

Proposal of Novel Temperature-Independent Zero-Zero-Birefringence Polymer with High Heat-Resistance

Kohei WATANABE[†], Yuma KOBAYASHI[†], *Nonmembers*, and Yasuhiro KOIKE^{†,††a)}, *Member*

SUMMARY Temperature-independent zero-zero-birefringence polymer (TIZZBP), which exhibits very small birefringence over the wide temperature range, is required to realize real-color images for displays, particularly vehicle-mounted displays. Previously, a TIZZBP was synthesized, but they did not put into practical use because of their too complex composition and low mechanical strength. In this paper, we propose a practical TIZZBP that has high heat resistance, high transparency and sufficient mechanical strength, using a simple binary copolymerization system. Our proposed novel polymer exhibits very low photoelastic birefringence and very low orientational birefringence. Both types of birefringence of this TIZZBP satisfy the negligible levels for displays, which are defined as follows: the absolute values of photoelastic coefficient and intrinsic birefringence are less than $1 \times 10^{-12} \text{ Pa}^{-1}$ and 1×10^{-3} , respectively. In addition, temperature dependency of orientational birefringence was very low. Orientational birefringence satisfies the negligible level all over the temperature range from around -40°C to 85°C . This temperature range is important because it is the operational temperature range for vehicle-mounted display. Furthermore, our proposed novel TIZZBP showed high heat resistance, high transparency and sufficient mechanical strength. The glass transition temperature was 194°C . The total light transmittance and the haze value is more than 91% and less than 1%, respectively. The tensile strength of non-oriented films was $35 \sim 50 \text{ MPa}$. These results suggest our proposed novel TIZZBP has high practicality in addition to very low birefringence. Therefore, this TIZZBP film will be very useful for various displays including vehicle-mounted displays and flexible displays.

key words: *birefringence, copolymerization, orientational birefringence, photoelastic birefringence, temperature dependency of birefringence*

1. Introduction

Optical polymer materials have advantages of lower manufacturing cost, light weight, flexibility and higher moldability. In displays such as liquid crystal displays (LCDs) and organic light-emitting displays (OLEDs), several kinds of optical polymer materials are used, for example, polarizer protecting films and plastic substrates. However, optical polymer films generally exhibit birefringence, which means anisotropy of refractive index. Regarding displays, the birefringence in optical polymer films degrades the image quality of displays such as the degradation of the contrast ratio and the color change with angle [1]–[3]. Therefore, an optical polymer film which exhibits no birefringence is required to realize real-color displays.

The birefringence of polymer is typically classified into two types depending on the mechanism of generation [4]. One of them is photoelastic birefringence, which is generated by elastic deformation below glass transition temperature (T_g). The other is orientational birefringence. Orientational birefringence is generated by the orientation of the polymer main chain, which is caused by drawing of the polymer above T_g . Optical polymer films tend to exhibit both types of birefringence because the residual stress and the orientation of polymer chain are generally caused in the manufacturing processes.

Random copolymerization methods have been proposed to realize optical polymers that exhibit neither photoelastic birefringence nor orientational birefringence [4], [5]. In the random copolymerization method, positive birefringent monomers and negative birefringent monomers are randomly copolymerized at a specified composition ratio. By using this method, we have synthesized zero-zero-birefringence polymers (ZZBPs), which exhibit neither photoelastic birefringence nor orientational birefringence [6]–[8]. ZZBP has an advantage where both types of birefringence become almost zero at room temperature. However, the ZZBP has temperature dependency of orientational birefringence as shown in a paper [9]. Although the ZZBP does not exhibit any birefringence at room temperature, it exhibits high orientational birefringence at other temperature. This temperature dependency of orientational birefringence causes a problem in the car internal environment, where the ambient temperature is largely changed. Therefore, temperature-independent zero-zero-birefringence polymer (TIZZBP), which exhibits no birefringence over the wide temperature range, is required to realize real-color displays for vehicle-mounted displays.

