Design of Zero–Zero-Birefringence Polymers in Methacrylate Copolymer Systems Containing Trichloroethyl Methacrylate

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ABSTRACT: Polymers that exhibit neither orientational nor photoelastic birefringence, called zero–zero-birefringence polymers, are candidate materials for preparing optical components of liquid crystal displays (LCDs). Analyzing the birefringences for various methacrylate polymers is an issue of current importance in developing zero–zero-birefringence polymers with appropriate characteristics for LCDs. The researchers have investigated different types of birefringence for poly(2,2,2-trichloroethyl methacrylate) (PTCEMA) and have shown that PTCEMA exhibits negative orientational and photoelastic birefringences. By using TCEMA as a comonomer, a zero–zero-birefringence polymer having much higher glass transition temperature (T_g) compared with previous researches has been prepared by ternary copolymerization. Moreover, the researchers have fabricated zero–zero-birefringence polymers in a quaternary system containing TCEMA. The property analyses indicate that T_g can be controlled while maintaining the zero–zero-birefringence property, which shows that designing a quaternary zero–zero-birefringence polymer permits selective synthesis with the most appropriate characteristics. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 138–144, 2013

INTRODUCTION

Polymeric materials are now widely used for preparing optical components of liquid crystal displays (LCDs) because of their advantages of light weight and ease of processing. LCDs have recently been applied to various display devices, such as mobile phones, tablet-type PCs, and LCD televisions. To manufacture LCDs at a lower cost, it is important to produce these optical polymer components, such as polarizer protective films, by melt extrusion method with high productive efficiency. However, this method typically aligns the polymer main chains and causes orientational birefringence. In addition, a polarizer in LCD tends to be contracted in its usage environment, which elastically deforms the optical polymer films and generates photoelastic birefringence. These birefringences significantly degrade the image quality of LCDs that require the maintenance of the polarization state of incident light. Thus, a polymer that exhibits no birefringence in any state of orientation and elastic deformation is desirable for the optical components of LCDs.

Typically, the birefringence of polymers is classified into two types, depending on the method whereby it is generated.[1] The first type of birefringence is orientational birefringence. This is caused by the alignment of polymer main chains, typically by stretching of the polymer heated above its glass-transition temperature (T_g) during the processing. Most polymer chains have intrinsic optical anisotropy that arises from the anisotropy of the polarizability of each monomer unit. A polymer that is randomly oriented remains macroscopically isotropic and exhibits no orientational birefringence, because the optical anisotropies of the monomer units cancel each other out. However, such polymeric materials do become birefringent when the polymer chains are aligned, because the optical anisotropies of the monomer units then no longer cancel each other out. The orientational birefringence, Δn_{or}, can be expressed by the following equation:

$$\Delta n_{or} = \Delta n^0 \times f \qquad (1)$$

where Δn^0 and f are the intrinsic birefringence and degree of orientation of the polymer main chain, respectively.

The other type of birefringence is photoelastic birefringence. This is caused by elastic deformation below the T_g when a polymer is in its elastic deformation region. The photoelastic birefringence Δn_{ph} can be expressed by using the following equation:

$$\Delta n_{ph} = C \times \sigma \qquad (2)$$

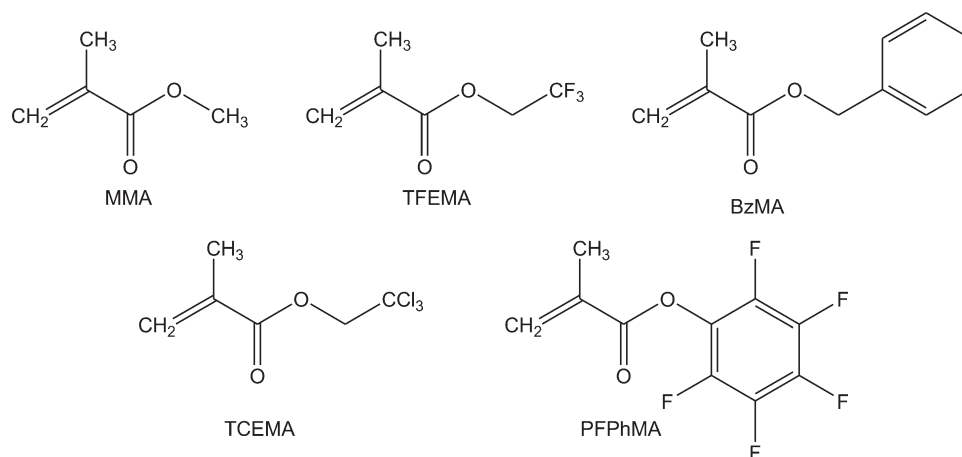where C and σ are the photoelastic coefficient and stress, respectively.

