films, alignment defects in micro regions have come to be considered problematic. When the homeotropically-aligned
20 liquid crystal film disclosed in Patent Document 1 is observed under a polarizing microscope, local light leakages due to minute alignment defects are observed. In view of such a problem, it is an object of the present invention to provide a homeotropically-aligned liquid crystal film having few alignment defects.

25 MEANS FOR SOLVING THE PROBLEMS

[0007] In order to achieve the above object, the inventors have intensively studied, and resultantly found that a homeotropically-aligned liquid crystal film having few alignment defects can be obtained by appropriately selecting a film substrate onto which a liquid crystalline composition is to be applied or adjusting
30 conditions for aligning liquid crystal molecules.

[0008] The present invention relates to a homeotropically-aligned liquid crystal film in which a side chain-type liquid crystal polymer and a polymer of a

photopolymerizable liquid crystal compound are homeotropically aligned, and a method for manufacturing the same.

[0009] A liquid crystalline composition containing a side chain-type liquid crystal polymer and a photopolymerizable liquid crystal monomer is applied onto a first main surface of a film substrate which is not provided with a vertical alignment film (application step), and the liquid crystal polymer and the liquid crystal monomer are homeotropically aligned in a liquid crystal state (liquid crystal aligning step), and the liquid crystal monomer is polymerized or crosslinked by photoirradiation (photopolymerization step). In this way, a homeotropically-aligned liquid crystal film is formed on the film substrate.

[0010] The side chain-type liquid crystal polymer preferably has a monomer unit containing a liquid crystalline fragment side chain and a monomer unit containing a non-liquid crystalline fragment side chain. A content of the photopolymerizable liquid crystal monomer in the liquid crystalline composition is preferably 1.1 to 10 times a content of the side chain-type liquid crystal polymer.

[0011] It is preferable that a heating temperature T (°C) during alignment of liquid crystal and an in-plane birefringence Δn of the film substrate satisfy $T \leq 100 - 3.5 \times 10^3 \Delta n$. By lowering the heating temperature during alignment of liquid crystal, alignment defects of the liquid crystal are reduced, and therefore a homeotropically-aligned liquid crystal film with high uniformity is obtained.

[0012] When the first main surface (which is a surface onto which the liquid crystalline composition is to be applied) of the film substrate is smooth, alignment defects tend to reduce. Therefore, an arithmetic mean roughness of the first main surface of the film substrate is preferably 3 nm or less. As such a film substrate having a small arithmetic mean roughness and high smoothness, a stretched film is preferably used. An in-plane retardation of the stretched film is, for example, 10 to 500 nm. When the liquid crystalline composition is applied onto a stretched film substrate, the alignment regulating force of the substrate may inhibit homeotropic alignment of the liquid crystalline composition. However, as described above, alignment defects can be reduced by lowering the temperature of heating for aligning liquid crystal.

[0013] The film substrate may have an easily-sliding layer on a second main

surface. It is preferable that an easily-sliding layer is not provided on the first main surface of the film substrate. A norbornene-based polymer film, for example, is used as the film substrate.

[0014] At least one surface of the homeotropically-aligned liquid crystal film preferably has an arithmetic mean roughness of 3 nm or less. In the homeotropically-aligned liquid crystal film, the number of alignment defects per 1 cm² is preferably 1 or less.

EFFECTS OF THE INVENTION

[0015] According to the present invention, it is possible to obtain a homeotropically-aligned liquid crystal film having few micro alignment defects and excellent in-plane uniformity.

MODE FOR CARRYING OUT THE INVENTION

[0016] A liquid crystal alignment film is formed by applying a liquid crystalline composition onto a substrate and fixing the alignment thereof.

[0017] [Liquid crystalline composition]

A liquid crystalline composition used for forming a homeotropically-aligned liquid crystal film contains a side chain-type liquid crystal polymer and a photopolymerizable liquid crystal monomer.

[0018] <Side chain-type liquid crystal polymer>

As the side chain-type liquid crystal polymer, a copolymer is used which has a monomer unit containing a liquid crystalline fragment side chain and a monomer unit containing a non-liquid crystalline fragment side chain. Since the polymer has a liquid crystalline fragment in the side chain, the polymer is homeotropically aligned when the liquid crystalline composition is heated to a specific temperature. Further, since the polymer has a non-liquid crystalline fragment in the side chain, a force for aligning the photopolymerizable liquid crystal monomer contained in the liquid crystalline composition acts so that the photopolymerizable liquid crystal monomer is homeotropically aligned together with the polymer. A homeotropically-aligned liquid crystal film can be obtained by aligning the liquid crystal monomer in association with the alignment of the side

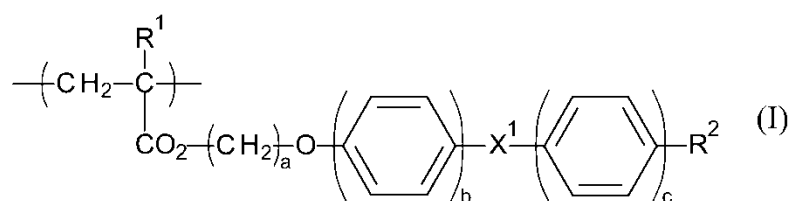
chain-type liquid crystal polymer and fixing their alignments.