A conventional TIZZBP was proposed in our previous research [10]. However, it is very brittle and its composition is too complex, thus it did not put into practical use. In this paper, we propose a practical TIZZBP that has high heat resistance, high transparency and sufficient mechanical strength, using a simple binary copolymerization system. The detail reaction mechanism of this TIZZBP will be separately reported in a chemical journal in near future. This paper is focusing on the characteristics of our novel polymer.

Manuscript received March 16, 2020.

Manuscript revised June 2, 2020.

Manuscript publicized July 22, 2020.

[†]The authors are with the Graduated School of Science and Technology, Keio University, Kawasaki-shi, 212-0032 Japan.

^{††}The author is with Keio Photonics Research Institute, Keio University, Kawasaki-shi, 212-0032 Japan.

a) E-mail: koike@appi.keio.ac.jp

DOI: 10.1587/transele.2020DII0004

2. Experimental

2.1 Preparation of Polymer Film

Our proposed novel TIZZBP is synthesized using a binary copolymerization system of commodity monomers; M1 and M2. In this binary system, its photoelastic birefringence is decreased by specific interactions between M1 unit and M2 unit.

A polymer film is fabricated in the following steps. First, a polymer was synthesized by using a bulk copolymerization method. The mixture of monomers was placed in a water bath at 70°C for 24 hours. Second, the polymer was purified by using a reprecipitation method. The polymer is dissolved in dichloromethane (FUJIFILM Wako Pure Chemical Corporation) and precipitated in methanol (FUJIFILM Wako Pure Chemical Corporation). Third, a polymer film was fabricated by using a solvent casting method. The purified polymers were dissolved in dichloromethane again and spread on a polyethylene terephthalate release film by knife coater. The thickness of films is controlled to 20 to 50 μm . To remove the solvent, the film was dried for 24 hours at 90°C under reduced pressure.

Polymer films of poly (methyl methacrylate) (PMMA) and polycarbonate (PC) were also prepared for comparison. These optical polymers are widely used for various optical devices. We synthesized PMMA films by using MMA monomer (FUJIFILM Wako Pure Chemical Corporation). The PC film was fabricated by using a pellet of poly (Bisphenol A carbonate) (Sigma-Aldrich Co. LLC).

2.2 Measurement of Birefringence

Photoelastic birefringence is defined as Eq. (1).

$$\Delta n_{\text{ph}} = C \cdot \sigma \quad (1)$$

Here, Δn_{ph} , C and σ are photoelastic birefringence, photoelastic coefficient and stress, respectively. As shown in this equation, photoelastic birefringence changes in proportional to the stress. Its proportionality constant is called photoelastic coefficient and this coefficient depends on the molecular structure of polymer. Photoelastic birefringence of polymer films was measured by utilizing optical heterodyne interferometry method at a wavelength of 633 nm while applying a uniaxial tensile stress at various levels (from 0% to 1% strain), using a birefringence measurement equipment (ABR-10A, Uniopt Corp., Ltd.). The measurement was performed at room temperature. Then, the C was estimated from this measurement results.

Oriental birefringence is defined as Eq. (2).

$$\Delta n_{\text{or}} = \Delta n^0 \cdot f \quad (2)$$

Here, Δn_{or} , Δn^0 and f are orientational birefringence, intrinsic birefringence and degree of orientation of main chains, respectively. As shown in Eq. (2), orientational birefringence changes in proportional to the degree of orientation.

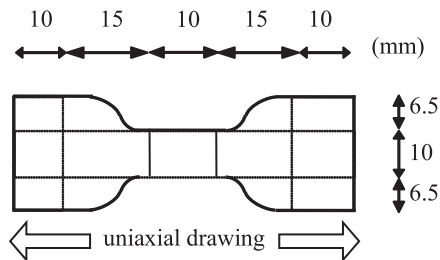


Fig. 1 Schematic representation of polymer film sample.

