Compensation of the Birefringence of a Polymer by a Birefringent Crystal

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We report 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 that of the polymer and has rod-shaped crystals that are oriented when the polymer chains are oriented. The birefringence of the polymer is thus compensated by the opposing birefringence of the crystal. Birefringence is minimized in various polymer optical devices by adjusting process conditions, because it degrades the performance of devices. This method minimizes it, independent of process conditions, which potentially improves the productivity of devices.

Optical polymers have been widely used as key materials for various optical devices—for example, as 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 processing by 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 assigned to the material for different polarizations. In the case of uniaxially drawn polymer samples, the orientational birefringence Δn is defined as $\Delta n = n_{\parallel} - n_{\perp}$, where $n_{\parallel}$ and $n_{\perp}$ are refractive indices for light that is polarized in a parallel direction and a perpendicular direction to the drawing direction, respectively. Although most 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 cancel each other. However, a polymer material becomes birefringent when polymer chains are oriented, because their intrinsic optical anisotropies do not cancel 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 optical device manufacturers attempt to reduce birefringence by increasing annealing time and temperature, which increases both processing time and cost (*1*, *2*). In addition, almost all low-birefringence optical films for LCDs are manufactured by solvent casting instead of extrusion to reduce birefringence, although the production rate of the former is only 1/10 that of the latter.

Methods have been proposed to realize a zero-birefringence polymer. They include polymer blending (*3*), random copolymerization (*4*, *5*), and doping anisotropic molecules (*6*, *7*). Polymer blending is a well-known method of obtaining a zero-birefringence polymer, in which negative- and positive-birefringence homopolymers are blended. In practice, it is difficult to completely blend two polymers during injection molding or extrusion, and thus difficult to achieve the transparency and homogeneity required for use in high-performance optical devices; the blends tend to phase separate into domains of the corresponding homopolymers on the order of more than several hundred nanometers, leading to scattering. The random copolymerization method was proposed to solve this problem by creating chemical bonding between the negative- and positive-birefringence monomers. This approach has proven to be somewhat successful for the fabrication of optical devices such as pick-up lenses for optical disks. However, the typical optical, mechanical, and thermal properties of most zero-birefringence polymers synthesized by these two methods were considerably different from the corresponding homopolymers, because the mixing ratio of the minority component was usually more than 10 weight % (wt %). For conventional optical polymers such as poly(methylmethacrylate) (PMMA), compensating the birefringence is still a challenge.

In the anisotropic molecule dopant method, molecules that have an anisotropic polarizability and a rodlike shape are chosen and doped into the polymers. When the polymer chains are oriented in processing, the molecules are also oriented because of their rodlike shape. The negative birefringence of the polymer can be compensated by doping with positive anisotropic molecules that have a higher polarizability in the direction of orientation than in the perpendicular direction. In principle, the positive birefringence of a polymer can be compensated by doping with negative anisotropic molecules. The orientational birefringence of PMMA was compensated by doping with 3.0 wt % trans-stilbene on the basis of the anisotropic molecule dopant method (*6*, *7*). The anisotropic molecule dopant method is available for compensating the orientational birefringence of conventional polymers while preserving transparency and processability. However, the glass transition temperature tends to decrease because of the plasticizing effect of the dopants, and few practical anisotropic molecule dopants have been found for compensating positive-

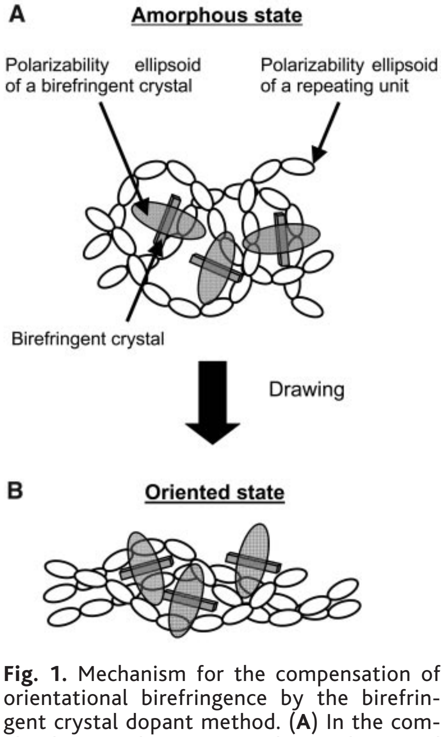

Fig. 1. Mechanism for the compensation of orientational birefringence by the birefringent crystal dopant method. (**A**) In the completely amorphous state, polymer chains and birefringent crystals are randomly oriented, so that the polymer containing the birefringent crystals exhibits no birefringence. (**B**) Polymer chains and birefringent crystals are oriented in the drawing direction. However, birefringence of the polymer is compensated by that of the crystal.