Figure 1. Chemical structures of MMA, 2,2,2-TFENA, BzMA, 2,2,2-TCEMA, and 2,3,4,5,6-PFPhMA.

Tagaya and coworkers have proposed a zero–zero-birefringence polymer that exhibits neither orientational birefringence nor photoelastic birefringence by using a ternary copolymerization system consisting of methyl methacrylate (MMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), and benzyl methacrylate (BzMA).[2,3] This polymer is free of both types of birefringence when subjected to any processing and usage environment.

Zero–zero-birefringence polymers can be designed as follows. First, the intrinsic birefringence Δn^0 and the photoelastic coefficient C for homopolymers are measured. Based on the results, the optimal composition ratios are calculated by using the following three simple eqs. (3)–(5).

$$\Delta n^0 = \Delta n_1^0 \times \frac{w_1}{100} + \Delta n_2^0 \times \frac{w_2}{100} + \Delta n_3^0 \times \frac{w_3}{100} + \cdots + \Delta n_i^0 \times \frac{w_i}{100} \tag{3}$$

$$C = C_1 \times \frac{w_1}{100} + C_2 \times \frac{w_2}{100} + C_3 \times \frac{w_3}{100} + \cdots + C_i \times \frac{w_i}{100} \tag{4}$$

$$w_1 + w_2 + w_3 + \cdots + w_i = 100 \tag{5}$$

where Δn_i^0, C_i, and w_i are the intrinsic birefringence, the photoelastic coefficient, and the weight fraction, respectively, of the ith polymer selected as a moiety ($i = 1, 2, 3 \ldots$). We determined the optimal compositions for compensating both types of birefringence with the condition of $\Delta n^0 = C = 0$. Moreover, we have proposed a quaternary copolymerization system for preparing advanced design of zero–zero-birefringence polymers.[4] In this system, it is possible to prepare zero–zero-birefringence polymers with multiple compositions from a quaternary system, which enable us to control the characteristics of zero–zero-birefringence polymers, such as T_g and refractive index, with high degree of accuracy.

Methacrylate polymers are now attracting a great deal of interest as candidate materials for optical films of LCDs, because their birefringences can be controlled by using the copolymerization method described above. However, both the intrinsic birefringence Δn^0 and the photoelastic coefficient C for most of the methacrylate polymers are yet to be determined. Thus, the analysis of birefringence properties for various methacrylates is a

pressing issue in the development of zero–zero-birefringence film with the most appropriate characteristics for LCDs.

In this article, we describe the birefringence analyses for poly(2,2,2-trichloroethyl methacrylate) (PTCEMA) and the design of the copolymer containing TCEMA. First, the intrinsic birefringence Δn^0 and the photoelastic coefficient C for PTCEMA are investigated in detail. Then, by using TCEMA as a comonomer, a zero–zero-birefringence polymer is synthesized in a ternary copolymerization system, and its T_g is evaluated. Moreover, the zero–zero-birefringence polymers are prepared in quaternary copolymerization system of TCEMA, MMA, TFEMA, and BzMA. We finally show that T_g of obtained copolymers can be controlled while maintaining the zero–zero-birefringence property, which enables the selective synthesis of the zero–zero-birefringence polymer in accordance with its intended application.