Its proportionality constant is called intrinsic birefringence and this coefficient depends on the molecular structure of polymer. To measure orientational birefringence, polymer films were uniaxially heat drawn above their T_g s by using a film biaxially stretching machine (IMC-C513, Imoto Machinery Corp., Ltd.). The degree of orientation f was determined from an infrared dichroic ratio measured by using a polarized Fourier-transform infrared spectrometer (7000e FT-IR, Varian Inc.). The orientational birefringence of the uniaxially drawn films was measured by utilizing an optical heterodyne interferometry method at a wavelength of 633 nm using a birefringence measurement device (ABR-10A, Uniopt Corp., Ltd.). The Δn^0 was estimated by Eq. (2), from this measurement results.

In general, orientational birefringence varies with changing temperature below the glass transition temperature T_g [9]. The $d\Delta n^0/dT$, which is the differential value of Δn^0 to temperature change, is called temperature coefficient of Δn^0 . It depends on the molecular structure of the polymer as well as C and Δn^0 . To evaluate the temperature dependency of orientational birefringence, orientational birefringence of the uniaxially drawn films was measured while changing the temperature from 15°C to 70°C at an interval of 5°C.

2.3 Other Measurement

Grass transition temperature (T_g) is one of the indexes of heat resistance of amorphous polymers. The T_g s of polymers were measured by using a differential scanning calorimeter (DSC-60, Shimadzu Corp.).

Total light transmittance and haze value of polymer films were measured by utilizing a spectral haze meter (SH 700, Nippon Denshoku Corp.). The thickness of films is about 30 μm .

Tensile strength was measured by utilizing a universal tensile testing machine (Tensilon RTC-1210A, A&D Co., Ltd.) at room temperature. For the measurement, more than three dumbbell shaped samples, whose thickness is about 30 μm , were prepared for each polymer. The sample shape was shown in Fig. 1. The samples were stretched at speed of 5 mm/min and at room temperature.

3. Result and Discussion

3.1 Photoelastic Birefringence

The photoelastic birefringence at room temperature was evaluated as shown in Fig. 2. This figure shows the relationships between photoelastic birefringence and the stress applied to the polymer films. Based on Eq. (1), these relationships were approximated by straight lines passing an origin. As shown in Fig. 2, our proposed novel TIZZBP showed very low photoelastic birefringence regardless of the value of the applied stress. The C s of these polymers were estimated from the slopes of these approximation lines in Fig. 2 and are shown in Table 1. The C of our novel TIZZBP is less than $1 \times 10^{-12} \text{ Pa}^{-1}$, which is negligible levels for displays. Although PMMA is generally known as a polymer material with low photoelastic birefringence, our proposed TIZZBP showed much lower photoelastic birefringence than the PMMA.

3.2 Orientational Birefringence

Next, we evaluated orientational birefringence at room temperature. The relationships between orientational birefringence and the degree of orientation of polymer main chain are shown in Fig. 3. These relationships were approximated by straight lines passing an origin based on Eq. (2) and the Δn^0 s of these polymers were estimated from the slopes of these approximation lines. The estimated Δn^0 s are shown in Table 2. As shown Table 2, the Δn^0 of our proposed novel TIZZBP is less than 1×10^{-3} , which is negligible levels. Comparing with PMMA and PC, our novel TIZZBP showed very much less orientational birefringence in Δn^0 .

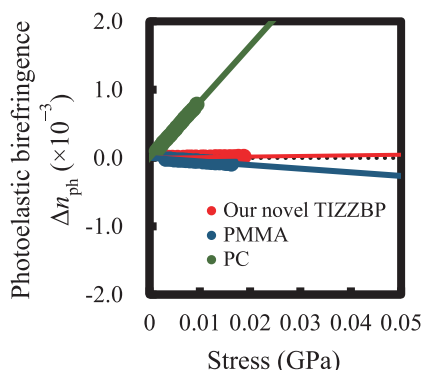


Fig. 2 The relationships between photoelastic birefringence and stress applied to the polymer of our novel TIZZBP, PMMA and PC.

Table 1 Photoelastic coefficient of our novel TIZZB, PMMA and PC.

