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Zero-Birefringence Optical Polymer by Birefringent Crystal and Analysis of the Compensation Mechanism

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Summary: We reported a method for compensating the birefringence of optical polymers by doping them with inorganic birefringent crystals. In this method, an inorganic birefringent material is chosen that has the opposite birefringence to the polymer and needle-like shape crystals which are oriented when the polymer chains are oriented. The birefringence of the polymer is thus compensated by the opposing birefringence of the crystal. Orientation behavior of the needle-like crystals and polymers was investigated. The orientation function of the needle-like crystal was increased with an increase in the aspect ratio of the needle-like crystal.

Keywords: birefringence; nanocomposites; nanoparticles; optical polymers; zero-birefringence polymers

Introduction

Optical polymers have been widely used as key materials for various optical devices, for example, lenses and functional films for liquid crystal displays (LCDs), because of their easy processing, light weight, high transparency, and low cost. Optical polymers tend to exhibit birefringence caused by the orientation of the chains during processes such as injection-molding, extrusion and drawing thus creating an optically anisotropic material. Birefringence is the division of a ray of light into two rays when it passes through an optically anisotropic material depending on the polarization of the light. Two different refractive-indices are assingned to the material for different polarizations. In the case of uniaxially drawn polymer samples, the orientational birefringence Δn is defined as $\Delta n = n_{\|} - n_{\perp}$ where $n_{\|}$ and $n_{\perp}$ are refractive-indices for light polarized in a parallel direction and a perpendicular direction to the drawing direction, respectively. Although most of polymer chains have intrinsic optical anisotropy derived from asymmetry of their chemical structures, a polymer material becomes macroscopically isotropic and exhibits no birefringence when polymer chains are randomly oriented because their intrinsic optical anisotropies are cancelled by each other. However, a polymer material becomes birefringent when polymer chains are oriented because their intrinsic optical anisotropies are not cancelled by each other. This hinders maintaining the polarization state of light or focusing by lenses and results in degradation of the performance of the optical devices. Most of the optical device manufacturers make a lot of efforts to minimize birefringence by improving processing method and their conditions, in other words, by inhibiting orientation of polymer main chains. For example, almost all of low birefringent optical films for LCDs are manufactured by solvent casting instead of extrusion to reduce birefringence although the production rate of the former do not exceed a tenth part of that of the latter, which increases their cost. Therefore, optical polymers that exhibit no birefringence at any orientation of the polymer chains are ideal for realizing high performance and low cost optical devices for handling polarized light. These

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polymers have been defined as zero-birefringence optical polymers.[1–4]

Methods have been proposed to realize a zero-birefringence polymer. They include the random copolymerization method[1] and the anisotropic molecule dopant method.[2] In the random copolymerization method, the positive and the negative birefringent monomers were randomly copolymerized with the specified monomer ratio. As a result, birefringence of the polymer can be compensated in a polymer molecule. This approach has proven to be somewhat successful for the fabrication of optical devices such as pick-up lenses for optical disks. In the anisotropic molecule dopant method, molecules that have an anisotropic polarizability and a rod-like shape are chosen and doped into the polymers. When the polymer chains are oriented in processes, the molecules are also oriented because of their rod-like shape. The negative birefringence of the polymer can be compensated by doping with positive anisotropic molecules which have a higher polarizability in the direction of orientation than in the perpendicular direction. The anisotropic molecule dopant method is available for compensating the orientational birefringence of conventional polymers such as poly(methylmethacrylate) while preserving transparency and processability. However, the glass transition temperature tends to decrease due to the plasticising effect of the dopants and few practical anisotropic molecule dopants have been found for compensating positive birefringent polymers because rod-like shaped molecules tend to have a higher polarizability along their long axis.

We proposed the birefringent crystal dopant method and demonstrated compensation of the positive birefringence of polymer without losing its thermostability[3–4]. In this article, we report the orientation behavior of the doped crystals and discuss the design of crystals.