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birefringence polymers because a rod-shaped molecule tends to have a higher polarizability along its long axis.

By using a birefringent crystal dopant, we show that it is possible to compensate the orientational birefringence of conventional polymers while preserving transparency and thermostability. Here, an inorganic birefringent crystal that has a higher refractive index for light polarized along its longer axis than along its shorter axis is defined as a positive crystal, and the opposite one is defined as a negative crystal. The compensation mechanism for the positive birefringence of a polymer by a negative crystal is shown in Fig. 1. The structural units of the polymer that correspond to the repeating units are illustrated by polarizability ellipsoids representing the polarizability anisotropy. The rectangular solids represent birefringent crystals, and ellipsoids overlapping with the birefringent crystals represent the polarizability anisotropy of the crystals. The polymer that contains the crystals exhibits no birefringence when the repeating units are randomly oriented in the amorphous state (Fig. 1A). The crystals are oriented when the polymer chains are oriented (Fig. 1B). As a result, the birefringence of the polymer is compensated by the birefringence (strictly, polarizability anisotropy) of the 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). The most important point is the size of the birefringent crystal dopant. The results of the anisotropic molecule dopant method (*6*, *7*) lead us to conclude that the birefringence of a polymer can be compensated by doping with birefringent crystals having molecular dimensions. However, it is difficult to synthesize such a small birefringent crystal that has a rodlike shape, which leads to the question: What are the maximum sizes of the units that have positive and negative optical anisotropy, respectively, that are needed to form an optically isotropic medium when they are randomly mixed? We believe that it is less than the size of an optical wavelength.

We showed that the compensation for the positive birefringence of poly[methylmethacrylate (MMA)-co-benzylmethacrylate (BzMA)] is 78/22 (wt/wt) by doping with strontium carbonate ($SrCO_3$) crystals. The refractive index for light polarized along the long axis of the needlelike $SrCO_3$ crystal is 1.5199, and along the other axes, the refractive indices are 1.666 and 1.6685. $SrCO_3$ was synthesized by injecting CO_2 gas into a $Sr(OH)_2/H_2O$ suspension. The crystals have a rodlike shape with a length of about 200 nm and a width of about 20 nm. The crystals were surface treated with bis(dioctyl pyrophosphate) oxyacetate titanate and were then added to a [poly(MMA-co-BzMA)/tetrahydrofuran] solution, and a film was prepared by casting from solution. The thickness of the polymer film was 30 μm. We chose poly(MMA-co-BzMA) because we can disperse the nanometer-size $SrCO_3$ particles into it, avoiding aggregation with the surface treatment, and because it exhibits a positive birefringence and high transparency. Figure 2 shows photographs of poly(MMA-co-BzMA) films placed between crossed Nicol polarizers. The samples look dark if the polarization state of the transmitted light is uniform; however, the samples look bright if the polarization state of the transmitted light is disturbed as a result of birefringence or depolarized scattering. The unoriented poly(MMA-co-BzMA) film exhibited no birefringence (Fig. 2A). The polarization state of the transmitted light was almost undisturbed through the poly(MMA-co-BzMA) film, which contained 0.5 and 1.0 wt % $SrCO_3$ (Fig. 2, B and C). In contrast, the film containing the large $SrCO_3$ crystals shows birefringence and depolarized scattering (Fig. 2D). The size of the crystals (3.0 μm × 300 nm) is too large to form an optically isotropic medium with the polymer. As a result, the light transmitted through a birefringent crystal and the light transmitted through the polymer around the birefringent crystal become independent of each other.

