

PROCESS FOR PRODUCING PHASE RETARDER FROM
A THERMOPLASTIC RESIN FILM OR SHEET

The present invention relates to a process for producing a phase retarder film or sheet used in liquid crystal display devices.

Phase retarder films or sheets each comprising a uniaxially oriented thermoplastic resin film or sheet have been used as optical compensators to enhance the display qualities of liquid crystal display devices.

10 A STN type liquid crystal display device using such phase retarder film or sheet as optical compensator is advantageous in that it is lighter in weight, thinner and less expensive, but disadvantageous in that it has a narrow viewing angle characteristic and exhibits a low contrast
15 ratio as compared with a STN double cell type liquid crystal display device using a liquid crystal cell as optical compensator. These disadvantages have been considerably eliminated by, for example, laminating two plies of phase retarder films or sheets, but the viewing
20 angle characteristic has not reached a satisfactory level.

The viewing angle characteristic of a liquid crystal display device using phase retarders as optical compensators depends greatly not only upon the angular dependence of the birefringence of the liquid crystal cell
25 used therein but also upon the angular dependence of the birefringence (i.e. retardation) of the phase retarder. In conventional phase retarders, it is known that lower

angular dependence of retardation gives a superior result. The angular dependence of retardation of a phase retarder film or sheet is expressed by the retardation ratio R_{40}/R_0 . In this case, the retardation R_{40} is a value measured with
5 the phase retarder film or sheet being tilted by 40° from the horizontal condition by rotating around an axis which corresponds to the slow axis if the phase retarder consists of a thermoplastic resin having a positive intrinsic birefringence, or to the fast axis if the phase retarder
10 consists of a thermoplastic resin having a negative intrinsic birefringence; the retardation R_0 is a value measured with the phase retarder film or sheet not being tilted (i.e. arranged horizontally); and the measurement is made using a polarizing microscope equipped with a
15 Sénarmont compensator. As the retardation ratio of a phase retarder becomes closer to 1, its angular dependence of retardation becomes lower.

In order to reduce the angular dependence of retardation of a phase retarder film or sheet, there have
20 been proposed, for example, the following methods.

JP-A-2-16024 describes stretching a film whose molecules are oriented in a direction normal to the film surface.

JP-A-2-191904 discloses shrinking a film in a
25 direction perpendicular to the stretching axis at the time of the uniaxial stretching.

JP-A-285303 discloses stretching a film produced from

a molten polymer or a polymer solution under an electric field applied.

None of these methods, however, is satisfactory for mass production.

5 We have made an extensive study in order to solve the above problems. As a result, we found that a phase retarder film or sheet having a low angular dependence of retardation can be produced by subjecting a stretched thermoplastic resin film or sheet to thermal relaxation to
10 shrink it in the stretching axis direction while suppressing its expansion in a direction parallel to its surface and perpendicular to the stretching axis.

A stretched thermoplastic resin film or sheet shrinks in the stretching direction when it is subjected to thermal
15 relaxation in an unrestricted condition at a temperature not lower than the glass transition temperature of the thermoplastic resin. During this thermal relaxation, the film or sheet tends to expand in a direction parallel to the film or sheet surface and perpendicular to the
20 stretching axis, because the film or sheet has a neck-in (shrinkage) generated during the stretching, in the direction parallel to the film or sheet surface and perpendicular to the stretching axis.

When a stretched film or sheet is subjected to thermal
25 relaxation while suppressing its expansion (length increase) in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, to a

length smaller than that obtained in an unrestricted condition, the length in the stretching axis direction shrinks and the thickness of the film or sheet expands and exhibits improved angular dependence of retardation.

5 Herein, the term "stretching axis" refers to an axis of uniaxial stretching in the case of uniaxial stretching, and to an axis of main stretching in the case of unbalanced biaxial stretching.

 "Perpendicular to stretching axis" refers to an angle
10 of 60-120° to the stretching axis. Suppression of expansion in a direction of, in particular, 85-95° to the stretching axis is preferable in view of the improvement in angular dependence of retardation. Suppression of expansion in a direction parallel to the film or sheet surface and
15 perpendicular to the stretching axis, as compared with the suppression in other directions, gives higher improvement in angular dependence of retardation.