[0019] Examples of the monomer having a liquid crystalline fragment side chain include polymerizable compounds having a nematic liquid crystalline substituent containing a mesogen group. Examples of the mesogen group include cyclic structures such as a biphenyl group, a phenylbenzoate group, a phenylcyclohexane group, an azoxybenzene group, an azomethine group, an azobenzene group, a phenylpyrimidine group, a diphenylacetylene group, a diphenylbenzoate group, a bicyclohexane group, a cyclohexylbenzene group, and a terphenyl group. These cyclic units may have a substituent, such as a cyano group, an alkyl group, an alkoxy group, or a halogen group, at its terminal. Among them, the mesogen group is preferably one having a biphenyl group or a phenylbenzoate group.

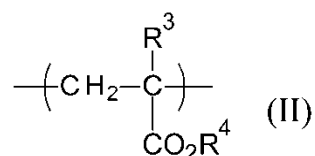
[0020] Examples of the monomer having a non-liquid crystalline fragment side chain include polymerizable compounds having a linear substituent such as a long-chain alkyl having 7 or more carbon atoms. A polymerizable functional group of the liquid crystalline monomer and the non-liquid crystalline monomer may be, for example, a (meth)acryloyl group.

[0021] As the side chain-type liquid crystal polymer, a copolymer is preferably used which has a liquid crystalline monomer unit represented by the general formula (I) and a non-liquid crystalline monomer unit represented by the general formula (II).

[0022]



[0023]

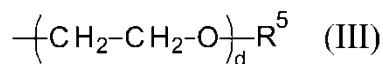


[0024] In the formula (I), R¹ is a hydrogen atom or a methyl group, R² is a cyano group, a fluoro group, an alkyl group having 1 to 6 carbon atoms, or an alkoxy group having 1 to 6 carbon atoms, and X¹ is -CO₂- or -OCO-. In the formula (I), "a" is an

integer of 1 to 6, and “b” and “c” are each independently 1 or 2.

[0025] In the formula (II), R³ is a hydrogen atom or a methyl group, R⁴ is an alkyl group having 7 to 22 carbon atoms, a fluoroalkyl group having 1 to 22 carbon atoms, or a group represented by the following general formula (III).

5 [0026]



[0027] In the formula (III), R⁵ is an alkyl group having 1 to 5 carbon atoms, and d is an integer of 1 to 6.

[0028] The ratio between the liquid crystalline monomer unit and the non-liquid crystalline monomer unit in the side chain-type liquid crystal polymer is not particularly limited. When the ratio of the non-liquid crystalline monomer unit is small, alignment of the photopolymerizable liquid crystal compound associated with alignment of the side chain-type liquid crystal polymer is insufficient so that the alignment of a liquid crystal layer after photo curing may be nonuniform. On the other hand, when the ratio of the liquid crystalline monomer unit is small, the side chain-type liquid crystal polymer hardly shows a liquid crystal monodomain alignment property. Therefore, the molar ratio of the non-liquid crystalline monomer to the total of the liquid crystalline monomer unit and the non-liquid crystalline monomer unit is preferably 0.01 to 0.8, more preferably 0.1 to 0.6, further preferably 0.15 to 0.5. From the viewpoint of achieving both the film formability and alignment property of the liquid crystalline composition, the weight-average molecular weight of the side chain-type liquid crystal polymer is preferably about 2000 to 100000, more preferably about 2500 to 50000.

[0029] The side chain-type liquid crystal polymer can be polymerized by various known methods. For example, when the monomer units have a (meth)acryloyl group as a polymerizable functional group, a side chain-type liquid crystal polymer having a liquid crystalline fragment and a non-liquid crystalline fragment can be obtained by radical polymerization using light or heat.

[0030] <Photopolymerizable liquid crystal compound>

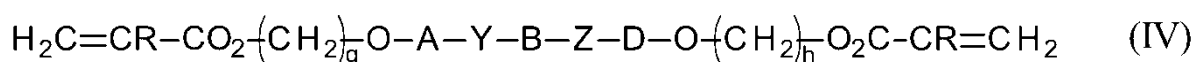
30 The photopolymerizable liquid crystal compound (monomer) has a mesogen group and at least one photopolymerizable functional group in one

molecule. Examples of the mesogen group include those described above with reference to the liquid crystalline fragment of the side chain-type liquid crystal polymer. Examples of the photopolymerizable functional group include a (meth) acryloyl group, an epoxy group, a vinyl ether group. Among them, a (meth) acryloyl group is preferred.

[0031] The photopolymerizable liquid crystal monomer is preferably one having two or more photopolymerizable functional groups in one molecule. When the liquid crystal monomer containing two or more photopolymerizable functional groups is used, a cross-linked structure is introduced into a liquid crystal layer after photopolymerization, which tends to improve the durability of the homeotropically-aligned liquid crystal film.

[0032] Examples of the photopolymerizable liquid crystal monomer having a mesogen group and two or more (meth)acryloyl groups in one molecule include compounds represented by the following general formula (IV).

[0033]



[0034] In the formula (IV), R is a hydrogen atom or a methyl group, A and D are each independently a 1,4-phenylene group or a 1,4-cyclohexylene group, B is a 1,4-phenylene group, a 1,4-cyclohexylene group, a 4,4'-biphenylene group, or a 4,4'-bicyclohexylene group, and Y and Z are each independently -COO-, -OCO-, or -O-. In the formula (IV), g and h are each independently an integer of 2 to 6.

[0035] As a commercially-available product of the photopolymerizable liquid crystal monomer represented by the general formula (IV), "Paliocolor LC242" manufactured by BASF can be exemplified.