The orientational birefringence of the compensated poly(MMA-co-BzMA) film uniaxially heat-drawn at 130°C is shown in Fig. 3. The poly(MMA-co-BzMA) film containing 0.4 wt % $SrCO_3$ (length 200 nm) showed a negative orientational birefringence, whereas the poly(MMA-co-BzMA) film showed a positive orientational birefringence. The negative value of the orientational birefringence increased as the crystal concentration increased. At a doping level of 0.3 wt %, the orientational birefringence of poly(MMA-co-BzMA) was almost eliminated for draw ratios of less than 2.0. Figure 4 shows a micrograph of the heat-drawn poly(MMA-co-BzMA) film containing 1 wt % $SrCO_3$ with a length of about 200 nm at a draw ratio of 2.0 obtained with a scanning electron microscope. The $SrCO_3$ needlelike crystal particles were statistically oriented in the drawing direction. A decrease in the degree of orientation of the polymer chains when doped with optically isotropic nanoparticles in a uniaxial heat-drawing process was reported in (*8*). Although a similar effect may have occurred here, the positive orientational birefringence does not become negative because of the decrease in overall chain orientation.

The poly(MMA-co-BzMA) film containing 0.3 wt % $SrCO_3$ (length 200 nm) exhibited the same glass transition temperature (109.5°C) as the poly(MMA-co-BzMA) film. The $SrCO_3$ crystals induced no plasticization because the size of the crystals was much larger than that of the polymer molecules. The transmittance of the poly(MMA-co-BzMA) film containing 0.3 wt % $SrCO_3$ is shown in Fig. 5. The polymer film showed

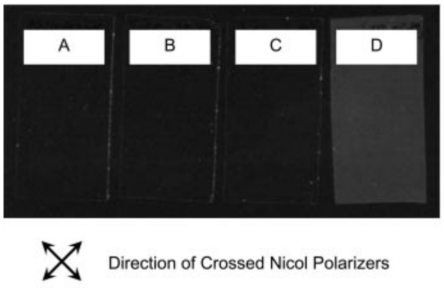

Fig. 2. A photograph of polymer films placed between crossed Nicol polarizers. (**A**) Poly(MMA-co-BzMA), (**B**) containing 0.5 wt % $SrCO_3$ with a length of 200 nm and a width of 20 nm, (**C**) containing 1.0 wt % $SrCO_3$ with a length of 200 nm and a width of 20 nm, and (**D**) containing 0.5 wt % $SrCO_3$ with a length of 3.0 μm and a width of 300 nm.

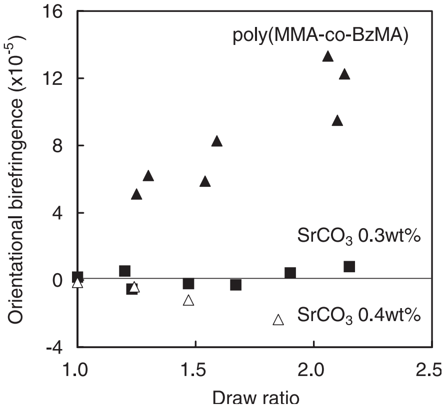

Fig. 3. Orientational birefringence of the poly(MMA-co-BzMA) films containing $SrCO_3$ with respect to draw ratio.

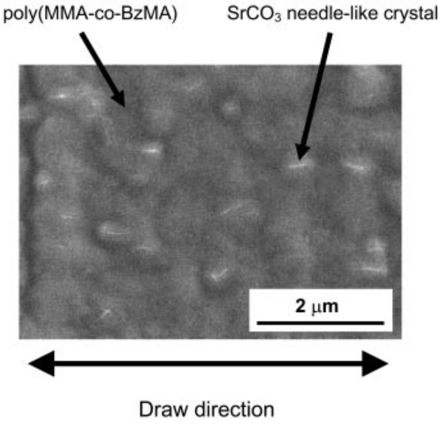

Fig. 4. A photograph of the heat-drawn poly(MMA-co-BzMA) film containing 1.0 wt % $SrCO_3$. Draw ratio = 2.0; drawing temperature = 130°C; drawing speed = 4 mm/min.

Fig. 5. Transmittance of pure poly(MMA-co-BzMA) and a film containing 0.3 wt % $SrCO_3$. Film thickness = 30 μm.

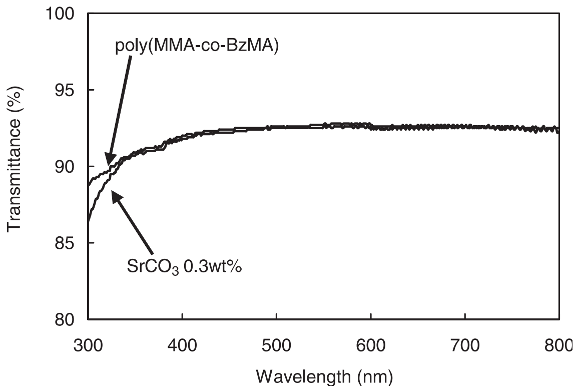

Table 1. Haze of the films.

