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Synthesis of a zero-birefringence optical polymer by the birefringent crystal dopant method and analysis of its characteristics

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Birefringence induced by the orientation of polymer main chains during an injection- molding or extrusion processing restricts the application of optical polymers to optical devices that require maintaining the polarization state of incident light. We propose the "birefringent crystal dopant method" to compensate the birefringence of polymers by homogeneous doping with an opposite birefringent needle-like crystal. Strontium carbonate ($SrCO_3$) was selected for this method and synthesized, with a length of about 200nm and a width of about 20nm. $SrCO_3$ was doped into poly(MMA/BzMA= 78/22(wt./wt.)) film. The film was uniaxially drawn at 130°C and 4mm/min. For the first time, the positive birefringence of the drawn copolymer film at a wavelength of 633nm was compensated by doping with 0.3wt.% of $SrCO_3$ without losing transparency and thermostability. The orientational birefringence of the zero-birefringence film was lower than that of blank copolymer film at any angle of incidence of light.

Key words: zero-birefringence, optical polymer, birefringent crystal dopant method, strontium carbonate, birefringence, inorganic crystal

1. INTRODUCTION

Optical devices that can transmit and store mass information are indispensable to the recent highly information-oriented society. Many optical devices based on polymer materials have been widely studied for the recent optical technology, for example, polymer optical fibers [1, 2], optical films for liquid-crystal displays, optical disks [3], lenses [4] and optical waveguides [5]. Polymers have the advantage of easy processing, easy handling, light weight, and low cost as compared with glasses. However, polymers have one serious drawback: they are birefringent. Birefringence degrades the performance of optical devices that require focusing by lenses or maintaining the polarization state of incident light. Birefringence does not occur if polymer main chain orientations are perfectly random without any stress. One of the main sources of birefringence development is the orientation of polymer main chains during a melt flow in injection-molding, extrusion or drawing processing. During the cooling stage in such processing, the orientation of polymer chains does not completely relax and causes orientational birefringence.

In order to prepare zero-birefringence polymers, we proposed two methods—the random copolymerization method [6, 7] and the anisotropic molecule dopant method [8, 9]. Two types of monomers that compose positive and negative birefringent polymers, respectively, were randomly copolymerized. A rod-like molecule that has a polarizability anisotropy was chosen and doped into polymers in the anisotropic molecule dopant method. The negative birefringence of poly(methyl methacrylate) (PMMA) based polymers was compensated by both the methods.

Compensating the birefringence of conventional polymers that have high glass transition temperatures (T_g), such as polycarbonate, is required in many applications where polymers have replaced glasses. However, such polymers generally exhibit a positive birefringence which has not been eliminated yet.

2. BIREFRINGENT CRYSTAL DOPANT METHOD

In this report, we propose a novel "birefringent crystal dopant method" to compensate the birefringence of polymers by homogeneous doping with an inorganic birefringent crystal [10]. The crystal for this method must have opposite orientational birefringence to that of the polymers. We describe the method and the optical and thermal characterization of the zero-birefringence polymer obtained.

The mechanism of the compensation of orientational birefringence by the birefringent crystal dopant method is shown in Fig. 1. Ellipsoids represent polarizability anisotropies of a monomer unit and a crystal, respectively. It is important to choose a crystal whose shape is needle-like for the method. In the completely random state shown in Fig. 1(a), polymer chains and crystals exhibit no birefringence. When the polymer chains are oriented as shown in Fig. 1(b), the crystals are also oriented because of their shape.

In the case of uniaxially drawn polymer samples, the orientational birefringence Δn is defined as

$$\Delta n = n_{\parallel} - n_{\perp}. \quad (1)$$

where $n_{\parallel}$ and $n_{\perp}$ are refractive-indices for incident light

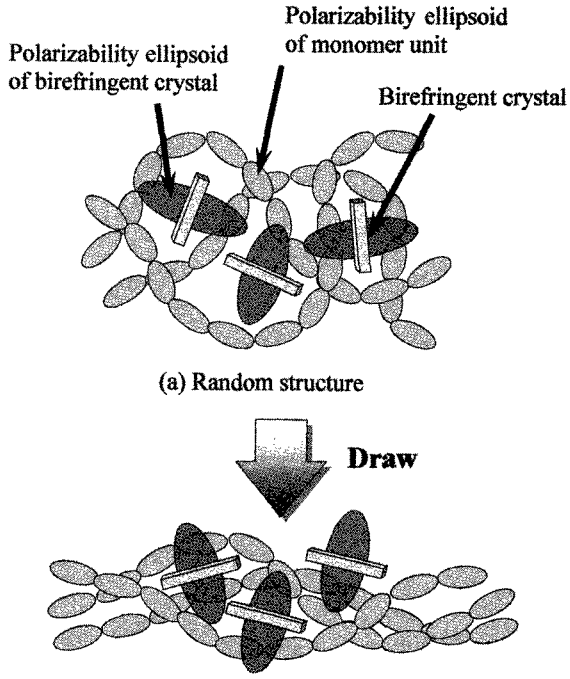

Figure 1 Mechanism of the compensation of orientational birefringence by the birefringent crystal dopant method.