Birefringent Crystal Dopant Method

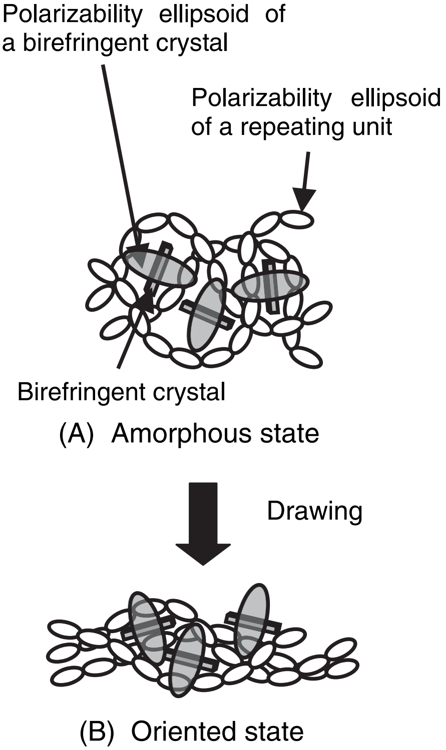

Figure 1.
Mechanism for the compensation of orientational birefringence by the birefringent crystal dopant method.

The compensation mechanism for the orientational birefringence of a polymer by the birefringent crystal dopant method is shown in Figure 1. In this method, nano-size birefringent crystals are added to polymers. The structural units of the polymer that correspond to the repeating units are illustrated by polarizability ellipsoids representing the polarizability anisotropy. The rectangular solids signify birefringent crystals, and ellipsoids overlapping with the birefringent crystals signify the polarizability anisotropy of the crystals. The polymer containing the crystals exhibits no birefringence when the repeating units are randomly oriented in the amorphous state as shown in Figure 1A. The crystals are oriented when the polymer chains are oriented as shown in Figure 1B. As a result, the birefringence of the polymer is compensated by the birefringence (strictly, polarizability anisotropy) of the crystal. In the following, an inorganic birefringent crystal that has a higher refractive-index for light polarized along its longer axis than that along its shorter axis is defined as a positive crystal, and the opposite one is a negative crystal. The orientational birefringence of positive and negative polymers can be compensated by a small amount of negative and positive crystals, respectively, because of their relatively large birefringence (typically >0.1).

Experimental

Preparation of Polymer Films Containing Strontium Carbonate Crystals

We selected strontium carbonate ($SrCO_3$) crystal as a dopant because it is needle-like and a negative crystal. The refractive-index for light polarized along the long axis of the needle-like $SrCO_3$ crystal is $n_x = 1.5199$ and along the other axes are $n_y = 1.666$ and $n_z = 1.6685$. $SrCO_3$ crystals in a polymer are oriented with its long axis along its draw direction by tensile stress. Therefore, we defined the intrinsic birefringence Δn_c^0 of $SrCO_3$ crystal as

$$\Delta n_c^0 = n_x - \sqrt{\frac{n_y^2 + n_z^2}{2}} = -0.147 \tag{1}$$

$SrCO_3$ was synthesized by injecting CO_2 gas into a $Sr(OH)_2/H_2O$ suspension. The crystals were surface treated with bis(dioctyl pyrophosphate) oxyacetate titanate.

We selected methyl methacrylate (MMA) and benzyl methacrylate (BzMA) as monomers. A mixture of MMA, BzMA, benzoyl peroxide as an initiator and *n*-butyl mercaptan as a chain transfer agent was placed in a glass tube, in which the ratio of MMA/BzMA was 78/22 (w/w). Polymerization was carried out at 70 °C for 1 day yielding poly(MMA/BzMA) that had a positive birefringence. The bulk polymer obtained was heat-treated at 90 °C for 1 day in order to finalize the polymerization, and the bulk was dissolved in acetone. The polymer solution was filtered through a 0.2 μm membrane filter, and dropped into methanol to precipitate the polymer and remove the remaining monomers. The polymer flakes obtained were dried under a reduced pressure for 2 days. The composition of the obtained copolymer was determined to be MMA/BzMA = 77.4/22.6 (w/w) based on the analysis of ^1H-NMR spectrum. Poly(MMA/BzMA) was dissolved in tetrahydrofuran with the $SrCO_3$ crystals. The polymer solution was spread onto a glass plate using a knife coater to prepare film samples with a thickness of approximately 30 μm.

These films were dried for 3 days at 90 °C at a reduced pressure (<1.33 Pa) to eliminate the solvent. The dried polymer films were uniaxially heat-drawn at a rate of 4 mm/min at 130 °C using a universal tensile testing machine (TENSILON RTC-1210A, A&D Company, Ltd.).

The birefringence Δn of the drawn films was calculated by dividing the retardation of the films by the distance that the light propagated the films. The retardation was determined at a wavelength of 633 nm by optical heterodyne interferometry using birefringence measurement equipment (ABR-10A, Uniopt Corporation, Ltd.).