[0036] <Composition>

The ratio between the photopolymerizable liquid crystal compound (monomer) and the side chain-type liquid crystal polymer in the liquid crystalline composition is not particularly limited. From the viewpoint of obtaining a durable homeotropically-aligned liquid crystal film, the content of the photopolymerizable liquid crystal compound is preferably higher than the content of the side chain-type liquid crystal polymer. From the viewpoint of obtaining a homeotropically-aligned liquid crystal film having high durability and excellent alignment uniformity, the

content (weight) of the photopolymerizable liquid crystal compound in the liquid crystalline composition is preferably 1.5 to 15 times, more preferably 2 to 10 times, further preferably 2.5 to 6 times the content of the side chain-type liquid crystal polymer.

5 **[0037]** In order to accelerate curing of the photopolymerizable liquid crystal compound by photoirradiation, the liquid crystalline composition preferably contains a photopolymerization initiator. Examples of the photopolymerization initiator include Irgacure 907, Irgacure 184, Irgacure 651, and Irgacure 369 manufactured by BASF. The content of the photopolymerization initiator in the
10 liquid crystalline composition is usually about 0.5 to 20 parts by weight, preferably about 3 to 15 parts by weight, more preferably about 5 to 10 parts by weight per 100 parts by weight of the photopolymerizable liquid crystal compound.

[0038] The liquid crystalline composition can be prepared by mixing the side chain-type liquid crystal polymer, the photopolymerizable liquid crystal compound,
15 the photopolymerization initiator, and a solvent. The solvent is not particularly limited as long as it can dissolve the side chain-type liquid crystal polymer and the photopolymerizable liquid crystal compound and does not erode the film substrate (or has low erosivity). Examples of such a solvent include: halogenated hydrocarbons such as chloroform, dichloromethane, carbon tetrachloride,
20 dichloroethane, tetrachloroethane, trichloroethylene, tetrachloroethylene, chlorobenzene, and orthodichlorobenzene; phenols such as phenol and parachlorophenol; aromatic hydrocarbons such as benzene, toluene, xylene, methoxybenzene, and 1,2-dimethoxybenzene; ketone-based solvents such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, cyclopentanone, 2-
25 pyrrolidone, and N-methyl-2-pyrrolidone; ester-based solvents such as ethyl acetate and butyl acetate; alcohol-based solvents such as t-butyl alcohol, glycerol, ethylene glycol, triethylene glycol, ethylene glycol monomethyl ether, diethylene glycol dimethyl ether, propylene glycol, dipropylene glycol, and 2-methyl-2,4-pentanediol; amide-based solvents such as dimethylformamide and dimethylacetamide; nitrile-
30 based solvents such as acetonitrile and butyronitrile; ether-based solvents such as diethyl ether, dibutyl ether, and tetrahydrofuran; and ethyl cellosolve and butyl cellosolve. The concentration of the liquid crystalline composition is usually about 3

to 50% by weight, preferably about 7 to 35% by weight.

[0039] [Film substrate]

In the present invention, a film substrate having no vertical alignment film is used as a substrate for applying the liquid crystalline composition. As described above, since the side chain-type liquid crystal polymer contained in the liquid crystalline composition is homeotropically aligned by heating, the substrate does not need to be provided with a vertical alignment film. The use of the film substrate makes it possible to perform a series of processes from application of the liquid crystalline composition onto the substrate to curing of the liquid crystal monomer by photopolymerization in a roll-to-roll manner, and therefore the productivity of the homeotropically-aligned liquid crystal film can be improved.

[0040] The film substrate has a first main surface and a second main surface, and the liquid crystalline composition is applied onto the first main surface. A resin material constituting the film substrate is not particularly limited as long as it is not dissolved in the solvent of the liquid crystalline composition and has heat resistance during heating for aligning the liquid crystalline composition. Examples of resin material include polyesters such as polyethylene terephthalate and polyethylene naphthalate; polyolefins such as polyethylene and polypropylene; cyclic polyolefins such as norbornene-based polymers; cellulose-based polymers such as diacetylcellulose and triacetylcellulose; acrylic polymers; styrene-based polymers; and polycarbonates, polyamides, and polyimides. Among them, a norbornene-based polymer film is particularly preferably used as the film substrate because flowability during molding is excellent and a highly smooth film is easily obtained. A norbornene-based polymer film is preferred also for the reason that it is excellent in releasability when the homeotropically-aligned liquid crystal film is transferred onto another substrate. Examples of the norbornene-based polymer include ZEONOR and ZEONEX manufactured by Zeon Corporation and ARTON manufactured by JSR Corporation.

[0041] The film substrate may be a stretched film. By stretching the film, surface irregularities such as die lines formed during film formation are leveled, and therefore the smoothness of the film substrate is improved so that the arithmetic mean roughness Ra of the film substrate tends to reduce. The film

substrate is particularly preferably a biaxially-stretched film due to its high surface uniformity.

[0042] The in-plane retardation R_0 of a stretched film used as the film substrate is generally 10 nm or more. When the film substrate is a stretched film having an in-plane retardation of 10 nm or more, a polymer constituting the film is preferentially aligned in a predetermined direction (slow axis direction or fast axis direction), and therefore an alignment regulating force for homogeneously aligning liquid crystal molecules is likely to act so that homeotropic alignment of the liquid crystalline composition tends to be inhibited. However, as will be described later, by lowering the temperature of heating for homeotropically aligning liquid crystal molecules, a homeotropically-aligned liquid crystal film having few alignment defects is obtained even when the stretched film substrate is used.