Polymer	Our novel TIZZBP	PMMA	PC
$C (\times 10^{-12} \text{ Pa}^{-1})$	0.90	-5.31	82.07

3.3 Temperature Dependency of Birefringence

Orientational birefringence varies with changing temperature. We measured the changes of orientational birefringence with temperature change and the $d\Delta n^0/dT$ s of the polymers were estimated from these results. The estimated $d\Delta n^0/dT$ s are shown in Table 3. As shown in Table 3, our proposed novel TIZZBP has much lower temperature dependency of orientational birefringence than PMMA and PC. Figure 4 shows the change of Δn^0 with temperature

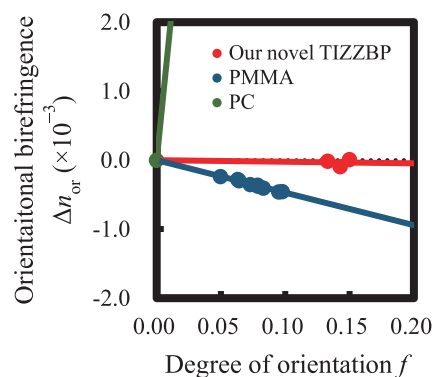


Fig. 3 The relationships between orientational birefringence and degree of orientation of our novel TIZZBP, PMMA and PC.

Table 2 Intrinsic birefringence of our novel TIZZB, PMMA and PC.

Polymer	Our novel TIZZBP	PMMA	PC
$\Delta n^0 (\times 10^{-3})$	-0.23	-4.71	184.33

Table 3 Temperature coefficient of intrinsic birefringence of our novel TIZZBP, PMMA and PC.

Polymer	Our novel TIZZBP	PMMA	PC
$d\Delta n^0/dT (\times 10^{-5} \text{ } ^\circ\text{C}^{-1})$	0.72	3.11	-2.49

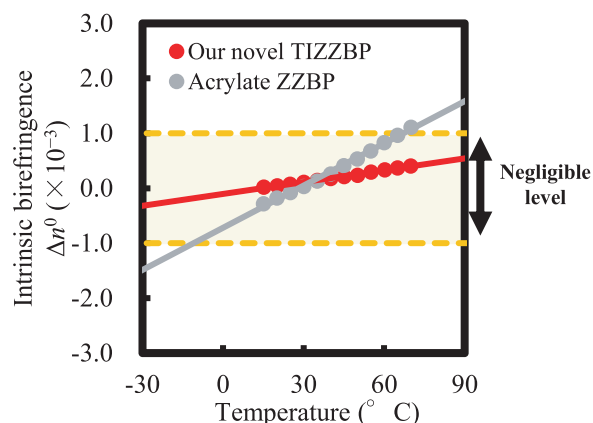
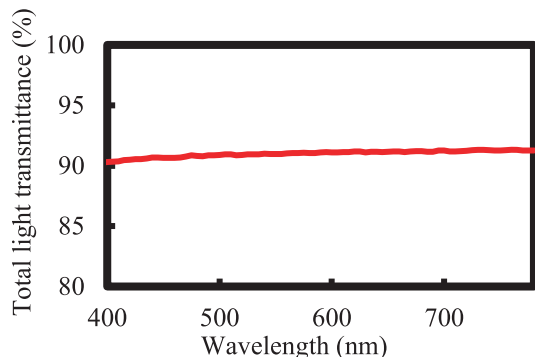


Fig. 4 The relationships between intrinsic birefringence and temperature of our novel TIZZBP and acrylate ZZBP which degree of orientation f at room temperature are 0.15 and 0.107, respectively.