Analysis of the Orientation of Polymers

In order to measure the degree of orientation of drawn polymer chains, the orientation function was determined from an infrared dichroic ratio measured by polarized Fourier-transform infrared spectroscopy.[5] In a drawn polymer film, the polymer chains are preferentially oriented in the draw direction. The dichroic ratio D is defined by

$$D = A_{\parallel}/A_{\perp}, \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ are absorbances for linearly polarized infrared light in the parallel and perpendicular direction to the draw direction, respectively. $A_{\parallel}$ and $A_{\perp}$ of the drawn film were measured within the spectral range 400 cm^{-1} to 4000 cm^{-1} using a Fourier transform infrared spectrometer (Digilab FTS-60A, Japan Bio-Rad Laboratories Company). An orientation function f_D is related to the dichroic ratio

D as

$$f_D = \frac{D-1}{D+2}\frac{2\cot^2\alpha+2}{2\cot^2\alpha-1} \tag{3}$$

where α is the angle between the transition moment vector of the absorbing group and the chain axis. We selected the symmetric bending of C-αCH$_3$ at 1388 cm^{-1} as the characteristic band of poly(MMA/BzMA). We used the angle α of 90 degrees for the C-αCH$_3$ bending band that was determined by Zhao *et al.*[6]

Results and Discussion

Figure 2 shows the size distribution of the synthesized SrCO$_3$ crystals which was measured from the scanning electron microscope micrographs. The crystals had a needle-like shape with an average length of about 193 nm, an average width of about 74 nm and an average aspect ratio of about 2.6. The transmission electron microscope (TEM) micrograph of the SrCO$_3$ crystals doped into poly(MMA/BzMA) film with a concentration of 0.3 wt% is shown in Figure 3. Dark images in the photograph are SrCO$_3$ crystals. The crystals were dispersed without aggregation in the polymer film.

The orientational birefringence of the films against the draw ratio at an incident angle of 0 degrees is shown in Figure 4. Absolute value of the orientational birefringence of the heat-drawn films became larger in proportion to the draw ratio. Poly(MMA/BzMA) film not containing the crystals exhibited a positive birefringence because of the orientation of polymer chains. On the other hand, poly(MMA/BzMA) film containing 0.3 wt% of the crystals exhibited a negative birefringence because of the negative birefringent effect of SrCO$_3$. Based on these results, birefringence of poly(MMA/BzMA) is estimated to be eliminated by 0.1–0.2wt% of the SrCO$_3$ crystal.

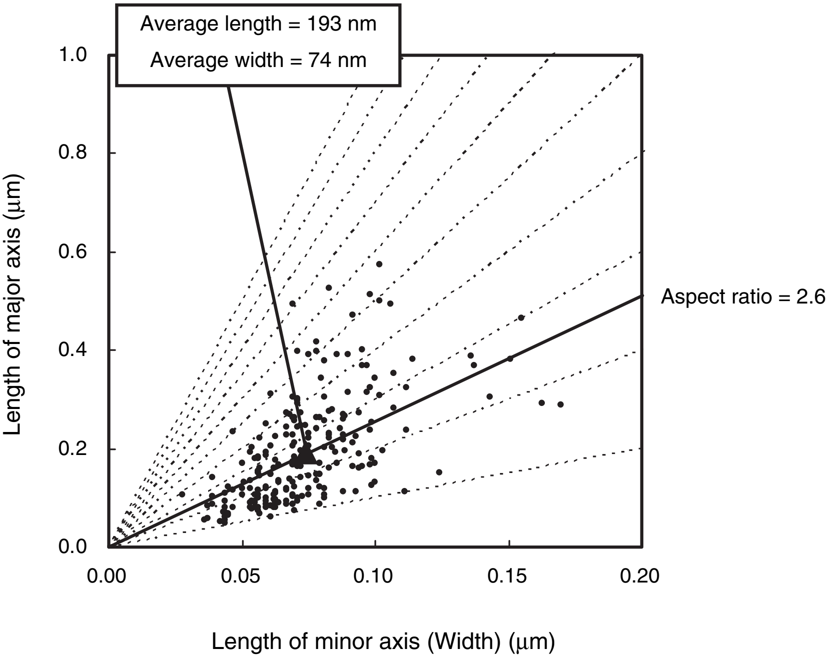

Figure 2.