Film	Haze (%)
PMMA	0.4
PC	0.3
poly(MMA-co-BzMA)	0.5
$SrCO_3$ (0.3 wt %)/poly(MMA-co-BzMA)	0.6

sufficient transmittance for optical films used in LCDs in the visible region. Despite doping with 0.3 wt % $SrCO_3$, the transmittance of the doped film was the same as the undoped one in the visible region because $SrCO_3$ has no large absorption band in the visible region.

The decrease in transmittance was caused by light scattering by the crystals. Table 1 lists haze values for PMMA, polycarbonate (PC), poly(MMA-co-BzMA), and [$SrCO_3$/poly(MMA-co-BzMA)] films with a thickness of 40 μm. The haze measurements were carried out according to American Society for Testing and Materials (ASTM) D1003. The haze value of the [$SrCO_3$/poly(MMA-co-BzMA)] film was almost the same as those of PMMA and PC films. The increase in haze by doping with 0.3 wt % $SrCO_3$ was 0.1%. Although the scattering loss cannot become zero, it can be reduced to a tolerable level by reducing the size of the birefringent crystal particles to less than the optical wavelength (less than about 200 nm × about 20 nm).

It follows from our discussion that the birefringent crystal dopant method is applicable to other polymers, and other kinds of birefringent crystals can be potential dopant candidates. Strontium carbonate, which is a negative birefringent crystal, is applicable to conventional optical polymers that have the high thermal stability typified by PC, because such polymers tend to exhibit a positive birefringence.

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Catalytic, Oxidative Condensation of CH_4 to CH_3COOH in One Step via CH Activation

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Acetic acid is an important petrochemical that is currently produced from methane (or coal) in a three-step process based on carbonylation of methanol. We report a direct, selective, oxidative condensation of two methane molecules to acetic acid at 180°C in liquid sulfuric acid. Carbon-13 isotopic labeling studies show that both carbons of acetic acid originate from methane. The reaction is catalyzed by palladium, and the results are consistent with the reaction occurring by tandem catalysis, involving methane C-H activation to generate Pd-CH_3 species, followed by efficient oxidative carbonylation with methanol, generated in situ from methane, to produce acetic acid.

Natural gas, which is composed primarily of methane, is one of the most abundant, low-cost, carbon-based feed stocks available. In spite of this, we are dependent on dwindling petroleum reserves because efficient technology has not yet been developed to economically convert methane directly to useful products. This is primarily because the C-H bonds of methane are strong, and efficient catalysts have not been developed that can economically, selectively, and directly convert methane to functionalized molecules. Consequently, the development of new, selective, catalysts for direct conversion of methane to useful products is an important challenge in chemistry today (*1*–*14*).

Acetic acid is an important petrochemical that is currently synthesized from methane (or coal) in a three-step capital- and energy-intensive process based on the high-temperature conversion of methane (or coal) to syn-gas, conversion of syn-gas to methanol, and finally carbonylation of the methanol to acetic acid (Scheme 1). Research efforts are being directed at more direct methods to generate acetic acid, such as the oxidation of ethane to acetic acid (*15*, *16*) or the oxidative carbonylation of methane (*5*, *17*–*21*), but no new processes have yet been commercialized. We now report the observation of the direct, one-step, selective, oxidative condensation of two methane molecules to acetic acid in low yields (~10%) based on methane. It is anticipated that, with improvements in yield and efficiency, such a direct, one-step conversion of methane to acetic acid (Scheme 1) could be less expensive than the existing multistep processes.

Several new catalyst systems have been reported for the selective conversion of methane to functionalized methyl products such as methanol (*8*, *9*), esters (*9*, *10*, *22*, *23*), sulfonic acid (*24*–*26*), and acetic acid (*5*, *17*–*21*). In the reported cases of methane conversions to acetic acid, the methyl group of the acetic acid is derived from methane, whereas the carboxylic group is derived from various carbon sources, such as CO (*5*, *17*, *19*), CO_2 (*18*), or carboxylic acid (*21*) reactants. However, to our knowledge, no reaction has been reported where both carbons of acetic acid are derived directly from two methane molecules in a single reaction system.

We have reported two high-yield systems for the low-temperature conversion of methane to methanol based on Hg(II) (*22*) and Pt(II) (*10*) catalysts that operate in liquid sulfuric acid. Coupled with acid-stable cata-

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