EXPERIMENTAL

Materials

MMA, TFEMA, BzMA, TCEMA, and 2,3,4,5,6-pentafluorophenyl methacrylate (PFPhMA) were purchased from Mitsubishi Gas Chemical (Tokyo), Tosoh F-Tech (Tokyo), Wako Pure Chemical Industries (Osaka), Osaka Organic Chemical Industry (Osaka), and SynQuest Laboratories (Alachua, FL), respectively. The chemical structures of the monomers are shown in Figure 1. The initiator 1-*tert*-butyl-3-(2-ethylhexanoyl)trioxidane (PBO) was purchased from NOF Corp. (Tokyo) and the chain transfer agent butanethiol (BuSH) was purchased from Wako Pure Chemical Industries. The solvents, methanol and dichloromethane, were also purchased from Wako Pure Chemical Industries Inc. MMA, TFEMA, and BzMA monomers were freshly distilled before use, and all other chemicals were used without further purification.

Preparation of Polymer Samples

To investigate the intrinsic birefringence and the photoelastic coefficient of poly(TCEMA) (PTCEMA), we synthesized samples of poly(MMA-*co*-TCEMA) by bulk polymerization with various composition ratios containing 10–50 wt % of TCEMA. All polymerization reactions were carried out at 70°C in water bath for

24 h with 0.4 wt % of PBO as an initiator and 0.1 wt % of BuSH as a chain transfer agent. The obtained polymers were purified by dissolution in dichloromethane and precipitation in a large volume of methanol.

For the birefringence measurements, polymer films were prepared by dissolving poly(MMA-*co*-TCEMA) in dichloromethane and spreading the polymer solution onto a glass plate with a knife coater. The films were dried at room temperature for 1 h and then at 90°C for 24 h under reduced pressure to remove the solvent.

Based on the result of calculations on the optimal composition ratios for eliminating both types of birefringence, a ternary copolymer of MMA, TCEMA, and PFPhMA and quaternary copolymers of MMA, TFEMA, BzMA, and TCEMA with the optimal compositions were synthesized, purified, and fabricated into films in the same way as described above for the binary copolymers.

Infrared Spectroscopic Measurements

To investigate the relationship between the degree of orientation and the orientational birefringence of the polymer samples, each fabricated film was uniaxially heat drawn above its T_g with a universal tensile testing machine (Tensilon RTC-1210A; A&D, Tokyo). The degree of orientation was determined by measuring the IR dichroism of the stretched films at room temperature with a polarizing Fourier-transform IR spectrometer (7000e FTIR; Varian, Palo Alto, CA). The absorbance of polarized IR radiation was measured in the directions parallel and perpendicular to the drawing direction, which was assumed to correspond to the direction of the main chains of the polymers. For this analysis, we selected a wave number of 1388 cm^{-1}, which corresponds to the symmetric bending vibration of α-methyl group.[5] The dichroic ratio D is defined as shown in the following equation:

$$D = \frac{A_\parallel}{A_\perp} \tag{6}$$

where $A_\parallel$ and $A_\perp$ are the absorbances of polarized IR radiation in the directions parallel and perpendicular to the direction of drawing, respectively. The degree of orientation f is defined by the following equation:

$$f = \frac{D-1}{D+2} \times \frac{2\cot^2\alpha + 2}{2\cot^2\alpha - 1} \tag{7}$$

where α is the angle between the transition moment vector of the absorbing group and the chain axis. In the case of the symmetric bending vibration of the α-methyl group at the wave number of 1388 cm^{-1}, the angle α can be assumed to be 90°, because the direction of the transition moment vector is perpendicular to the direction of the main chain axis of the polymer.[5]

Birefringence

Both orientational birefringence and photoelastic birefringence were measured by optical heterodyne interferometry at a wavelength of 633 nm using a birefringence measurement device (ABR-10A; UNIOPT). From the measured degree of orientation f and the orientational birefringence Δn_{or}, the intrinsic birefrin-

gence Δn^0 was determined by using the eq. (1). Added stress was measured at the same time with photoelastic birefringence. The photoelastic coefficient C was determined from the relationship between stress σ and photoelastic birefringence Δn_{ph} as expressed in eq. (2). The thickness of the films used for measurement of birefringence was 33 ± 4 μm.