The size distribution of the synthesized SrCO$_3$ crystals measured from the SEM micrograph. The average length is about 193 nm, the average width is about 74 nm and the average aspect ratio is about 2.6. The position of the average value is indicated by ▲.

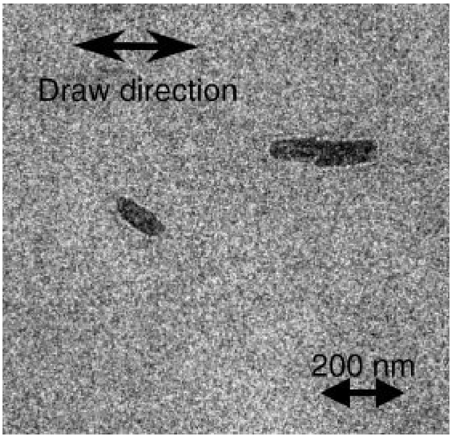

Figure 3.
A TEM micrograph of the $SrCO_3$ crystals doped into poly(MMA/BzMA) film with a concentration of 0.3 wt%.

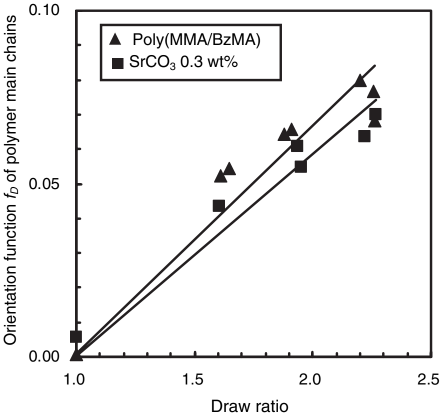

Figure 5.
Orientation function of the poly(MMA/BzMA) films containing $SrCO_3$, drawn at 130 °C and 4 mm/min with respect to draw ratio.

Figure 5 shows the orientation function f_D against the draw ratio of the films. Square and triangular plots are measured data, straight lines are approximation curves. The orientation function was calculated by Equation 3. From the approximation curves, orientation function f_D of poly(MMA/BzMA) and poly(MMA/BzMA) containing 0.3 wt% of $SrCO_3$ at draw ratio of 2.3 were about 0.0868 and about 0.0764, respectively, which means that the orientation function of the poly(MMA/BzMA) was reduced to about 88% by adding 0.3 wt% of $SrCO_3$. We called this effect, "the orientation-inhibition effect". The mechanism of the orientation-inhibition effect has not been clarified yet.

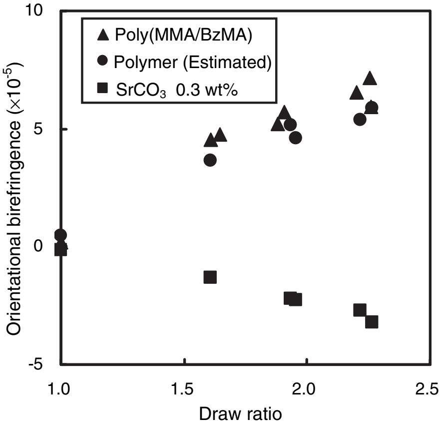

Figure 4.
Orientational birefringence of the poly(MMA/BzMA) films containing $SrCO_3$ with respect to draw ratio. ● = The estimated orientational birefringence value caused by the polymer molecules in the poly(MMA/BzMA) films containing 0.3 wt% of $SrCO_3$.

In the case of a polymer containing a birefringent crystal, the orientational birefringence may be formulated by

$$\Delta n = \Delta n_p^0 \cdot f_p \cdot \phi_p + \Delta n_c^0 \cdot f_c \cdot \phi_c + \Delta n_F, \quad (4)$$

where Δn_i^0 is the intrinsic birefringence of the i polymer, f_i is the orientation function, ϕ_i is the volume fraction, Δn_F is the form birefringence, subscripts p and c correspond to a polymer (poly(MMA/BzMA)) and a crystal ($SrCO_3$), respectively. The intrinsic birefringence of the polymer (Δn_p^0) was 0.00084 from the slope of the approximation curve in Figure 6, and that of the crystal (Δn_c^0) was -0.147 from Equation 1, respectively. The volume fraction of the polymer (ϕ_p) was 99.9055%, and that of the crystal (ϕ_c) was 0.0945%. The birefringence caused by only the polymer molecules of poly(MMA/BzMA) film containing $SrCO_3$ was estimated based on the relation shown in Figure 6 and its orientation function, and shown in Figure 4. Difference between the estimated birefringence and the measured