Table 4 Glass transition temperature T_g of our novel TIZZBP, PMMA, and PC

Polymer	Our novel TIZZBP	PMMA	PC
T_g	194	126	147

**Fig. 5** Total light transmittance of 23.4 μm film of our proposed novel TIZZBP.

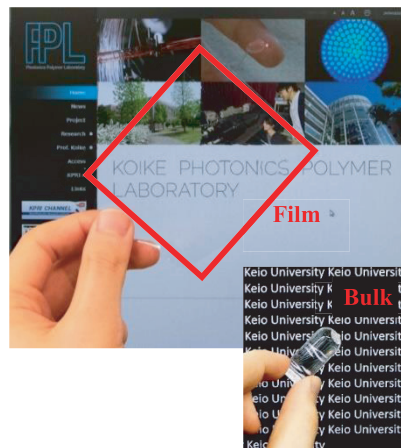
change from 15°C to 70°C of our novel TIZZBP. An acrylate ZZBP, which is synthesized in a ternary copolymerization system of MMA, 2, 2, 2-trifluoroethyl methacrylate and benzyl methacrylate, is one of the ZZBP [6]. The Δn^0 of the acrylate ZZBP is also shown in Fig. 4 for comparison. As shown in Fig. 4, the temperature dependency of Δn^0 of our novel TIZZBP was about one-third of the acrylate ZZBP and Δn^0 satisfies the negligible levels all over the temperature range of from -40°C to 85°C . This temperature range is important because it is the operational temperature range for vehicle-mounted displays [11]. This result suggests that our novel TIZZBP realizes real-color images for all over the operational temperature range of vehicle-mounted displays.

3.4 Heat Resistance

The glass transition temperatures (T_g s) of our novel TIZZBP, PMMA and PC were measured. The measured T_g s are shown in Table 4. The T_g of the novel TIZZBP is significantly higher than PC, which is generally known as a high heat resistant polymer. These results suggest that our novel TIZZBP has very high heat resistance that is required such as in flexible LCD and OLED.

3.5 Transparency

Figure 5 shows a spectrum transmittance of visible light from 380 nm to 780 nm of our proposed novel TIZZBP. Our novel TIZZBP shows high transparency over the whole visible light. The average of total light transmittance and haze value of our novel TIZZBP are 91.0% and 0.65%, respectively. Those of PMMA are 92.3% and 0.86% and, those of PC are 90.7% and 1.02%, respectively. The results show our novel TIZZBP is very transparent approximately equivalent to PMMA and PC. Figure 6 shows the photograph of the polymer film and bulk of our novel TIZZBP. As shown

**Fig. 6** The image of the film and bulk of our novel TIZZBP.

in Fig. 6, these shows high transparency.

3.6 Mechanical Strength

We measured tensile strength of polymer films. The measurement results of our novel TIZZBP, PMMA and PC were 35 ~ 46 MPa, 39 ~ 56 MPa and 40 ~ 45 MPa, respectively. Our proposed novel TIZZBP showed almost the same tensile strength as PMMA and PC. These results suggest our proposed novel TIZZBP has enough mechanical strength for display uses.

3.7 Comparison with Conventional TIZZBP

A conventional TIZZBP, which we proposed in a previous research, does not necessary satisfy mechanical properties such as brittleness [10]. In addition, its composition control is a little difficult because many kinds of monomers are needed for the synthesis. Therefore, the conventional TIZZBP is not practical. On the other hand, our proposed novel TIZZBP has sufficient mechanical strength and simple composition, thus it is very practical. The novel TIZZBP is synthesized in a simple binary copolymerization system although the conventional TIZZBP is synthesized in a quaternary system.

4. Conclusion

We proposed a novel TIZZBP that has high heat resistance, high transparency and sufficient mechanical strength. Both of photoelastic birefringence and orientational birefringence satisfies the negligible levels for displays. In addition, temperature dependency of orientational birefringence was very low and orientational birefringence the negligible level all over the operational temperature range for vehicle-mounted displays of from -40°C to 85°C . Furthermore, our proposed novel TIZZBP showed high heat resistance, high transparency and sufficient mechanical strength. Therefore, our proposed novel TIZZBP will achieve real-color images not only for vehicle-mounted LCD and OLED but also for

flexible LCD and OLED.