[0043] If the in-plane retardation of the film substrate is excessively large, the temperature at which alignment defects can be reduced is low, and therefore there is a case where it is difficult to cause the liquid crystal phase transition of the side chain-type liquid crystal polymer in such a temperature range. Therefore, the in-plane retardation R_0 of the film substrate is preferably 500 nm or less, more preferably 300 nm or less, further preferably 200 nm or less.

[0044] Although the thickness of the film substrate is not particularly limited, the thickness is usually about 10 to 200 μm in consideration of handleability. The in-plane birefringence Δn (determined by dividing the in-plane retardation R_0 by the thickness) of the stretched film is preferably 0.01 or less, more preferably 0.008 or less, further preferably 0.006 or less.

[0045] The arithmetic mean roughness R_a of the first main surface of the film substrate is preferably 3 nm or less, more preferably 2 nm or less, further preferably 1.5 nm or less. When the liquid crystalline composition is applied onto the surface of the film substrate having a small R_a and high smoothness, alignment defects of the homeotropically-aligned liquid crystal film tend to reduce. As described above, the R_a of the film tends to be reduced by stretching the film. Therefore, alignment defects of the homeotropically-aligned liquid crystal film tend to be reduced by using the stretched film substrate.

[0046] The surface shape of the first main surface of the film substrate is

transferred onto the homeotropically-aligned liquid crystal film formed on the first main surface of the film substrate, and therefore the Ra of the substrate-side surface of the homeotropically-aligned liquid crystal film is almost the same as that of the first main surface of the substrate. Therefore, when a film substrate whose first main surface has an Ra of 3 nm or less is used, the substrate-side surface of the liquid crystal alignment film also often has an Ra of 3 nm or less. Further, when the liquid crystalline composition is applied onto the film substrate, the Ra of the air-side surface tends to be smaller than that of the substrate-side surface. Therefore, when a film substrate whose first main surface has an Ra of 3 nm or less is used, the arithmetic mean roughness of both surfaces of the homeotropically-aligned liquid crystal film is often 3 nm or less.

[0047] In order to achieve the arithmetic mean roughness within the above range, the film substrate preferably contains no filler inside thereof. Films containing no filler and having high surface smoothness are poor in slidability, and therefore there is a case where blocking occurs or transfer failure or winding failure occurs in a roll-to-roll process. Examples of a method for preventing blocking or transfer failure resulting from high smoothness include bonding another film having high slidability to the film substrate and providing an easily-sliding layer on the film substrate. In a case where another film is bonded to the film substrate, the film is preferably bonded to the second main surface (which is a surface opposite to the surface onto which the liquid crystalline composition is to be applied), from the viewpoint of preventing defects (*e.g.*, alignment defects of liquid crystal or optical defects) resulting from transfer of an adhesive layer or the like onto the first main surface (which is a surface onto which the liquid crystalline composition is to be applied). It should be noted that even if the film is bonded to the second main surface of the film substrate, a pressure-sensitive adhesive or the like adhered to the second main surface may be transferred onto the first main surface when the film substrate is wound up in a roll-to-roll process, which may cause alignment defects or optical defects.

[0048] Therefore, slidability is preferably improved by disposing an easily-sliding layer on at least one of the surfaces of the film substrate. An example of the easily-sliding layer includes one having a microfiller with an average particle

diameter of 100 nm or less being contained in a binder such as a polyester or a polyurethane. The film substrate preferably has no easily-sliding layer on its surface onto which the liquid crystalline composition is to be applied, from the viewpoint of maintaining releasability when the homeotropically-aligned liquid crystal film is transferred onto another substrate and preventing defects such as transfer of the easily-sliding layer onto the homeotropically-aligned liquid crystal film when the homeotropically-aligned liquid crystal film is released from the film substrate. In other words, a film substrate having an easily-sliding layer on its second main surface but having no easily-sliding layer on its first main surface is preferably used.

[0049] [Formation of homeotropically-aligned liquid crystal film on film substrate]

The homeotropically-aligned liquid crystal film is obtained in the following manner: the liquid crystalline composition is applied onto the film substrate; heated to convert the liquid crystalline polymer to a liquid crystal state to homeotropically align liquid crystalline molecules, and then cooled to fix the alignment of the liquid crystalline polymer; and the liquid crystal monomer is polymerized or crosslinked by photoirradiation.

[0050] A method for applying the liquid crystalline composition onto the film substrate is not particularly limited, and examples thereof include spin coating, die coating, kiss roll coating, gravure coating, reverse coating, spray coating, Meyer bar coating, knife roll coating, and air knife coating. After applying the solution, a liquid crystalline composition layer is formed on the film substrate by removing the solvent. The thickness of the liquid crystalline composition applied onto the film substrate is preferably adjusted such that the thickness of the liquid crystalline composition layer after drying the solvent (*i.e.*, the thickness of the homeotropically-aligned liquid crystal film) is about 0.5 to 5 μm .