 "Suppression of expansion in a direction parallel to the film or sheet surface and perpendicular to the
20 stretching axis" refers to keeping the expansion in said direction substantially at zero, i.e. keeping constant the length of the film or sheet in said direction and further making the expansion in said direction smaller than the level obtained when the film or sheet is subjected to
25 thermal relaxation in an unrestricted condition until a desired R_0 value is obtained.

The method used for suppressing the expansion of a stretched film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, during the thermal relaxation, is not critical. The following are examples of this method.

(1) Contacting a film or sheet with a plate (e.g. a hot plate) and utilizing the frictional force generated by the contact for suppression of the expansion of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

(2) Arranging a film or sheet between a pair of parallel walls having a given distance between them, in such a manner that the film or sheet surface becomes perpendicular to the walls and the stretching axis of the film or sheet becomes parallel to the walls and thereby suppressing the expansion of the film or sheet in a direction parallel to its surface and perpendicular to the stretching axis, to a length not larger than the distance between the walls.

(3) Arranging a film or sheet in a frame having a structure in which the film or sheet is not allowed to expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis and thereby suppressing the expansion of the film or sheet in said direction.

Of these methods, there is preferred the methods (2) and (3).

Thus, by subjecting a film or sheet to thermal relaxation while suppressing the expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis, there can be easily obtained a thermoplastic resin film or sheet satisfying the following formula:

$$0.900 < R_{40}/R_0 < 1.100$$

Wrinkles may be generated when a film or sheet is subjected to thermal relaxation while suppressing the expansion in a direction parallel to the film or sheet surface and perpendicular to the stretching axis. In such cases, the thermal relaxation is preferably conducted while applying an appropriate pressure to the film or sheet surface.

The method used for conducting the thermal relaxation while applying an appropriate pressure perpendicularly to the film or sheet surface, is not critical. It can be any method provided that the heating of and the pressure application to the film or sheet can be conducted simultaneously. The following are examples of this method.

(1) Arranging a film or sheet in a frame having a structure in which the film or sheet is not allowed to stretch in a direction parallel to its surface and perpendicular to the stretching axis, mounting a weight
5 having the same bottom surface shape as the film or sheet surface, on the film or sheet, and conducting the thermal relaxation of the film or sheet while applying a pressure to the film or sheet surface.

(2) Interposing a film or sheet between releasable films,
10 tightly winding them around a cylindrical material so that the direction parallel to the surface and perpendicular to the stretching axis of the film or sheet becomes the same as the circumferential direction of the cylindrical material, to apply a pressure uniformly to the film or
15 sheet surface, and conducting the thermal relaxation of the film or sheet under a condition that both ends of the film or sheet are fixed so as not to allow the expansion of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

20 By subjecting a stretched thermoplastic resin film or sheet to thermal relaxation while applying a pressure thereto so that no wrinkle is generated in the film or sheet and there occurs increase of film or sheet thickness, there can be obtained a thermoplastic sheet or film
25 satisfying the following formula and having no wrinkles:

$$0.900 < R_{40}/R_0 < 1.100$$

A pressure of 0.1 g/cm² to 10 kg/cm² is generally applied in view of the uniformity of the film or sheet after thermal relaxation and the relaxation rate.

5 The stretched thermoplastic resin film or sheet has no restriction as to its orientation provided that it can, during the thermal relaxation, shrink in the stretching axis direction and expand in a direction parallel to the film or sheet surface and perpendicular to the stretching
10 axis.

 The method of production of such a film or sheet is not critical. It can be produced, for example, by preparing an unstretched film or sheet by a known method such as solution casting, press molding or extrusion and
15 then stretching the unstretched film or sheet by a known method, such as tentering, stretching between rolls or rolling.

 In view of, for example, the molecular orientation in the film or sheet thickness direction during thermal
20 relaxation and the uniformity of in-plane retardation of the film or sheet, it is preferred that a film or sheet be prepared by solution casting and then subjected to longitudinal uniaxial stretching between rolls.

