Zero-Birefringence Optical Polymers

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ABSTRACT: Here we demonstrate, for the first time, that it is possible to synthesize a polymer that exhibits no orientational birefringence and no photoelastic birefringence using two methods. In these methods, the contributions of monomers and an anisotropic dopant to orientational birefringence and photoelastic birefringence are analyzed experimentally, after which the composition of a ternary copolymer or a binary copolymer including the dopant is adjusted, based on the results, to compensate for both types of birefringence. By the methods and fine adjustment of the composition, we synthesized poly(methyl methacrylate (MMA)/2,2,2-trifluoroethyl methacrylate (3FMA)/benzyl methacrylate = 52.0/42.0/6.0(w/w/w)) and poly(MMA/3FMA = 85.0/15.0(w/w)) containing 2.8 wt % of *trans*-stilbene that exhibited close to zero birefringence.

I. Introduction

Optical polymers are widely used as key materials for various optical devices, for example, lenses, optical disks, and functional films for liquid crystal displays, due to their ease of processing, light weight, high transparency, and low cost. However, they tend to exhibit birefringence in processes such as injection molding, extrusion, and drawing. The caused birefringence degrades the performance of optical devices that require fine focusing by lenses or maintaining the polarization state of incident light.

In the case of a typical thermoplastic polymer used in ordinary optical polymer devices, the major types of birefringence are orientational birefringence and photoelastic birefringence. The birefringence of polymers derives from the asymmetry of their molecular structures. 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, since their intrinsic optical anisotropies cancel each other out. However, a polymer material becomes birefringent when its polymer chains are oriented, because their intrinsic optical anisotropies do not cancel each other out. This type of birefringence is called orientational birefringence. In the case of uniaxially heat-drawn polymer films above their glass transition temperature (T_g), the orientational birefringence Δn is defined as $\Delta n = n_{\|} - n_{\perp}$, where $n_{\|}$ and $n_{\perp}$ are, respectively, the refractive indices for light polarized in the parallel direction and the direction perpendicular to the drawing (tensile stress) direction. Positive polymers show orientational birefringence of $\Delta n > 0$ and negative polymers show $\Delta n < 0$. Photoelastic birefringence of a typical thermoplastic polymer is mainly caused in elastic deformation below its T_g. The sign of photoelastic birefringence is defined in the same way as the orientational birefringence in the tensile stress direction. Although the behavior of optical polymer molecules in elastic deformation has not been clarified in detail, the orientation of the side chains of the polymer molecules is believed to make a major contribution to photoelastic birefringence compared to the orientation of the main chains of the polymer molecules in photoelastic deformation of under 1%.[1] The sign of orientational birefringence in some kinds of polymers, for example polystyrene, is opposite to the sign of the photoelastic birefringence, which shows that the change in conformation of polymer molecules which causes the orientational birefringence is different from that causing photoelastic birefringence.

Several methods have been proposed to realize optical polymers that exhibit no orientational birefringence for any orientation of the polymer main chains. They are the random copolymerization method,[2,3] the anisotropic molecule dopant method,[4,5] the birefringent crystal dopant method,[6,7] and the polymer blending method.[8] In the random copolymerization method, positive and negative birefringent monomers that compose positive and negative birefringent homopolymers are randomly copolymerized. As a result, birefringence is mutually canceled at a specified monomer ratio. In the anisotropic molecule dopant method, molecules that have anisotropic polarizability, a rodlike shape, and a lower molecular weight than the polymers are chosen and doped into the polymers. When the polymer chains are oriented as a result of processes such as injection molding, extrusion, and drawing, 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, which have a higher polarizability in the direction of orientation than in the perpendicular direction. Elimination of photoelastic birefringence has been demonstrated by both the random copolymerization method[3] and the anisotropic molecule dopant method.[7] The anisotropic molecules used in the anisotropic molecule dopant method can be slightly oriented when the side chains of the polymer molecules are slightly oriented in elastic deformation of the optical polymer containing the anisotropic molecules. As a result, the photoelastic birefringence of the optical polymer is compensated for by the anisotropic molecules.