[0051] By heating the liquid crystalline composition layer formed on the film substrate to form a liquid crystal phase, the liquid crystalline composition is homeotropically aligned. Although the heating temperature is not particularly limited, the heating temperature is usually about 40 to 200°C. If the heating temperature is excessively low, transition to the liquid crystal phase tends to be

insufficient, and if the heating temperature is excessively high, alignment defects tend to increase. Therefore, the heating temperature is preferably 45 to 100°C, more preferably 50 to 95°C, further preferably 55 to 90°C. The heating time may be adjusted such that transition to the liquid crystal phase is sufficient, and is usually
5 about 30 seconds to 30 minutes.

[0052] When the stretched film substrate is used, a homogeneous alignment regulating force resulting from molecular alignment of the film substrate is likely to act as the heating temperature increases, and therefore alignment defects of the homeotropically-aligned liquid crystal film tend to increase. Therefore, when the
10 stretched film substrate is used, heating is preferably performed at a low temperature within a temperature range in which the liquid crystalline compound is converted to a liquid crystal phase. The heating temperature T (°C) during alignment of liquid crystal is preferably $100 - 3.5 \times 10^3 \Delta n$ or less. Δn is the in-plane birefringence of the stretched film substrate. The heating temperature T is more
15 preferably $100 - 4 \times 10^3 \Delta n$ or less, further preferably $100 - 4.5 \times 10^3 \Delta n$ or less. The heating temperature T is preferably $100 - 0.1 R_0$ or less, more preferably $100 - 0.12 R_0$ or less, further preferably $100 - 0.13 R_0$ or less. R_0 is the in-plane retardation of the stretched film substrate.

[0053] After heating, the liquid crystalline composition layer is cooled to a
20 temperature equal to or less than the glass transition temperature of the liquid crystal polymer so that the alignment of the liquid crystalline compound is fixed. A cooling method is not particularly limited. For example, the liquid crystalline composition layer may be transferred from a heating atmosphere to a room temperature atmosphere. Forced cooling such as air cooling or water cooling may
25 be performed.

[0054] The liquid crystalline composition layer in which the homeotropic alignment is fixed is irradiated with light to polymerize or crosslink the photopolymerizable liquid crystal compound so that the alignment of the photopolymerizable liquid crystal compound is fixed and the durability of the
30 homeotropically-aligned liquid crystal film is improved. As the irradiation light, light having a wavelength at which the photopolymerization initiator is cleaved may be selected. In general, ultraviolet ray is used. In order to promote a

photopolymerization reaction, photoirradiation is preferably performed in an inert gas atmosphere such as nitrogen gas.

[0055] [Properties and uses of homeotropically-aligned liquid crystal film]

The homeotropically-aligned liquid crystal film obtained in the above-described manner is a positive C plate having an in-plane retardation of almost 0 (*e.g.*, 5 nm or less, preferably 3 nm or less) and a negative thickness direction retardation (refractive index anisotropy of $n_z > n_x = n_y$). The thickness direction retardation R_t represented by the product of $(n_x - n_z)$ and thickness of the homeotropically-aligned liquid crystal film is, for example, about -50 to -500 nm.

[0056] When the homeotropically-aligned liquid crystal film is observed under a polarizing microscope, the number of light leakages (alignment defects) per cm^2 is preferably 1 or less, more preferably 0.7 or less, further preferably 0.5 or less. The number of alignment defects is determined as an average of the numbers of alignment defects observed in 10 areas in the film plane. As described above, a homeotropically-aligned liquid crystal film having few alignment defects is obtained by using a stretched film substrate having high smoothness and setting the temperature of heating for aligning liquid crystal to a value within a specific range.

[0057] The homeotropically-aligned liquid crystal film can be used as an optical film for displays intended to, for example, compensate for the viewing angle. The homeotropically-aligned liquid crystal film may be used in a state of being laminated on the film substrate or may be used after released from the film substrate. The homeotropically-aligned liquid crystal film may be released from the film substrate and laminated on a retardation film, a polarizing plate, or a substrate made of glass etc..

EXAMPLES

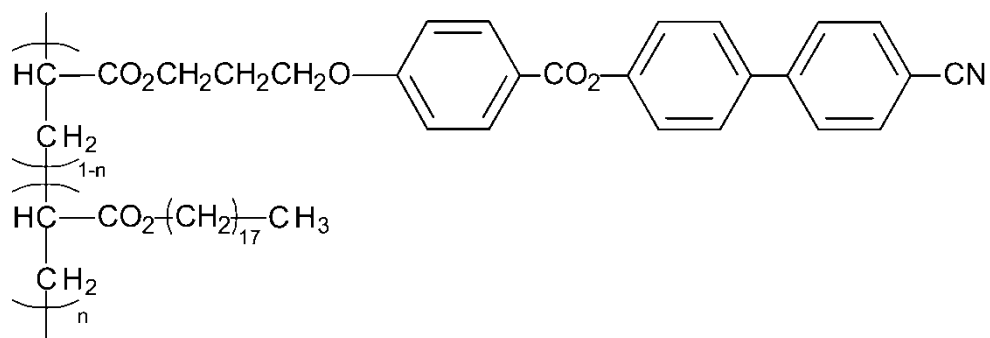
[0058] Hereinbelow, the present invention will be described in more detail with reference to production examples of homeotropically-aligned liquid crystal films, but the present invention is not limited to the following examples.

[0059] [Preparation of liquid crystalline composition]

Twenty parts by weight of a side chain-type liquid crystal polymer represented by the following chemical formula ($n = 0.35$, shown as a block polymer

for convenience) and having a weight-average molecular weight of 5000, 80 parts by weight of a polymerizable liquid crystal compound ("Paliocolor LC242" manufactured by BASF) exhibiting a nematic liquid crystal phase, and 5 parts by weight of a photopolymerization initiator ("Irgacure 907" manufactured by BASF) were dissolved in 400 parts by weight of cyclopentanone to prepare a liquid crystalline composition.