The temperature at which the stretched thermoplastic resin film or sheet is relaxed thermally can be any temperature which is not lower than the glass transition temperature (T_g) of the thermoplastic resin and is lower than the melting point (T_m) and permits the thermal relaxation of the thermoplastic resin film or sheet. The temperature of thermal relaxation varies depending upon the T_g and T_m of the resin used, but is preferably in the range of T_g to $(T_g + 50^\circ\text{C})$ in view of, for example, the control of in-plane retardation and the molecular orientation in thickness direction.

In conducting the thermal relaxation of a stretched thermoplastic resin film or sheet while applying a pressure to its surface, a cushioning medium may be used in order to reduce the unevennesses in temperature and pressure. Such a medium enables the uniform transfer of temperature and pressure to the film or sheet via the cushioning medium.

It is also possible to interpose a stretched thermoplastic resin film or sheet between releasable materials (e.g. releasable polyester films) or to coat the surface of said film or sheet with a lubricant (e.g. silicone oil or molten surfactant), in order to enhance the transformation rate or uniformity in transformation rate, of said film or sheet during the thermal relaxation.

The thermoplastic resin used for preparation of a stretched thermoplastic resin film or sheet is not critical as long as it has intrinsic birefringence. However, it preferably has excellent optical properties (e.g. excellent
5 transparency).

As the thermoplastic resin, there can be used, for example, thermoplastic resins having positive intrinsic birefringence, such as a polycarbonate, polysulfone, polyarylate, polyethersulfone or cellulose diacetate, and
10 thermoplastic resins having negative intrinsic birefringence, such as polystyrene, α -methylpolystyrene, polyvinylpyridine, polyvinyl naphthalene or polymethyl methacrylate. Of these, a polycarbonate is preferred in view of its transparency, heat and humidity resistance and
15 expression of birefringence.

The present invention permits easy industrial production of a phase retarder which is low in angular dependence of retardation. A liquid crystal display device having the phase retarder(s) mounted thereon shows a
20 significantly improved viewing angle characteristic.

We refer also to the disclosure of Japanese Patent Application No. 03-324644.

The present invention is hereinafter illustrated by the following specific examples.

5 Example 1

A polycarbonate film of 185 μm in thickness, obtained by solvent casting was stretched to a 2.1-fold length at 184°C by longitudinal uniaxial stretching to obtain a stretched film of thickness = 98 μm , $R_0 = 867 \text{ nm}$ and R_{40}/R_0
10 = 1.108. The stretched film was cut into a size of 9.9 cm (direction perpendicular to stretching axis) x 2.4 cm (stretching axis direction), and the cut film was placed in a frame having such a temperature in which the cut film was not allowed to expand in a direction parallel to the film
15 surface and perpendicular to the stretching axis. On the cut film in the frame was mounted a weight having the same bottom surface shape as the cut film shape, to apply a pressure of 70 g/cm^2 uniformly on the film surface in a direction perpendicular to the film surface. Under this
20 condition, the stretched film was subjected to thermal relaxation at 165°C for 120 minutes while suppressing the expansion of the film in a direction parallel to the film surface and having an angle of 90° to the stretching axis of the film. As a result, there was obtained a phase
25 retarder film of size = 9.9 cm (direction perpendicular to

1 stretching axis) $\times$ 2.0 cm (stretching axis direction),
thickness = 120 μm , $R_0 = 445 \text{ nm}$, and $R_{40}/R_0 = 1.000$.

Example 2

The same stretched film as in Example 1 was
5 cut into a size of 9.9 cm (direction perpendicular to
stretching axis) $\times$ 2.4 cm (stretching axis direction),
and the cut film was placed in a frame having such a
structure in which the cut film was not allowed to
expand in a direction parallel to the film surface and
10 perpendicular to the stretching axis. On the cut film
in the frame was mounted a weight having the same bottom
surface shape as the cut film shape, to apply a pressure
of 235 g/cm^2 uniformly on the film surface in a direc-
tion perpendicular to the film surface. Under this
15 condition, the stretched film was subjected to thermal
relaxation at 165°C for 180 minutes while suppressing
the expansion of the film in a direction parallel to the
film surface and having an angle of 90° to the stretch-
ing axis of the film. As a result, there was obtained a
20 phase retarder film of size = 9.9 cm (direction perpen-
dicular to stretching axis) $\times$ 2.1 cm (stretching axis
direction), thickness = 118 μm , $R_0 = 586 \text{ nm}$, and R_{40}/R_0
= 1.047.