References

- [1] R. Suzuki, M. Nagura, Y. Sasada, N. Fukagawa, K. Kawato, and Y. Ito, "31.1: Evolution of cellulose triacetate (TAC) films for LCDs: Novel technologies for high hardness, durability, and dimensional stability," Proc. the Society for Information Display 2015, California, United States, pp.446–449, June 2015.
- [2] H. Nakayama, N. Fukagawa, Y. Nishiura, T. Yasuda, T. Ito, and K. Mihayashi, "Development of Low-Retardation TAC Film for Protection Films of LCD's Polarizer," J. Photopolym. Sci. Technol., vol.19, no.2, pp.169–173, June 2006.
- [3] T. Ishinabe, T. Miyashita, and T. Uchida, "Wide-Viewing-Angle Polarizer with a Large Wavelength Range," Jpn. J. Appl. Phys., vol.41, pp.4553–4558, July 2002.
- [4] S. Iwata, H. Tsukahara, E. Nihei, and Y. Koike, "Transparent zero-birefringence copolymer and its optical properties," Appl. Opt., vol.36, no.19, pp.4549–4555, July 1997.
- [5] S. Iwata, H. Tsukahara, E. Nihei, and Y. Koike, "Compensation for Birefringence of Oriented Polymers by Random Copolymerization Method," Jpn. J. Appl. Phys., vol.35, part. 1, no.7, pp.3896–3901, July 1996.
- [6] A. Tagaya, H. Ohkita, T. Harada, K. Ishibashi, and Y. Koike, "Zero-Birefringence Optical Polymers," Macromolecules, vol.39, no.8, pp.3019–3023, April 2006.
- [7] S. Beppu, S. Iwasaki, H. Shafiee, A. Tagaya, and Y. Koike, "Design and synthesis of zero-zero-birefringence polymers in a quaternary copolymerization system," Polymer, vol.53, no.15, pp.3287–3296, July 2012.
- [8] A. Tagaya and Y. Koike, "Compensation and control of the birefringence of polymers for photonics," Polym. J., vol.44, pp.306–314, Jan. 2012.
- [9] M.D. Shikanai, A. Tagaya, and Y. Koike, "Temperature-independent zero-birefringence polymer for liquid crystal displays," Applied Physics Letters, vol.108, 131902, March 2016.
- [10] A. Tagaya, M. Shikanai, H. Nagahama, and Y. Koike, "Temperature-independent zero-zero-birefringence polymers for optical films," Proc. 23rd International Display Workshops in conjunction with Asia Display, Fukuoka, Japan, pp.961–964, Dec. 2016.
- [11] G. Pettitt, J. Ferri, and J. Thompson, "47.1: Invited paper: Practical application of TI DLP® technology in the next generation head-up display system," Proc. Society for Information Display 2015, California, United States, pp.700–703, July 2015.



Yuma Kobayashi obtained a B.S. and M.S. degrees in applied physics and physics-informatics from Keio University, Yokohama, Japan, in 2017 and 2019, respectively.



Yasuhiro Koike obtained a B.S., M.S., and Ph.D. degrees in applied chemistry from Keio University, Yokohama, Japan, in 1977, 1979, and 1982, respectively. He was a Visiting researcher with AT&T Bell Laboratories from 1989 to 1990. He has been a professor at Keio University since 1997 and a director of Keio Photonics Research Institute since 2010. He is known as the inventor of high-bandwidth graded-index plastic optical fiber "GI POF," and has been a general chair of the International Cooperative of Plastic Optical Fiber (ICPOF). He has been pursuing an extended research project based on his original technologies supported by the "First" Program of the Cabinet Office of Japan in 2010-2014. Prof. Koike has received several awards, including the International Engineering Award, the honor of the Society of Plastics Engineers, the Fujiwara Award, the honor of the Medal with Purple Ribbon in Palace, and SID Special Recognition Award.



Kohei Watanabe obtained a B.S. degree in applied physics and physics-informatics from Keio University, Yokohama, Japan, in 2019.