[0060]



[0061] [Experimental Example 1]

Using a bar coater, the above-described liquid crystalline composition was applied onto an unstretched norbornene-based film ("ZEONOR film" manufactured by Zeon Corporation, thickness: 50 μm , in-plane retardation: 0 nm, arithmetic mean roughness: 2.3 nm) such that its thickness after drying was 1 μm , and heated at a temperature (50 to 100°C) shown in Table 1 for 2 minutes to align liquid crystal. Then, the liquid crystalline composition was cooled to room temperature to fix the alignment of the liquid crystal polymer, and irradiated with ultraviolet ray of 700 mJ/cm² in a nitrogen atmosphere to photocure the liquid crystal monomer. In this way, a liquid crystal alignment film was produced.

[0062] [Experimental Example 2]

A biaxially-stretched norbornene-based film having an easily-sliding layer on its one of surfaces ("ZEONOR film" manufactured by Zeon Corporation, thickness: 52 μm , in-plane retardation: 50 nm, arithmetic mean roughness of easily-sliding layer-free surface: 1.2 nm) was prepared. The above-described liquid crystalline composition was applied onto the easily-sliding layer-free surface of the biaxially-stretched norbornene-based film, and a liquid crystal alignment film was produced in the same manner as in Experimental Example 1.

[0063] [Experimental Example 3]

A biaxially-stretched norbornene-based film having an easily-sliding layer on its one of surfaces ("ZEONOR film" manufactured by Zeon Corporation, thickness: 33 μm , in-plane retardation: 135 nm, arithmetic mean roughness of easily-sliding layer-free surface: 1.0 nm) was prepared. The above-described liquid crystalline composition was applied onto the easily-sliding layer-free surface of the biaxially-stretched norbornene-based film, and a liquid crystal alignment film was produced in the same manner as in Experimental Example 1.

[0064] [Experimental Example 4]

A biaxially-stretched norbornene-based film having an easily-sliding layer on its one of surfaces ("ZEONOR film" manufactured by Zeon Corporation, thickness: 34 μm , in-plane retardation: 270nm, arithmetic mean roughness of easily-sliding layer-free surface: 0.9 nm) was prepared. The above-described liquid crystalline composition was applied onto the easily-sliding layer-free surface of the biaxially-stretched norbornene-based film, and a liquid crystal alignment film was produced in the same manner as in Experimental Example 1.

[0065] [Experimental Example 5]

The above-described liquid crystalline composition was applied onto a biaxially-stretched polyethylene terephthalate film ("DIAFOIL T302" manufactured by Mitsubishi Chemical Corporation, thickness: 75 μm), and a liquid crystal alignment film was produced in the same manner as in Experimental Example 1.

[0066] [Experimental Example 6]

A liquid crystalline composition was prepared in the same manner as described above except that the amount of the side chain-type liquid crystal polymer was changed to 50 parts by weight and the amount of the polymerizable liquid crystal compound was changed to 50 parts by weight. The thus prepared liquid crystalline composition was applied onto the same biaxially-stretched film as used in Experiment Example 2, heated at 80°C for 2 minutes, cooled, and photocured to produce a liquid crystal alignment film.

[0067] [Evaluation]

(Arithmetic mean roughness)

Each of the liquid crystal alignment films was observed with a scanning probe microscope (AFM) to determine an arithmetic mean roughness from its 1 μm

square AFM observation image.

[0068] (Retardation)

The retardation of each of the liquid crystal alignment films was measured under an environment of 23°C using a polarization/retardation measurement system (manufactured by Axometrics under the trade name of “AxoScan”) at a wavelength of 590 nm. More specifically, the retardation of each of the liquid crystal alignment films was measured in the following manner. A glass plate having a pressure-sensitive adhesive-coated surface was prepared, and the liquid crystal alignment film was transferred onto the pressure sensitive adhesive-coated surface of the glass plate to prepare a sample. The in-plane retardation R_0 of the sample was measured, and the retardation of the sample at a tilt angle of 40° was measured. From these measured values, the thickness direction retardation R_t of the sample was calculated by setting the average refractive index of the liquid crystal alignment film to 1.52.

[0069] (Alignment defect)

A glass plate having a pressure sensitive adhesive-coated surface was prepared, and the liquid crystal alignment film was transferred onto the pressure sensitive adhesive-coated surface of the glass plate. An area of 1 cm² of the liquid crystal alignment film was observed under a cross-nicoled polarizing microscope to count the number of local light leakages. The observation under the polarizing microscope was performed in 10 areas (10 cm² in total) per sample, and the average of the numbers of light leakages was determined as the number of alignment defects per cm². The number of alignment defects per cm² of the liquid crystal alignment film obtained in each of Experimental Examples is shown in Table 1.