Example 3

25 The same stretched film as in Example 1 was
cut into a size of 9.9 cm (direction perpendicular to

1 stretching axis) $\times$ 2.4 cm (stretching axis direction),
and the cut film was placed in a frame having such a
structure in which the cut film was not allowed to
expand in a direction parallel to the film surface and
5 perpendicular to the stretching axis. On the cut film
in the frame was mounted a weight having the same bottom
surface shape as the cut film shape, to apply a pressure
of 87 g/cm² uniformly on the film surface in a direction
perpendicular to the film surface. Under this condi-
10 tion, the stretched film was subjected to thermal
relaxation at 170°C for 120 minutes while suppressing
the expansion of the film in a direction parallel to the
film surface and having an angle of 90° to the
stretching axis of the film. As a result, there was
15 obtained a phase retarder film of size = 9.9 cm
(direction perpendicular to stretching axis) $\times$ 2.1 cm
(stretching axis direction), thickness = 122 μ m, R_0 =
519 nm, and R_{40}/R_0 = 1.059.

Example 4

20 A polycarbonate film of 200 μ m in thickness,
obtained by solvent casting was stretched to a 1.1-fold
length at 190°C by longitudinal uniaxial stretching to
obtain a stretched film of thickness = 187 μ m, R_0 = 613
nm and R_{40}/R_0 = 1.124. The stretched film was cut into
25 a size of 9.9 cm (direction perpendicular to stretching
axis) $\times$ 2.4 cm (stretching axis direction), and the cut
film was placed in a frame having such a structure in

1 which the cut film was not allowed to expand in a
direction parallel to the film surface and perpendicular
to the stretching axis. On the cut film in the frame
was mounted a weight having the same bottom surface
5 shape as the cut film shape, to apply a pressure of 63
g/cm² uniformly on the film surface in a direction
perpendicular to the film surface. Under this condi-
tion, the stretched film was subjected to thermal
relaxation at 165°C for 120 minutes while suppressing
10 the expansion of the film in a direction parallel to the
film surface and having an angle of 90° to the stretch-
ing axis of the film. As a result, there was obtained a
phase retarder film of size = 9.9 cm (direction
perpendicular to stretching axis) × 2.2 cm (stretching
15 axis direction), thickness = 200 μm, $R_0 = 351$ nm, and
 $R_{40}/R_0 = 1.035$.

Example 5

A polycarbonate film of 185 μm in thickness,
obtained by solvent casting was stretched to a 1.1-fold
20 length at 178°C by longitudinal uniaxial stretching to
obtain a stretched film of thickness = 170 μm, $R_0 = 650$
nm and $R_{40}/R_0 = 1.100$. The stretched film was cut into
a size of 30 cm (direction perpendicular to stretching
axis) × 20 cm (stretching axis direction). The cut film
25 was interposed between two same releasable films
(Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co.,
Ltd.). Thereon was mounted a metal plate and a pressure

1 of 4.5 g/cm² was applied uniformly on the film surface
in a direction perpendicular to the film surface. Under
this condition, the stretched film was subjected to
thermal relaxation at 153°C for 120 minutes while
5 suppressing the expansion of the film in a direction
parallel to the film surface and having an angle of 90°
to the stretching axis of the film. As a result, there
was obtained a phase retarder film of size = 30.85 cm
(direction perpendicular to stretching axis) × 18.8 cm
10 (stretching axis direction), thickness = 185 μm, R₀ =
200 nm, and R₄₀/R₀ = 1.063.