Characterization

Copolymer composition ratios were analyzed by using ^{1}H NMR spectrometer (JNM-LA400; JOEL, Tokyo) and ^{13}C NMR spectrometer (AVANCEIII 600; Bruker BioSpin K.K., Kanagawa). TMS was used as a reference for both measurements.

The T_g values of all polymers were measured by using a differential scanning calorimeter (DSC-60; Shimadzu). All polymer samples were heated under air from room temperature to 160°C, held at 160°C for 5 min, then cooled to 50°C and reheated to 160°C at a scanning rate of 10°C/min. The T_g was measured during the second heating scan.

The weight percent of the remaining monomer in polymer bulks was measured by gas chromatography (GC-2010, Shimadzu). The polymer bulks were dissolved in a small amount of dichloromethane and then added to a large amount of methanol to precipitate the polymer. Based on the results of the gas chromatographic analyses of the supernatant liquid, the concentration of monomers was determined.

RESULTS AND DISCUSSION

Poly(TCEMA)

To design zero–zero-birefringence polymers containing TCEMA, the birefringence of PTCEMA was evaluated. Considering the mechanical brittleness of the TCEMA homopolymer film, binary copolymer films of MMA and TCEMA with various composition ratios were fabricated and two types of birefringence for each film were measured.

Figure 2 shows a plot of the intrinsic birefringence as a function of the proportion of MMA, where w_{MMA} represents the weight percentage of MMA in the copolymer. The relation between them is described by the following equation.
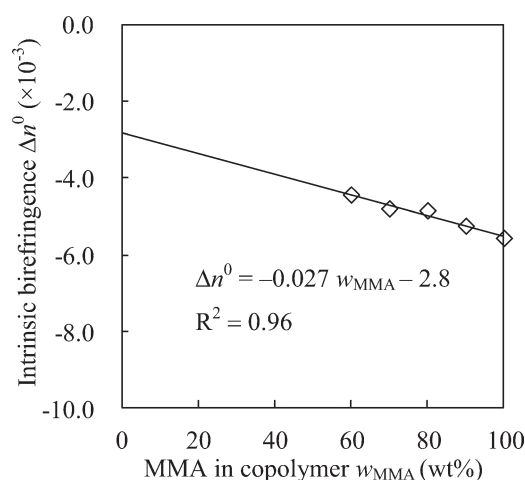

Figure 2. Intrinsic birefringence of poly(MMA-*co*-TCEMA) as a function of the proportion of MMA in the copolymer, w_{MMA} (wt %).

$$\Delta n^0 = -0.027 w_{MMA} - 2.8 \qquad (8)$$

From the intercept of the approximated line, the intrinsic birefringence of PTCEMA could be estimated, because it corresponds to the case where the proportion of MMA is 0 wt %. As shown in Figure 2, the intrinsic birefringence Δn^0 for PTCEMA was estimated to be $\Delta n^0 = -2.8 \times 10^{-3}$. The value for PTCEMA was equivalent to a half of the intrinsic birefringence of PMMA, which is typically used for the optical applications. Because the PTCEMA exhibits negative orientational birefringence, it was found that the orientational birefringence could be compensated by copolymerizing PTCEMA with a polymer that has positive intrinsic birefringence.

The plot of the dependence of photoelastic coefficient on the proportion of MMA is shown in Figure 3 and the relation between them is described by the following equation.

$$C = 0.034 w_{MMA} - 8.9 \qquad (9)$$

The photoelastic coefficient of PTCEMA was estimated to be $C = -2.9 \times 10^{-12}$ (Pa^{-1}) by the extrapolation. The absolute value of the measured photoelastic coefficient was ~1.6 times larger than that of PMMA. It was also found that PTCEMA exhibited the largest negative photoelastic birefringence among the methacrylate polymers that have previously been measured.[4,6]

The birefringence analyses described above show that both PTCEMA and PMMA exhibit negative orientational and photoelastic birefringences. Thus, a polymer with positive orientational and photoelastic birefringences is suitable for the design of a zero–zero-birefringence polymer in a ternary system.