[0070] Table 1

	Experimental Example 1	Experimental Example 2	Experimental Example 3	Experimental Example 4	Experimental Example 5	Experimental Example 6
Substrate	biaxially-stretched norbornene	biaxially-stretched norbornene	biaxially-stretched norbornene	biaxially-stretched norbornene	biaxially-stretched PET	biaxially-stretched norbornene
type						
Ra (nm)	2.3	1.2	1	0.9	N.D.	1.2
R _o (nm)	0	50	135	270		50
50	0.3	0	0	0		
55	0.6	0.1	0	0.1	>10	
60	0.2	0	0.1	0	>10	
65	0.5	0	0	0.1	>10	
70	0.5	0.1	0	0.5	>10	
75	0.9	0	0	5.1	>10	
80	0.2	0	0.2	8.3	>10	
85	0.5	0	0.8	>10	>10	
90	0.9	0.7	7.2	>10	>10	
95	0.8	1	>10	>10	>10	
100	0.6	5.5	>10	>10	>10	
heating temperature (°C)						0

[0071] (Durability test)

A 5 cm square glass plate having a pressure sensitive adhesive-coated surface was prepared, and the liquid crystal alignment film produced at a heating temperature of 80°C in Experimental Example 2 or the liquid crystal alignment film produced in Experimental Example 6 was transferred onto the pressure sensitive adhesive-coated surface of the glass plate. The liquid crystal alignment film was subjected to 100 heat cycles between -40°C and 85°C. The ratio of the thickness direction retardation after the heat cycle test to the thickness direction retardation before the heat cycle test (retardation retention rate), the number of cracks detected by visually observing the sample after the heat cycle test, and the number of alignment defects per cm² are shown in Table 2.

[0072] Table 2

		Experimental Example2	Experimental Example6
composition	liquid crystal monomer / side chain-type liquid crystal polymer	80/20	50/50
heat cycle test	alignment defect (/cm ²)	0	0
	crack (/25cm ²)	0	7
	retardation retention rate (%)	92	85

As can be seen from the results shown in Table 2, alignment defects were not detected both before and after the heat cycle test in Experimental Example 2 and Experimental Example 6, and the homeotropic alignment of liquid crystal was fixed. However, in Experimental Example 6 in which the content of the photopolymerizable liquid crystal monomer was small, cracking occurred after the heat cycle test, and the retardation retention rate was lower than that of Experimental Example 2. As can be seen from the result, a homeotropically-aligned liquid crystal film having high temperature cycle durability can be obtained by increasing the ratio of the photopolymerizable liquid crystal monomer in the liquid crystalline composition.

In Experimental Example 5 using a biaxially-stretched PET film having a large in-plane birefringence, 10 or more alignment defects were detected per cm² at any heating temperature in the range of 50 to 100°C. On the other hand, the

number of alignment defects of each of Experimental Examples 1 to 4 was smaller than that of Experimental Example 5, and was more likely to reduce when the heating temperature was lower. As can be seen from these results, a homeotropically-aligned liquid crystal film having few alignment defects can be
5 obtained by using a film substrate whose in-plane birefringence is within a specific range and lowering the temperature of heating for aligning liquid crystal.

[0075] Comparing Experimental Example 1 with Experimental Example 2, the number of alignment defects of Experimental Example 2 was smaller when the heating temperature was in the range of 50 to 90°C. On the other hand, the
10 number of alignment defects of Experimental Example 2 was larger when the heating temperature was 95°C or 100°C. The number of alignment defects of Experimental Example 2 using a stretched film substrate having an in-plane retardation R_0 of 50 nm was smaller than that of Experimental Example 1 when the heating temperature was 90°C or less. In contrast, the temperature range in which
15 the number of alignment defects of Experimental Example 3 using a stretched film substrate having an R_0 of 135 nm was smaller than that of Experimental Example 1 was 50 to 80°C, and the temperature range in which the number of alignment defects of Experimental Example 3 using a stretched film substrate having an R_0 of 270 nm was smaller than that of Experimental Example 1 was 50 to 70°C.

[0076] The film substrates used in Experimental Examples 2 to 4 have almost the same R_a , and therefore it can be said that the temperature range in which the number of alignment defects can be reduced is wider when the R_0 of the stretched film is smaller. The reason for this is considered to be that a polymer constituting the film substrate is more preferentially aligned in a predetermined direction when
25 the R_0 is larger, and therefore an alignment regulating force for homogeneously aligning liquid crystal molecules is likely to act due to the film substrate.

[0077] As can be seen from the above results, a homeotropically-aligned liquid crystal film having few alignment defects can be obtained by adjusting the temperature of heating for aligning liquid crystal. Further, it is considered that a
30 small R_a of the surface of the stretched film substrate onto which the liquid crystalline composition is applied contributes to a reduction in the number of alignment defects.

CLAIMS

1. A method for manufacturing a homeotropically-aligned liquid crystal film, the method comprising:

an application step of applying a liquid crystalline composition onto a film substrate, the film substrate has a first main surface and a second main surface and no vertical alignment film is provided, the liquid crystalline composition contains a side chain-type liquid crystal polymer and a photopolymerizable liquid crystal monomer,

a liquid crystal aligning step of homeotropically aligning the liquid crystal polymer and the liquid crystal monomer in a liquid crystal state; and

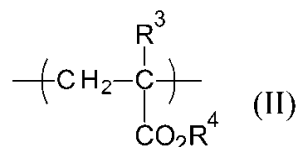
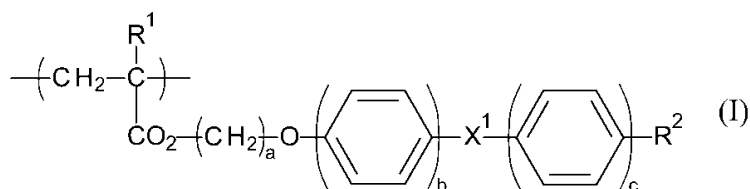
a photopolymerization step of polymerizing or crosslinking the liquid crystal monomer by photoirradiation,

wherein

the side chain-type liquid crystal polymer has a monomer unit containing a liquid crystalline fragment side chain and a monomer unit containing a non-liquid crystalline fragment side chain, and

a heating temperature T (°C) in the liquid crystal aligning step and an in-plane birefringence Δn of the film substrate satisfy $T \leq 100 - 3.5 \times 10^3 \Delta n$.