In the case of the random copolymerization method, it should be pointed out that the composition of the copolymer for

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eliminating orientational birefringence is different from that for eliminating photoelastic birefringence. For example, in the case of poly(methyl methacrylate (MMA)/benzyl methacrylate (BzMA)), the composition for eliminating orientational birefringence is MMA/BzMA = 82/18 (w/w) and the composition for eliminating photoelastic birefringence is MMA/BzMA = 92/8 (w/w). Therefore, simultaneous compensation of the orientational birefringence and the photoelastic birefringence by means of the random copolymerization method has not been demonstrated. Similarly, in the case of the anisotropic molecule dopant method, the concentration of the anisotropic molecule for eliminating orientational birefringence is different from that for eliminating photoelastic birefringence. For example, the concentration of *trans*-stilbene is 3.0 wt % for eliminating the orientational birefringence of poly(methyl methacrylate) (PMMA), and that for eliminating the photoelastic birefringence of PMMA is 2.2 wt %. Therefore, simultaneous compensation of the orientational birefringence and the photoelastic birefringence by the anisotropic molecule dopant method has not been demonstrated either.

We have so far defined polymers that exhibit no birefringence either with any orientation of the polymer main chains or in elastic deformation as zero-birefringence optical polymers. In this article, however, we define polymers as zero-birefringence optical polymers that exhibit no birefringence with any orientation of the polymer main chains and in elastic deformation (i.e., both the orientational birefringence and the photoelastic birefringence are zero). As far as we know, any zero-birefringence optical polymer has not been reported, and realization of zero-birefringence optical polymers is still a challenge.

During typical injection molding and extrusion, both the orientational birefringence and the photoelastic birefringence tend to be caused in molded or extruded polymer samples, because polymer main chains tend to be oriented in the molten state and the polymer samples tend to be elastically deformed by contraction in volume during the cooling process from around T_g to room temperature. Manufacturers have been making a lot of efforts to reduce both types of birefringence by increasing annealing time and temperature[9,10] or adopting solvent casting method instead of extrusion method,[11] which increases both process time and cost. Nevertheless, birefringence in most optical polymer devices cannot be completely eliminated. Therefore, zero-birefringence optical polymers are ideal for realizing high performance and low cost optical devices for handling polarized light or fine focusing.

The purpose of this article is to show that zero-birefringence optical polymers can be realized in a system that is composed of more than three components, in which at least one of the components exhibits the opposite orientational birefringence effect and the opposite photoelastic birefringence effect to those of the other components. We describe the examples of a ternary copolymer and a binary copolymer including the dopant.

II. Experimental Section

MMA (99.8%, Mitsubishi Gas Chemical Company, Inc.), 2,2,2-trifluoroethyl methacrylate (3FMA) (99.95%, Jemco Inc.), and BzMA (95%, Tokyo Ksei Kogyo Co. Ltd.) were distilled under reduced pressure prior to use. *tert*-Butyl peroxy-2-ethylhexanoate (98%, NOF Corporation) and *n*-butyl mercaptan (95%, Wako Pure Chemical Industries, Ltd.) were used as received. Mixtures of MMA and 3FMA (MMA/3FMA(w/w) = 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100) were prepared. *tert*-Butyl peroxy-2-ethylhexanoate as an initiator and *n*-butyl mercaptan as a chain transfer agent were added to the monomer mixtures with ratios to the monomer mixture of 0.5 and 0.3 wt %, respectively. After the mixtures were filtered via PTFE membrane filters (pore size: 0.2 μm), the mixtures were injected into cylindrical glass tubes. The glass tubes were placed in a water bath at 70 °C for 24 h for polymerization, after which they were placed in a furnace at 90 °C for 24 h. Finally, cylindrical bulk polymers were obtained by breaking the glass tubes. Preparation of poly(MMA/BzMA) bulks and PMMA bulks containing *trans*-stilbene was carried out in the same way. *trans*-Stilbene was added to monomer mixtures, and then the obtained mixtures were polymerized. The compositions of the obtained polymers (MMA/3FMA, MMA/BzMA, and PMMA containing *trans*-stilbene) were determined by ^{1}H NMR analysis.