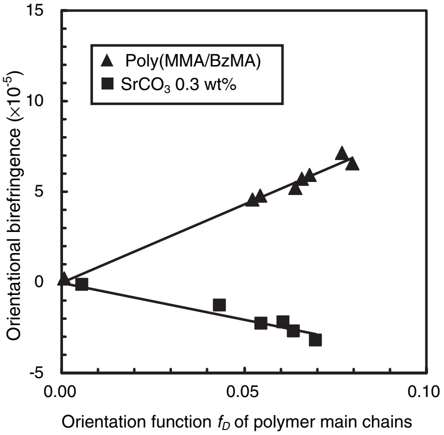

Figure 6.
Orientational birefringence of the poly(MMA/BzMA) films containing $SrCO_3$, drawn at 130 °C and 4 mm/min with respect to orientation function f_D of polymer main chains.

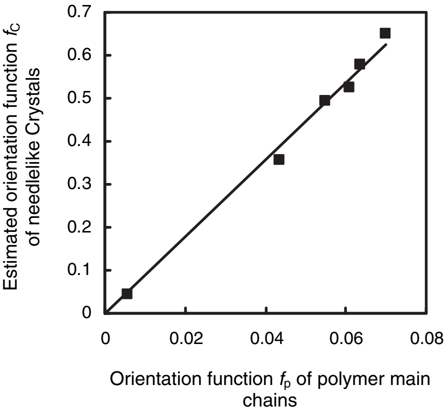

Figure 7.
Estimated orientation function f_c of $SrCO_3$ needle-like crystal in the poly(MMA/BzMA) films against the orientation function f_p of a polymer main chain in the films.

birefringence of poly(MMA/BzMA) film not containing $SrCO_3$ was the birefringence reduction by the orientation-inhibition effect. Furthermore, difference between the estimated birefringence and the measured birefringence of poly(MMA/BzMA) film containing $SrCO_3$ was the birefringence reduction by the negative birefringence of the $SrCO_3$ crystals.

The orientation function of $SrCO_3$ crystals was calculated by the following Equation 5,

$$f_c = \left(\Delta n - \Delta n_p^0 \cdot f_p \cdot \phi_p - \Delta n_F\right) \Big/ \left(\Delta n_c^0 \cdot \phi_c\right) \tag{5}$$

which leads from Equation 4. The birefringence shown in Figure 4 was used for Δn, and the orientation function of the polymer shown in Figure 6 was used for f_p. The above mentioned values were used for Δn_p^0, Δn_c^0, ϕ_p and ϕ_c. The estimated Δn_F was low ($<1.0 \times 10^{-5}$) and positive, and did not compensate the positive birefringence of the polymer; therefore Δn_F was assumed to be zero as,

$$\Delta n_F \cong 0. \tag{6}$$

f_c was calculated by substituting the values described above into Equation 5. The calculation of f_c against the orientation function of the polymer is shown in Figure 7. We found out the calculated orientation function of the crystal was about 9.0 times larger than that of the polymer in the drawing conditions. These results showed that the birefringence of the film was compensated by a low concentration of $SrCO_3$ because of its high orientation degree as compared with that of the polymer main chains and its orientation-inhibition effect.

In the previous article[4], we reported that the estimated orientation function of the crystal was about 12.0 times larger than that of the polymer. Regarding the crystal, the average length, the average width and the average aspect ratio were about 195 nm, about 65 nm, about 3.0, which were measured from the TEM micrograph. These results showed that the orientation function of the needle-like crystal was increased with an increase in the aspect ratio of the needle-like crystal.

Conclusions

We have demonstrated the birefringent crystal dopant method by homogeneous doping with $SrCO_3$ to compensate for the orientational birefringence of a polymer.

The positive birefringence of heat-drawn poly(MMA/BzMA) films at a wavelength of 633 nm was changed into negative birefringence by doping with 0.3 wt% of $SrCO_3$ while maintaining film transparency and thermostability, which showed that the birefringence of the polymer was compensated by the birefringence of the crystal. The orientation function of the needle-like crystals was estimated to be about 9.0 times larger than that of the polymer. We found that the orientation function of the needle-like crystal was increased with an increase in the aspect ratio of the needle-like crystal. These results showed the strategy for designing needle-like crystals to realize high-efficiency compensation of birefringence of polymers.

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