polarized parallel and perpendicular to the drawing direction, respectively. Positive polymers show orientational birefringence $\Delta n > 0$ and negative polymers show $\Delta n < 0$.

3. EXPERIMENTAL DETAILS

3.1 Preparing Strontium Carbonate and Polymer films

We selected strontium carbonate ($SrCO_3$) crystals for a negative birefringent needle-like crystal to compensate the positive birefringence of polymers. The refractive-indices of $SrCO_3$ are n_a= 1.6685, n_b= 1.666 and n_c= 1.5199. $SrCO_3$ has a negative birefringence, because refractive-index n_c of the longer axis is lower than the other refractive-indices n_a and n_b of the shorter axes. We selected methyl methacrylate (MMA) as a negative birefringent monomer and benzyl methacrylate (BzMA) as a positive birefringent monomer. The monomers were randomly copolymerized yielding poly(MMA-co-BzMA) that had a positive birefringence, with the composition of MMA/BzMA=78/22(wt./wt.).

$SrCO_3$ was prepared by reaction of a suspension of strontium hydroxide with carbon dioxide. The surface of the crystal was treated by a titanate-based coupling agent [bis(dioctyl pyrophosphate) oxyacetate titanate] in order to disperse the crystal in a polymer homogeneously. The crystal length and the width of the obtained $SrCO_3$ were about 200nm and 20nm, respectively. Poly(MMA/BzMA=78/22) was dissolved in ethyl acetate with $SrCO_3$. The polymer solution was cast onto a glass plate to prepare film samples with a thickness of approximately 30μm using a knife coater. Three types of film samples were prepared to evaluate the birefringent crystal dopant method. Film 1 was poly(MMA/BzMA=78/22), Film 2 was 0.3wt.% of $SrCO_3$ doped copolymer and Film 3 was 0.4wt.% of $SrCO_3$ doped copolymer. These films were dried at a temperature of 90°C and at a reduced pressure (<1.33 Pa) for 3days to eliminate the solvent.

3.2 Analyzing the characteristics of $SrCO_3$ doped polymer

The dried polymer films were uniaxially heat-drawn at a rate of 4mm/min and at a temperature of 70°C using a universal tensile testing machine (TENSILON RTC-1210A, A&D Company, Ltd.). The birefringence of the drawn films was determined at a wavelength of 633nm by an optical heterodyne technique using Auto Birefringence Measurement Equipment (ABR-10A, Uniopt Corporation, Ltd.).

The normalized light intensity at a wavelength of 633nm through the center of the drawn films between a polarizer and an analyzer was measured using a power meter (Q8221, Advantest Corporation) and a digital lock-in amplifier (LI5640, NF Corporation) to investigate the polarization maintaining property of the films. Experimental set-up is shown in Fig. 2. Glan-Taylor prisms with an extinction ratio of 5×10^{-5} were used as a polarizer and an analyzer. The films were placed with their drawn direction oriented axis at 45° to the polarizer. The normalized light intensity was measured as the analyzer was rotated every 0.2° from 0°