Table 1. Sign of Birefringence Effect of Monomers and a Dopant

monomer and dopant	orientational birefringence	photoelastic birefringence
MMA	negative	negative
3FMA	positive	negative
BzMA	positive	positive
trans-stilbene	positive	positive

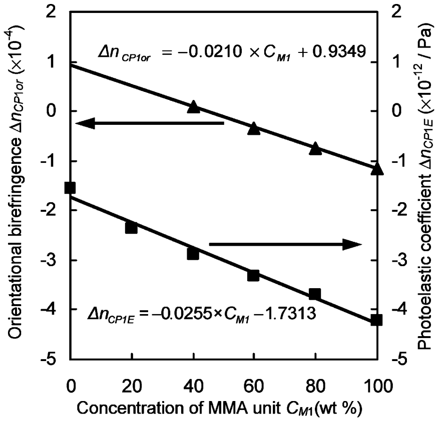
The end faces of the obtained cylindrical polymers were polished to enable measurement of photoelastic birefringence. Optical heterodyne interferometry was employed, using birefringence measurement equipment (ABR-10A, Uniopt Corp., Ltd.) at a wavelength of 633 nm while applying a load in the diametrical parallel direction of the cylindrical polymers (diameter, 18 mm; length, 10 mm). The photoelastic coefficients of the polymers were determined based on the results of the photoelastic birefringence measurements.

For the orientational birefringence measurements, polymer films were prepared as follows. The cylindrical bulk polymers mentioned above were dissolved in tetrahydrofuran to prepare polymer solutions. The polymer solutions were spread onto a glass plate using a knife coater, then dried at room temperature for 24 h followed by the drying process at 60 °C under reduced pressure for 48 h. The obtained polymer films with a thickness of about 40 μm were uniaxially drawn above their T_g using a universal tensile testing machine (Tensilon RTC-1210A, A&D Co., Ltd.), in which the orientation degrees of the main chains of the polymers were adjusted to 0.03 by optimizing the drawing temperature and the drawing rate. The orientation degrees of the main chains of the polymers were confirmed from an infrared dichroic ratio measured by polarized Fourier transform infrared spectroscopy. The orientational birefringence of the uniaxially drawn films was measured at a wavelength of 633 nm by optical heterodyne interferometry using birefringence measurement equipment (ABR-10A, Uniopt Corp., Ltd.).

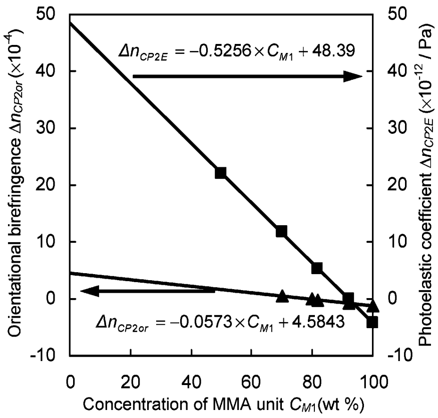
On the basis of the experimental results, we estimated the optimum compositions for a ternary copolymer and a binary copolymer containing an anisotropic dopant by the calculation, and adjusted them experimentally as described in section III. Preparation, birefringence measurements and determination of compositions of poly(MMA/3FMA/BzMA) bulks and poly(MMA/3FMA) bulks containing *trans*-stilbene with the optimized composition were carried out in the same way.