Example 6

A polycarbonate film of 185 μm in thickness,
obtained by solvent casting was stretched by transverse
15 uniaxial stretching to obtain a stretched film of
thickness = 138 μm, R₀ = 619 nm and R₄₀/R₀ = 1.112. The
stretched film was cut into a size of 200 cm (direction
perpendicular to stretching axis) × 12 cm (stretching
axis direction). The cut film was interposed between
20 two same releasable films (200 cm × 15 cm) (Cerapeel Q-1,
#188 manufactured by Toyo Metallizing Co., Ltd.). The
resultant sandwich, together with a cushioning medium
(200 cm × 15 cm) covered with flannel at both sides,
was tightly wound around an aluminum pipe of 9 cm
25 (diameter) × 3 mm (wall thickness). In this case, the
polycarbonate film was fixed at the ends to prevent the
expansion in a direction parallel to the film surface

1 and perpendicular to the stretching axis. Under this
condition, the stretched film was subjected to thermal
relaxation at 152°C for 25 hours while suppressing the
expansion of the film in a direction parallel to the
5 film surface and having an angle of 90° to the
stretching axis of the film. As a result, there was
obtained a phase retarder film of size = 200 cm
(direction perpendicular to stretching axis) × 11.5 cm
(stretching axis direction), thickness = 158 μm, $R_0 =$
10 421 nm, and $R_{40}/R_0 = 0.978$.

Example 7

A polycarbonate film of 185 μm in thickness,
obtained by solvent casting was stretched by transverse
uniaxial stretching to obtain a stretched film of
15 thickness = 148 μm, $R_0 = 990$ nm and $R_{40}/R_0 = 1.167$. The
stretched film was cut into a size of 200 cm (direction
perpendicular to stretching axis) × 12 cm (stretching
axis direction). The cut film was interposed between
two same releasable films (200 cm × 15 cm) (Cerapeel Q-1
20 #188 manufactured by Toyo Metallizing Co., Ltd.). The
resultant sandwich, together with a cushioning medium
(200 cm × 15 cm) covered with flannel at the both sides,
was tightly wound around an aluminum pipe of 9 cm
(diameter) × 3 mm (wall thickness). In this case, the
25 polycarbonate film was fixed at the ends to prevent the
expansion in a direction parallel to the film surface
and perpendicular to the stretching axis. Under this

1 condition, the stretched film was subjected to thermal
relaxation at 153°C for 25 hours while suppressing the
expansion of the film in a direction parallel to the
film surface and having an angle of 90° to the
5 stretching axis of the film. As a result, there was
obtained a phase retarder film of size = 200 cm
(direction perpendicular to stretching axis) × 10.2 cm
(stretching axis direction), thickness = 182 μm, $R_0 =$
467 nm, and $R_{40}/R_0 = 1.007$.

10 Example 8

A polycarbonate film of 185 μm in thickness,
obtained by solvent casting was stretched by transverse
uniaxial stretching to obtain a stretched film of
thickness = 160 μm, $R_0 = 1333$ nm and $R_{40}/R_0 = 1.110$.
15 The stretched film was cut into a size of 200 cm
(direction perpendicular to stretching axis) × 12 cm
(stretching axis direction). The cut film was
interposed between two same releasable films (200 cm ×
15 cm) (Cerapeel Q-1 #188 manufactured by Toyo
20 Metallizing Co., Ltd.). The resultant sandwich,
together with a cushioning medium (200 cm × 15 cm)
covered with flannel at the both sides, was tightly
wound around an aluminum pipe of 9 cm (diameter) × 3 mm
(wall thickness). In this case, the polycarbonate film
25 was fixed at the ends to prevent the expansion in a
direction parallel to the film surface and perpendicular
to the stretching axis. Under this condition, the



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1 stretched film was subjected to thermal relaxation at
153°C for 25 hours while suppressing the expansion of
the film in a direction parallel to the film surface and
having an angle of 90° to the stretching axis of the
5 film. As a result, there was obtained a phase retarder
film of size = 200 cm (direction perpendicular to
stretching axis) × 10.1 cm (stretching axis direction),
thickness = 198 μm, R_0 = 692 nm, and R_{40}/R_0 = 0.954.

Comparative Example 1

10 A polycarbonate film of 185 μm in thickness,
obtained by solvent casting was stretched to a 2.1-fold
length at 190°C by longitudinal uniaxial stretching.
The resultant stretched film had thickness = 93 μm, R_0
= 589 nm and R_{40}/R_0 = 1.114.