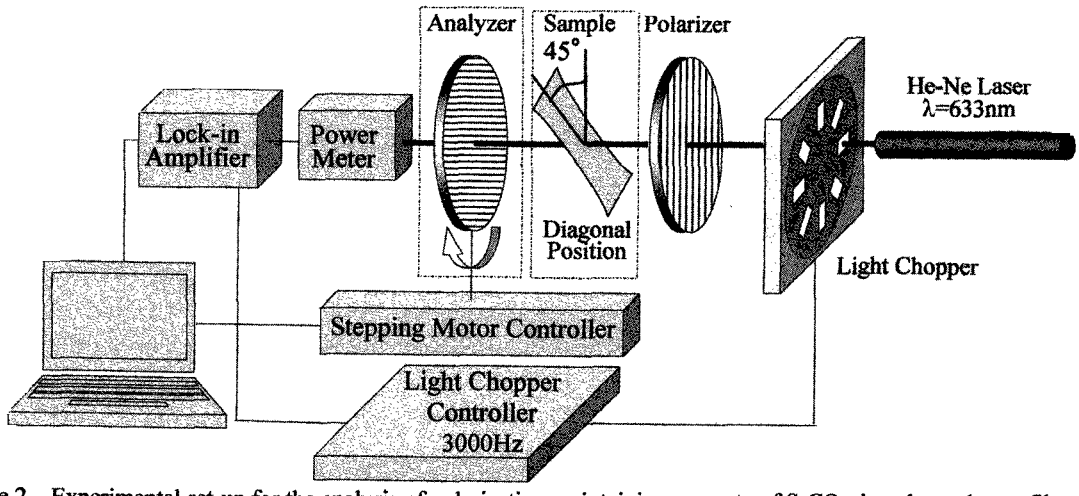

Figure 2 Experimental set-up for the analysis of polarization maintaining property of $SrCO_3$ doped copolymer films.

(parallel polarizers state) to 90° (crossed polarizers state).

The transmittance of undrawn films was measured using a spectrophotometer (U-2001, Hitachi instruments service Company, Ltd.). Furthermore, the *Tg* of the films was measured at a heating rate of 10°C/min using a differential scanning calorimeter (DSC-50, Shimadzu Corporation).

4. RESULTS AND DISCUSSION

4.1 Observation of $SrCO_3$ in polymer films

Figure 3 shows SEM photographs of $SrCO_3$ doped into poly(MMA/BzMA=78/22) film at a concentration of 0.3wt.%. Black images are $SrCO_3$ crystals. The orientation of $SrCO_3$ to the drawing direction was observed after uniaxial heat-drawing at a draw ratio of 2.15.

4.2 Birefringence of drawn copolymer films

Figure 4 shows the orientational birefringence Δn of the films against the draw ratio. Undrawn films did not exhibit birefringence, and the birefringence of the heat-drawn films became larger in proportion to the draw ratio. Figure 4(a) shows that Film 1 generated a positive birefringence because of the orientation of polymer chains. On the other hand, the 0.4wt.% $SrCO_3$ doped film (Film 3) exhibited a negative birefringence because of the orientation of negative birefringent $SrCO_3$ as shown in Fig. 4(c). In the case of Film 2, the positive birefringence of the blank copolymer was compensated by doping with 0.3 wt.% of $SrCO_3$, as shown in Fig. 4(b). Based on these results, we confirmed that Film 2 is a zero-birefringence optical polymer.

The orientational birefringence Δn of the drawn films against an angle of incidence of light was also measured. Figure 5 illustrates a scheme of the measurement and Fig. 6 shows the result. A plane of incidence of light was parallel to a draw direction of the sample films as shown in Fig. 5. A draw ratio of the films was nearly 2.

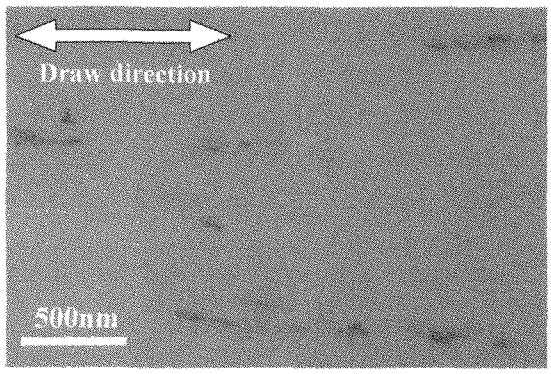

Figure 3 TEM photograph of $SrCO_3$ doped into poly(MMA/BzMA=78/22) film at a concentration of 0.3wt.% and with a thickness of 40μm (× 20,000, at a draw ratio of 2.15).

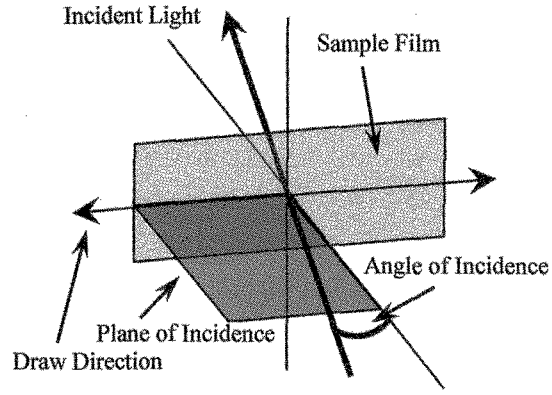

Figure 5 Scheme of an orientational birefringence measurement of drawn films at several incident angle of light.