III. Results and Discussion

Design of a Ternary Copolymer as a Zero-Birefringence Polymer. Ternary copolymers were synthesized from MMA, 3FMA, and BzMA. The signs of the birefringence effect of these monomers are listed in Table 1. Poly(MMA/3FMA) and poly(MMA/BzMA) with several compositions were synthesized for the design of a ternary copolymer. Figure 1 shows the orientational birefringence and the photoelastic coefficients in terms of the concentration of MMA units in poly(MMA/3FMA) and poly(MMA/BzMA). The relations between them were



(a) Poly(MMA/3FMA)



(b) Poly (MMA/BzMA)

Figure 1. Orientational birefringence and photoelastic coefficient of copolymers as a function of the composition of the copolymers: (a) poly(MMA/3FMA); (b) poly(MMA/BzMA).

described by the approximate eqs 1−4.

$$\Delta n_{\mathrm{CP1or}} = -\ 0.0210 \times C_{\mathrm{M1}} + 0.9349 \tag{1}$$

$$\Delta n_{\mathrm{CP1E}} = -\ 0.0255 \times C_{\mathrm{M1}} - 1.7313 \tag{2}$$

$$\Delta n_{\mathrm{CP2or}} = -\ 0.0573 \times C_{\mathrm{M1}} + 4.5843 \tag{3}$$

$$\Delta n_{\mathrm{CP2E}} = -\ 0.5256 \times C_{\mathrm{M1}} + 48.39 \tag{4}$$

Here, $\Delta n_{\mathrm{CP1or}}$ and Δn_{CP1E} are respectively the orientational birefringence and the photoelastic coefficient for poly(MMA/3FMA), and $\Delta n_{\mathrm{CP2or}}$ and Δn_{CP2E} are respectively the orientational birefringence and the photoelastic coefficient for poly(MMA/BzMA). C_{M1} is the concentration of MMA units in poly(MMA/3FMA) and poly(MMA/BzMA).

The contributions of MMA to the orientational birefringence and the photoelastic coefficient are $\Delta n_{\mathrm{P1or}} = -1.1651$ and $\Delta n_{\mathrm{P1E}} = -4.2813$ which are obtained when $C_{\mathrm{M1}} = 100$ wt % in eqs 1−2, respectively. In addition, the contributions of 3FMA to the orientational birefringence and the photoelastic coefficient are $\Delta n_{\mathrm{P2or}} = 0.9349$ and $\Delta n_{\mathrm{P2E}} = -1.7313$, which are obtained when $C_{\mathrm{M1}} = 0$ wt % in eqs 1−2, respectively. Similarly, the contributions of BzMA to the orientational birefringence and the photoelastic coefficient are $\Delta n_{\mathrm{P3or}} = 4.5843$ and $\Delta n_{\mathrm{P3E}} = 48.39$ which are obtained when $CM1 = 0$ wt % in eqs 3 and 4, respectively.

For a terpolymer comprising MMA, 3FMA and BzMA, the weight fractions of the monomers are written as α (wt %), β (wt %), and γ (wt %), and

$$\alpha + \beta + \gamma = 100 \tag{5}$$

On the basis of the contributions mentioned above, the orientational birefringence Δn_{or} and the photoelastic coefficient Δn_{E} for a terpolymer, poly(MMA/3FMA/BzMA), can be written as

$$\begin{aligned}\Delta n_{\mathrm{or}} &= \Delta n_{\mathrm{P1or}} \times \frac{\alpha}{100} + \Delta n_{\mathrm{P2or}} \times \frac{\beta}{100} + \Delta n_{\mathrm{P3or}} \times \frac{\gamma}{100} \\ &= -1.1651 \times \frac{\alpha}{100} + 0.9349 \times \frac{\beta}{100} + 4.5843 \times \frac{\gamma}{100}\end{aligned} \tag{6}$$

$$\begin{aligned}\Delta n_{\mathrm{E}} &= \Delta n_{\mathrm{P1E}} \times \frac{\alpha}{100} + \Delta n_{\mathrm{P2E}} \times \frac{\beta}{100} + \Delta n_{\mathrm{P3E}} \times \frac{\gamma}{100} \\ &= -4.2813 \times \frac{\alpha}{100} - 1.7313 \times \frac{\beta}{100} + 48.39 \times \frac{\gamma}{100}\end{aligned} \tag{7}$$