15 Comparative Example 2

A polycarbonate film of 185 μm in thickness,
obtained solvent casting was stretched by transverse
uniaxial stretching to obtain a stretched film of
thickness = 137 μm, R_0 = 619 nm and R_{40}/R_0 = 1.112. The
20 stretched film was cut into a size of 10 cm (direction
perpendicular to stretching axis) × 10 cm (stretching
axis direction). The cut film was subjected to thermal
relaxation at 153°C for 2 hours on the releasable films
(Cerapeel Q-1 #188 manufactured by Toyo Metallizing Co.,
25 Ltd.). As a result, there was obtained a phase retarder
film of size = 10.15 cm (direction perpendicular to



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1 stretching axis) x 9.65 cm (stretching axis direction),
thickness = 141 μm , $R_0 = 406 \text{ nm}$, and $R_{40}/R_0 = 1.109$.

Comparative Example 3

A polycarbonate film of 185 μm in thickness,
5 obtained solvent casting was stretched by transverse
uniaxial stretching to obtain a stretched film of
thickness = 160 μm , $R_0 = 1333 \text{ nm}$ and $R_{40}/R_0 = 1.110$.
The stretched film was cut into a size of 10 cm
(direction perpendicular to stretching axis) x 10 cm
10 (stretching axis direction). The cut film was subjected
to thermal relaxation at 153°C for 2 hours on the
releasable films (Cerapeel Q-1 #188 manufactured by Toyo
Metallizing Co., Ltd.). As a result, there was obtained
a phase retarder film of size = 10.4 cm (direction
15 perpendicular to stretching axis) x 9.1 cm (stretching
axis direction), thickness = 169 μm , $R_0 = 621 \text{ nm}$, and
 $R_{40}/R_0 = 1.113$.

Comparative Example 4

A polycarbonate film of 185 μm in thickness,
20 obtained solvent casting was stretched by transverse
uniaxial stretching to obtain a stretched film of
thickness = 137 μm , $R_0 = 619 \text{ nm}$ and $R_{40}/R_0 = 1.112$. The
stretched film was cut into a size of 10 cm (direction
perpendicular to stretching axis) x 10 cm (stretching
25 axis direction). The cut film was subjected to thermal
relaxation at 158°C for 4 minutes on the releasable

- 1 films (Cerapeel Q-1 #188 manufactured by Toyo
Metallizing Co., Ltd.). As a result, there was obtained
a phase retarder film of size = 10.1 cm (direction
perpendicular to stretching axis) x 9.65 cm (stretching
5 axis direction), thickness = 141 μm , $R_0 = 415 \text{ nm}$, and
 $R_{40}/R_0 = 1.118$.



CLAIMS:

1. A process for producing a phase retarder film or sheet, which comprises subjecting a stretched thermoplastic resin film or sheet to thermal relaxation at a temperature not lower than the glass transition temperature of the thermoplastic resin so as to shrink the film or sheet in the direction of its stretching axis or main stretching axis in the case of an unbalanced biaxially stretched film or sheet, while suppressing the expansion of the film or sheet in a direction parallel to the film or sheet surface and approximately perpendicular to the stretching axis.

2. A process according to Claim 1, wherein the thermal relaxation is conducted while keeping constant the length of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis.

3. A process according to Claim 1, wherein the thermal relaxation is conducted while applying a pressure in a direction perpendicular to the film or sheet surface.

4. A process according to Claim 2, wherein the length of the film or sheet in a direction parallel to the film or sheet surface and perpendicular to the stretching axis is kept constant by arranging the film or sheet in a frame having a structure in which the film or sheet is not allowed to expand in a direction parallel to the film or sheet surface and perpendicular to the stretching axis of the film or sheet, thereby suppressing the expansion of the film or sheet in said direction.



5. A process according to any preceding claim, wherein the temperature of the thermal relaxation is in the range of the transition temperature of the thermoplastic resin to 50°C above said temperature.

6. A process according to any preceding claim, wherein said thermoplastic resin is a polycarbonate.

7. A liquid crystal display having mounted thereon a phase retarder film or sheet made by a process as claimed in any preceding claim.