Figure 4 shows the changes of T_g of the bulk and purified polymers and the amount of remaining monomer against the copolymer compositions of the obtained bulks. As shown in Figure 4, the T_g of the bulk samples decreased when the bulks have a lot of remaining monomer due to the plasticizing effect. However, the T_g of the purified samples increased with increasing TCEMA content because the remaining monomer was removed through the reprecipitation process. The homopolymer of partially
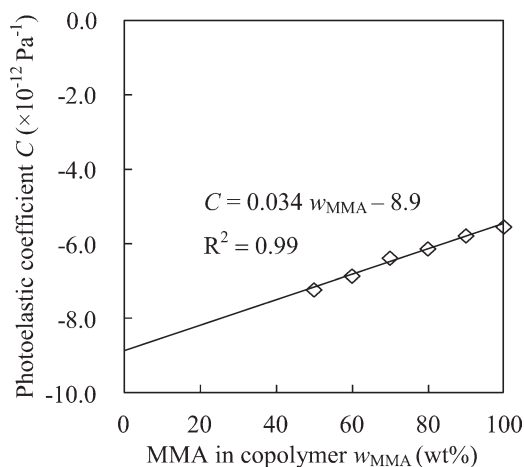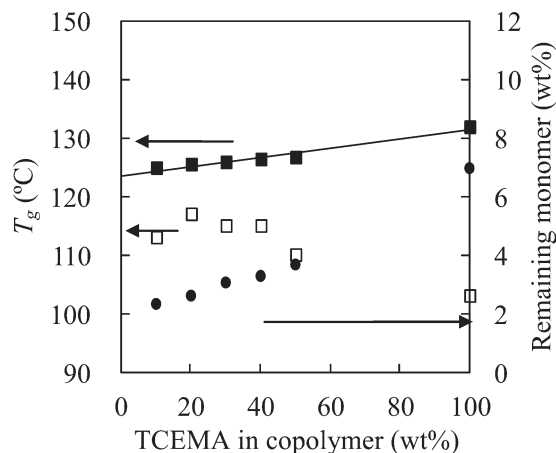

Figure 4. T_g of bulk ($\square$) and purified ($\blacksquare$) poly(MMA-*co*-TCEMA) and the amount of remaining monomer in bulks ($\bullet$) against the proportion of TCEMA in the copolymer (wt %).

chlorinated methacrylate has been found to exhibit higher T_g compared with that of poly(MMA) (PMMA).[7,8] By copolymerizing with TCEMA, the T_g values of the copolymer slightly increased as the fraction of TCEMA increased and were fitted with the Gordon-Taylor equation.[9] As shown in Figure 4, PTCEMA has a high T_g. It was found that the T_g of the zero–zero-birefringence polymer could be improved from the value of the previous work by designing a copolymerization system containing TCEMA.

Copolymer Design

The intrinsic birefringence and the photoelastic coefficient for PTCEMA, PMMA, poly(TFEMA) (PTFEMA), poly(BzMA) (PBzMA), and poly(PFPhMA) (PPFPhMA) are summarized in Table I. The relation between them is also shown in Figure 5, where the origin ($\Delta n^0 = C = 0$) represents zero–zero-birefringence. In the copolymerization system, we can design desirable birefringence inside the polygonal area formed by connecting the plots for each moiety, because both constants are generally described by the additivity expressed in eqs. (3) and (4). As shown in Figure 5, a zero–zero-birefringence polymer can be designed in the ternary system of TCEMA, MMA, and PFPhMA, because the three plots surround the origin of the figure. By using the Δn^0 and C listed in Table I, we calculated the monomer composition to adjust both types of birefringence

Figure 3. Photoelastic coefficient of poly(MMA-*co*-TCEMA) as a function of the proportion of MMA in the copolymer, w_{MMA} (wt %).