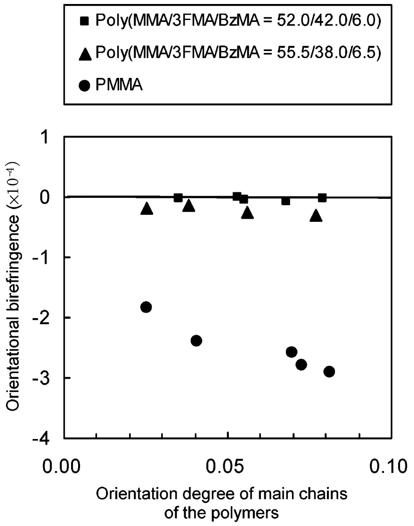
We obtained the specified composition MMA/3FMA/BzMA = 55.5/38.0/6.5(w/w/w) by solving eqs 5−7 simultaneously, on the condition that $\Delta n_{\mathrm{or}} = \Delta n_{\mathrm{E}} = 0$. We synthesized the poly(MMA/3FMA/BzMA) of the specified composition and measured its orientational birefringence and photoelastic birefringence. The results are shown in Figure 2 and Table 2. The poly(MMA/3FMA/BzMA) of the specific composition exhibited significantly low orientational birefringence and significantly low photoelastic birefringence (close to zero birefringence) which were negligible amounts of birefringence for a typical optical device. Although the orientational birefringence and the photoelastic birefringence of PMMA are already known to be fairly low, poly(MMA/3FMA/BzMA) at the specific composition exhibited much lower birefringences than those of PMMA. By fine adjustment of the composition to MMA/3FMA/BzMA = 52.0/42.0/6.0(w/w/w), we obtained an optical polymer that exhibits close to zero birefringence.

Design of a Binary Copolymer Containing an Anisotropic Dopant as a Zero-Birefringence Polymer. Poly(MMA/3FMA) containing *trans*-stilbene as an anisotropic dopant was investigated. The birefringence effects that *trans*-stilbene exhibits in bulk polymer are shown in Table 1. *trans*-Stilbene molecules dispersed as a molecule in bulk polymer are oriented and exhibit their effects when the polymer main chains and the polymer side chains are oriented. We synthesized PMMA containing *trans*-stilbene and poly(MMA/3FMA) and then measured the birefringence of them in the same way as described in the previous section. Here, we use the results of poly(MMA/3FMA) described in the previous section. Figure 3 shows the results, in which the concentration of *trans*-stilbene C_{AM} (wt %) is defined as the weight ratio to MMA. The relations between the orientational birefringence Δn_{AMPor} and the photoelastic coefficient Δn_{AMPE} of PMMA containing *trans*-stilbene and the concentration of *trans*-stilbene C_{AM} are approximately written as

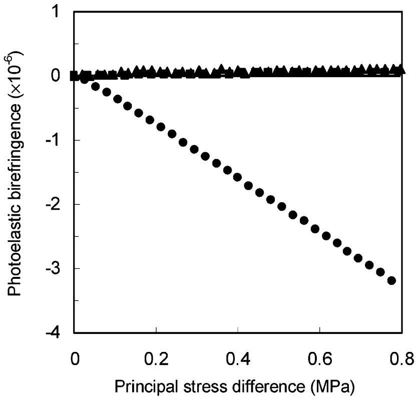
$$\Delta n_{\mathrm{AMPor}} = 0.2982 C_{\mathrm{AM}} - 1.1374 \tag{8}$$

$$\Delta n_{\mathrm{AMPE}} = 1.3778 C_{\mathrm{AM}} - 4.2132 \tag{9}$$

The contributions of *trans*-stilbene to the orientational birefringence and the photoelastic birefringence are $\Delta n_{\mathrm{AMor}} = 0.2982 C_{\mathrm{AM}}$ and $\Delta n_{\mathrm{AME}} = 1.3778 C_{\mathrm{AM}}$, respectively, and the intercepts of eqs 8 and 9 are the contributions of PMMA. Therefore, based on these contributions and eqs 1 and 2, the orientational birefringence Δn_{or} and the photoelastic birefringence Δn_{E} of