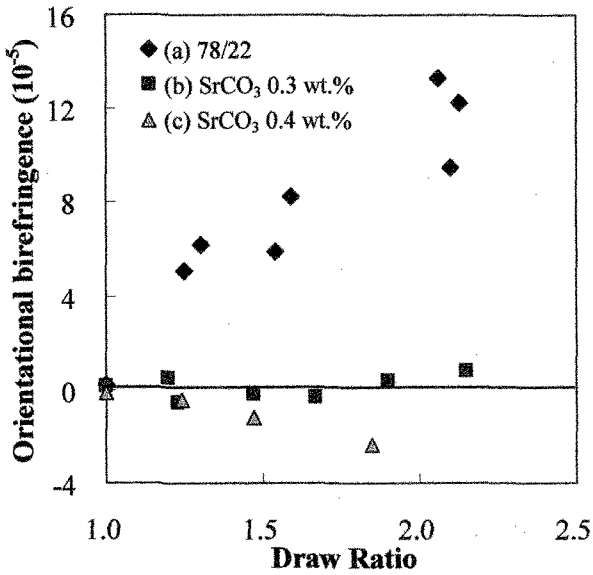

Figure 4 Orientational birefringence of $SrCO_3$ doped poly(MMA/BzMA=78/22) films, drawn at 130°C and 4mm/min. (a) Film 1, (b) Film 2 and (c) Film 3.

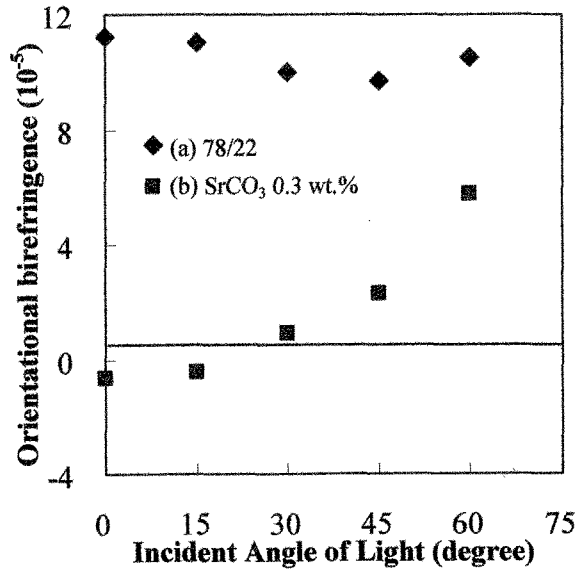

Figure 6 Orientational birefringence of $SrCO_3$ doped poly(MMA/BzMA=78/22) film against an incident angle of light, drawn at 130°C and 4mm/min, draw ratio 2. (a) Film 1 and (b) Film 2.

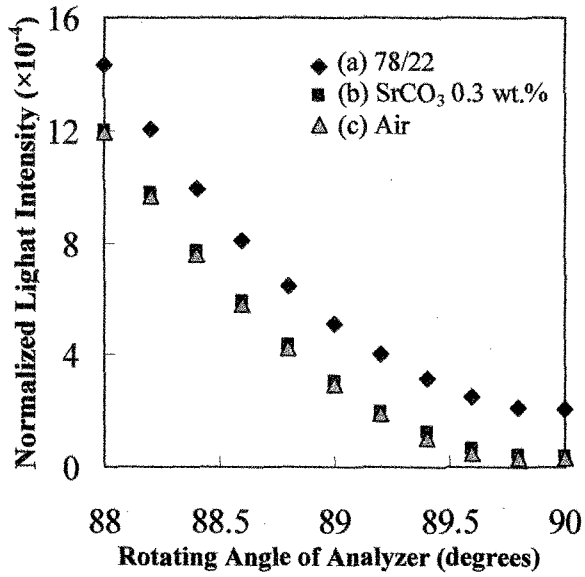

Figure 7 Normalized light intensity of $SrCO_3$ doped poly(MMA/BzMA=78/22) films at a draw ratio of 2.15 between a polarizer and an analyzer. (a) Film 1, (b) Film 2 and (c) Air.