Table I. Intrinsic Birefringence Δn^0 and Photoelastic Coefficient C of Polymers[a]

Polymer	Intrinsic birefringence Δn^0 ($\times 10^{-3}$)	Photoelastic coefficient C ($\times 10^{-12}$ Pa^{-1})
PTCEMA	−2.8	−8.9
PMMA	−5.6	−5.5
PTFEMA	3.5	−2.2
PBzMA	19.5	48.4
PPFPhMA	23.4	27.4

[a]The intrinsic birefringence and photoelastic coefficients of PMMA, PTFEMA, PBzMA, and PPFPhMA were analyzed in the previous work.[2,10]
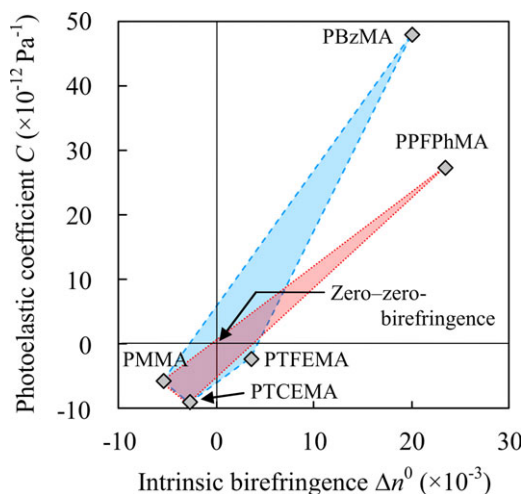
Figure 5. The relationship between the intrinsic birefringence and the photoelastic coefficient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to zero, which was determined as MMA/TCEMA/PFPhMA = 69 : 13 : 18 (wt %).

Figure 5 also indicates that zero–zero-birefringence polymers can be designed by using TCEMA as a fourth moiety in addition to MMA, TFEMA, and BzMA, which have been used in previous researches.[2,3] Figure 6 shows the change of the calculated compositions of MMA, TFEMA, and BzMA against the composition of TCEMA to eliminate both types of birefringence. In a quaternary copolymerization system, zero–zero-birefringence polymers can be designed with multiple compositions, because the simultaneous eqs. (3)–(5) theoretically have an indefinite number of solutions. As can be seen in Figure 6, we can design the zero–zero-birefringence polymers in the cases where the fraction of TCEMA varies from 0 to 70 wt %, where the eqs. (3)–(5) give positive solutions. For example, by selecting a composition with high TCEMA content, a zero–zero-birefringence with high T_g can be obtained. Based on the above
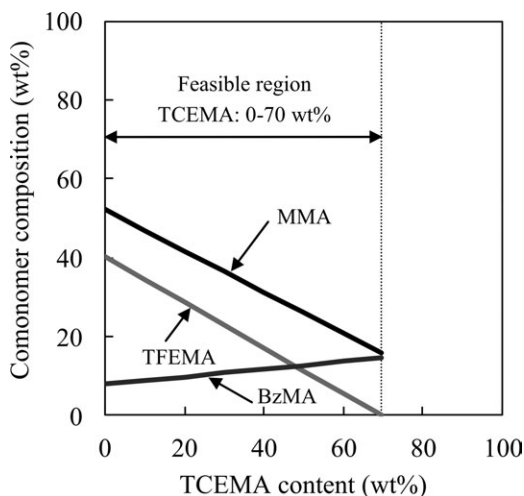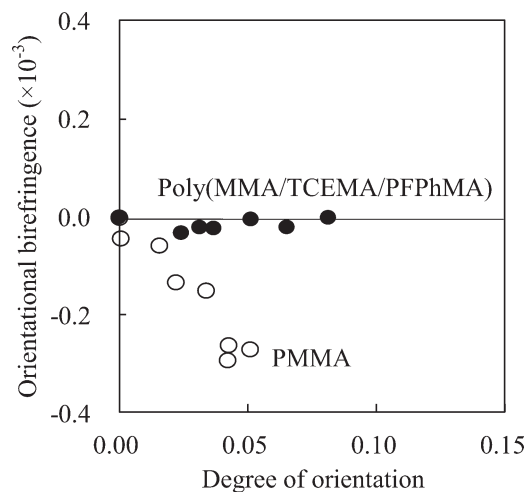
Figure 7. Orientational birefringence of poly(MMA/TCEMA/PFPhMA) (●) and PMMA (○).