(a) Orientational birefringence



(b) Photoelastic birefringence

Figure 2. Orientational birefringence and photoelastic birefringence of a ternary copolymer compared with PMMA: (a) orientational birefringence as a function of the orientational degree of the main chains of poly(MMA/3FMA/BzMA); (b) photoelastic birefringence as a function of the principal stress difference in poly(MMA/3FMA/BzMA).

Table 2. Photoelastic Coefficient of a Ternary Copolymer

optical polymer	photoelastic coeff (Pa^{-1})
poly(MMA/3FMA/BzMA = 55.5/38.0/6.5)	0.119×10^{-12}
poly(MMA/3FMA/BzMA = 52.0/42.0/6.0)	0.074×10^{-12}
PMMA	-4.225×10^{-12}

poly(MMA/3FMA) containing *trans*-stilbene are written as

$$\Delta n_{\mathrm{or}} = \Delta n_{\mathrm{CP1or}} + \Delta n_{\mathrm{Amor}}$$

$$= -0.0210C_{\mathrm{M1}} + 0.9349 + 0.2982C_{\mathrm{AM}} \quad (10)$$

$$\Delta n_{\mathrm{E}} = \Delta n_{\mathrm{CP1E}} + \Delta n_{\mathrm{AME}}$$

$$= -0.0255C_{\mathrm{M1}} - 1.7313 + 1.3778C_{\mathrm{AM}} \quad (11)$$

We obtained the specified composition MMA/3FMA = 85/15(w/w) and $C_{\mathrm{AM}} = 2.8$ wt % by solving eqs 10−11 simultaneously on the condition that $\Delta n_{\mathrm{or}} = \Delta n_{\mathrm{E}} = 0$. We synthesized the poly(MMA/3FMA) containing *trans*-stilbene of the specified composition and measured its orientational birefringence and photoelastic birefringence. The results are shown in Figure 4 and Table 3. The poly(MMA/3FMA) containing *trans*-stilbene of the specific composition exhibited close to zero birefringence with any orientation from 0.00 to 0.09 and in elastic deformation.

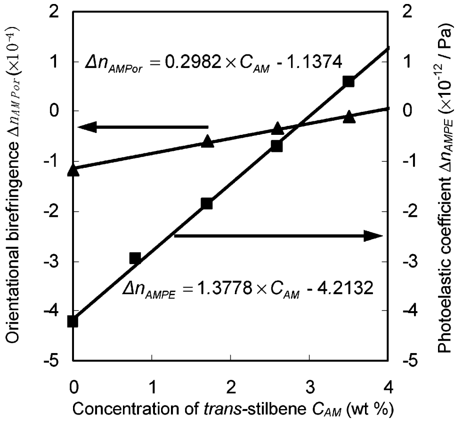
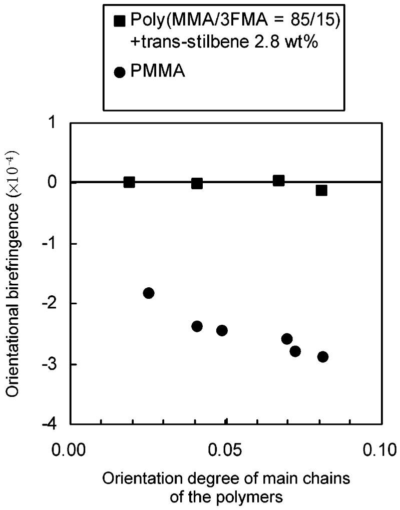
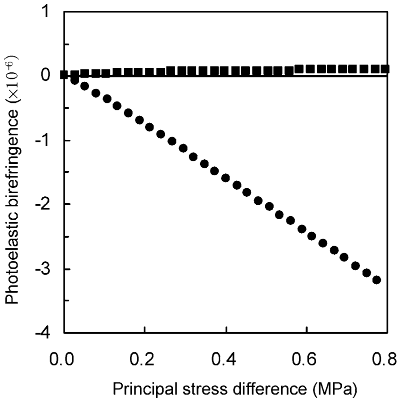