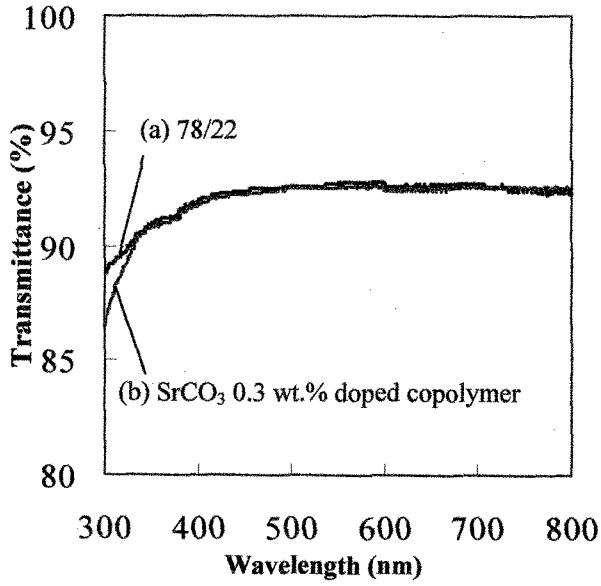

Figure 8 Transmittance of $SrCO_3$ doped poly (MMA/BzMA=78/22) films. (a) Film 1, and (b) Film 2.

Orientational birefringence of crystal doped Film 2 was almost compensated at the angle of 0°. A sign of the birefringence of Film 2 became positive and a value of the birefringence increased, when the angle of incidence of light became larger as shown in Fig.6 (b). A refractive index ellipsoid of the zero-birefringence polymer film may not be a sphere. However, the birefringence of Film 2 was lower than that of Film 1 at any incident angle of light.

4.3 Polarization maintaining property

Figure 7 shows the polarization-maintaining property of the heat-drawn films at a draw ratio of 2.15. Figure 7(a) shows that the normalized light intensity of the drawn Film 1 was 2.069×10^{-4} in crossed polarizers state because of the birefringence caused by the heat-drawing. On the other hand, Fig. 7(b) shows that the normalized light intensity of drawn zero-birefringence Film 2 was 0.396×10^{-4}. Film 2 maintained the polarization state of incident light nearly the same as air, because the birefringence of the copolymer was compensated.

4.4 Transparency and thermostability

Transmittances of Film 1 and Film 2 at a wavelength of 633 nm were 92.6% and 92.5%, respectively as shown in Fig 8. The *Tg* of Film 1 and Film 2 were 109.4°C and 109.6°C, respectively. It should be pointed out that $SrCO_3$ compensated the positive birefringence of polymers while nearly maintaining the transparency and thermostability of undoped films.

5. CONCLUSION

We have demonstrated the birefringent crystal dopant method to compensate the orientational birefringence of polymers by homogeneous doping with $SrCO_3$. $SrCO_3$ in a drawn polymer film was oriented to a drawing direction with a polymer main chain from SEM observation. As a result, the positive birefringence of heat-drawn poly(MMA/BzMA =78/22) films at a wavelength of 633 nm was compensated by doping with 0.3wt.% of $SrCO_3$ for the first time. The orientational birefringence of the zero-birefringence film was lower than that of blank copolymer film at any angle of incidence of light. We confirmed that the zero-birefringence film maintained the polarization state of incident light as air.

REFERENCES

[1] T. Ishigure, E. Nihei and Y. Koike, Appl. Opt., 33, 4261-66 (1994).
[2] Y. Koike, T. Ishigure and E. Nihei, J. Lightwave Technol., 13, 1475-89 (1995).
[3] E. Bernacki and M. Mansuripur, Appl. Opt., 32, 6747-55 (1993).
[4] Y. Koike, N. Tanio, E. Nihei, and Y. Ohtsuka, Polym. Eng. Sci., 29, 1200-04 (1989).
[5] Y. Koike, Y. Takezawa, and Y. Ohtsuka, Appl. Opt., 27, 486-91 (1988).
[6] S. Iwata, H. Tsukahara, E. Nihei and Y. Koike, Jpn. J. Appl. Phys., 35, 3896-901 (1996).
[7] S. Iwata, H. Tsukahara, E. Nihei and Y. Koike, Appl. Opt., 36, 4549-55 (1997).
[8] A. Tagaya, S. Shuichi, E. Kawanami, H. Tsukahara and Y. Koike, Appl. Opt., 40, 3677-83 (2001).
[9] A. Tagaya, S. Shuichi, E. Kawanami, H. Tsukahara and Y. Koike, Jpn. J. Appl. Phys., 40, 6117-23 (2001).
[10] A. Tagaya, H. Ohkita, M. Mukoh, R. Sakaguti and Y. Koike, Science, 301, 812-814 (2003).

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