2. The method for manufacturing a homeotropically-aligned liquid crystal film according to claim 1, wherein the side chain-type liquid crystal polymer contains a liquid crystalline monomer unit represented by the following general formula (I) and a non-liquid crystalline monomer unit represented by the following general formula (II):



wherein

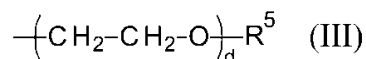
R¹ and R³ are each independently a hydrogen atom or a methyl group,

X¹ is -CO₂- or -OCO-,

R² is a cyano group, a fluoro group, an alkyl group having 1 to 6 carbon atoms, or an alkoxy group having 1 to 6 carbon atoms,

5 “a” is an integer of 1 to 6, and “b” and “c” are each independently 1 or 2, and

R⁴ is an alkyl group having 7 to 22 carbon atoms, a fluoroalkyl group having 1 to 22 carbon atoms, or a group represented by the following general formula (III),



10 wherein R⁵ is an alkyl group having 1 to 5 carbon atoms, and d is an integer of 1 to 6.

3. The method for manufacturing a homeotropically-aligned liquid crystal film according to claim 1 or 2, wherein the film substrate is a stretched film having an in-plane retardation of 10 to 500 nm

15

4. The method for manufacturing a homeotropically-aligned liquid crystal film according to any one of claims 1 to 3, wherein an arithmetic mean roughness of the first main surface of the film substrate is 3 nm or less

20 5. The method for manufacturing a homeotropically-aligned liquid crystal film according to any one of claims 1 to 4, wherein an easily-sliding layer is disposed on a second main surface of the film substrate, and easily-sliding layer is not disposed on the first main surface of the film substrate.

25 6. The method for manufacturing a homeotropically-aligned liquid crystal film according to any one of claims 1 to 5, wherein the film substrate is a norbornene-based polymer film.

30 7. The method for manufacturing a homeotropically-aligned liquid crystal film according to any one of claims 1 to 6, wherein a content of the photopolymerizable liquid crystal monomer is 1.1 to 10 times a content of the side chain-type liquid crystal polymer in the liquid crystalline composition.

8. A homeotropically-aligned liquid crystal film comprising a side chain-type liquid crystal polymer and a polymer of a photopolymerizable liquid crystal compound that are homeotropically aligned, wherein

both surfaces have an arithmetic mean roughness of 3 nm or less.

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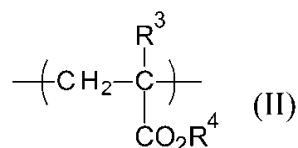
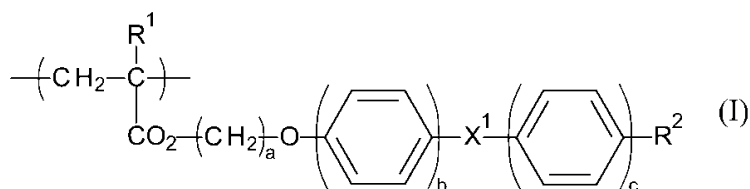
9. A homeotropically-aligned liquid crystal film comprising a side chain-type liquid crystal polymer and a polymer of a photopolymerizable liquid crystal compound that are homeotropically aligned, wherein

the side chain-type liquid crystal polymer has a monomer unit containing a

10 liquid crystalline fragment side chain and a monomer unit containing a non-liquid crystalline fragment side chain, and

at least one surface has an arithmetic mean roughness of 3 nm or less.

15 10. The homeotropically-aligned liquid crystal film according to claim 9, wherein the side chain-type liquid crystal polymer contains a liquid crystalline monomer unit represented by the following general formula (I) and a non-liquid crystalline monomer unit represented by the following general formula (II):



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wherein

R¹ and R³ are each independently a hydrogen atom or a methyl group,

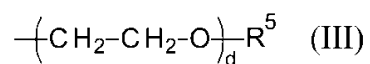
X¹ is -CO₂- or -OCO-,

R² is a cyano group, a fluoro group, an alkyl group having 1 to 6 carbon atoms,

25 or an alkoxy group having 1 to 6 carbon atoms,

“a” is an integer of 1 to 6, and “b” and “c” are each independently 1 or 2, and

R⁴ is an alkyl group having 7 to 22 carbon atoms, a fluoroalkyl group having 1 to 22 carbon atoms, or a group represented by the following general formula (III),



wherein R⁵ is an alkyl group having 1 to 5 carbon atoms, and d is an integer of 1 to 6.

- 5 11. The homeotropically-aligned liquid crystal film according to claim 9 or 10, wherein a content of the photopolymerizable liquid crystal monomer is 1.1 to 10 times a content of the side chain-type liquid crystal polymer.
12. The homeotropically-aligned liquid crystal film according to any one of claims
10 9 to 11, wherein a number of alignment defects per 1 cm² is 1 or less.