Figure 3. Orientational birefringence and photoelastic coefficient of PMMA containing *trans*-stilbene as a function of the concentration of *trans*-stilbene.



(a) Orientational birefringence



(b) Photoelastic birefringence

Figure 4. Orientational birefringence and photoelastic birefringence of a binary copolymer containing an anisotropic dopant compared with PMMA: (a) orientational birefringence as a function of the orientational degree of the main chains for poly(MMA/3FMA) containing *trans*-stilbene; (b) photoelastic birefringence as a function of the principal stress difference for poly(MMA/3FMA) containing *trans*-stilbene.

Validity and Potentiality of The Methods. The ternary copolymer of the specified compositions that was calculated as described above exhibited significantly low birefringence. We estimated that the calculated contribution from each component was slightly different from the contributions from each component in the polymers with the specified compositions. For example, the contribution of 3FMA determined in poly(MMA/

Table 3. Photoelastic Coefficient of a Binary Copolymer Containing *trans*-Stilbene

optical polymer	photoelastic coeff (Pa^{-1})
poly(MMA/3FMA = 85/15) + *trans*-stilbene 2.8 wt %	0.046×10^{-12}
PMMA	-4.225×10^{-12}

3FMA) might be different from that in poly(MMA/3FMA/BzMA), since the interaction between an MMA unit and a 3FMA unit is likely to be different from that between a 3FMA unit and a BzMA unit. However, we concluded that this method was effective, since the orientational birefringence and the photoelastic birefringence of the ternary copolymer of the specified compositions calculated using this method were significantly low, and both the birefringences were close to zero at the adjusted composition, near the calculated specified composition. Furthermore, the binary copolymer containing an anisotropic dopant of the specified compositions that were calculated as described above exhibited close to zero birefringence. Therefore, we concluded that this method was effective, too.

Using the methods described in this article, it is possible experimentally to obtain three equations related to orientational birefringence, such as eqs 6 and 10, the photoelastic birefringence such as eqs 7 and 11, and composition, such as eq 5. Therefore, if the number of the components increases further (more than 3), it is not possible to solve the equations analytically. Generally, in the case of optical polymers, the number of the components is not more than 10, and it is typically less than 5. Therefore, it is possible to solve the equations numerically for most actual cases using a computer. There may be several solutions for a polymer composed of more than three components, and there might be no solution for a polymer composed of inappropriate components. The number of solutions tends to increase with a greater number of components.

Clearly, these methods are applicable to other polymers composed of other monomers and anisotropic dopants, opening the way to synthesizing novel zero-birefringence optical polymers.

IV. Conclusions

We demonstrated that zero-birefringence optical polymers can be realized in a system that is composed of more than three components, in which at least one of the components exhibits the opposite orientational birefringence effect and the opposite photoelastic birefringence effect to those of the other components, and explained the methods to design the zero-birefringence optical polymers. Poly(MMA/3FMA/BzMA = 52.0/42.0/6.0(w/w/w)) and poly(MMA/3FMA = 85.0/15.0(w/w)) containing 2.8 wt % of *trans*-stilbene were designed by the methods and fine adjustment of the composition, and synthesized. We confirmed that these polymers exhibited close to zero birefringence in the oriented state and in elastic deformation. These methods are applicable to other polymers composed of other monomers and anisotropic dopants.

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