calculations, quaternary copolymers with MMA/TCEMA/ TFEMA/BzMA ratios of 50 : 4 : 38 : 8, 40 : 23 : 27 : 10, and 30 : 42 : 16 : 12 wt % in the feed were fabricated.

Zero–Zero-Birefringence Polymer

The orientational and photoelastic birefringences of the ternary copolymer poly(MMA/TCEMA/PFPhMA) are shown in Figures 7 and 8, respectively. While PMMA exhibited birefringences, in the copolymer both birefringences were eliminated. Therefore, we have successfully fabricated the zero–zero-birefringence polymer. The T_g of the zero–zero-birefringence polymer was measured and the result is shown in Table II. The obtained copolymer exhibited 29°C higher T_g than the value reported in the previous research (T_g = 93°C).[3] For the poly(MMA/ TCEMA/TFEMA/BzMA) quaternary copolymers, both birefringences were measured and the results are shown in Figures 9 and 10. As shown in the graphs, regardless of the composition, all copolymers were free of both types of birefringence. Moreover, as listed in Table II, the measured T_g values for the
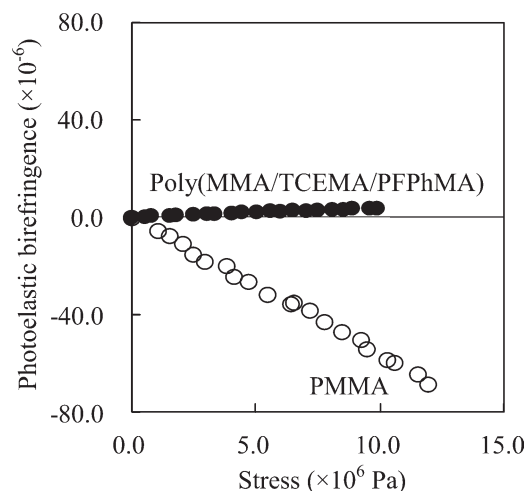

Figure 6. Feasible region for zero–zero-birefringence polymer in a quaternary copolymer of MMA, TCEMA, TFEMA, and BzMA.

Figure 8. Photoelastic birefringence of poly(MMA/TCEMA/PFPhMA) (●) and PMMA (○).

Table II. Birefringence Properties and T_g of the Zero–Zero-Birefringence Polymers and PMMA

Polymer	Copolymer composition (wt %)[a]	Δn^0 ($\times 10^{-3}$)	C ($\times 10^{-12}$ Pa^{-1})	T_g (°C)
Poly(MMA/TCEMA/PFPhMA)	69 : 13 : 18	−0.23	0.41	122
	50 : 4 : 38 : 8	0.09	0.28	106
Poly(MMA/TCEMA/TFEMA/BzMA)	40 : 23 : 30 : 7	−0.28	0.07	107
	29 : 43 : 16 : 12	−0.66	−0.27	111
PMMA	–	−5.6	−5.5	118

[a]The copolymer compositions were determined on the basis of the results of ^{1}H NMR measurement for poly(MMA/TCEMA/PFPhMA) and ^{13}C NMR measurements for poly(MMA/TCEMA/TFEMA/BzMA).

quaternary zero–zero-birefringence polymers increased with an increase in the TCEMA content. In the ternary system reported in the previous articles, the optimal composition for compensating the birefringences was determined as one specific value
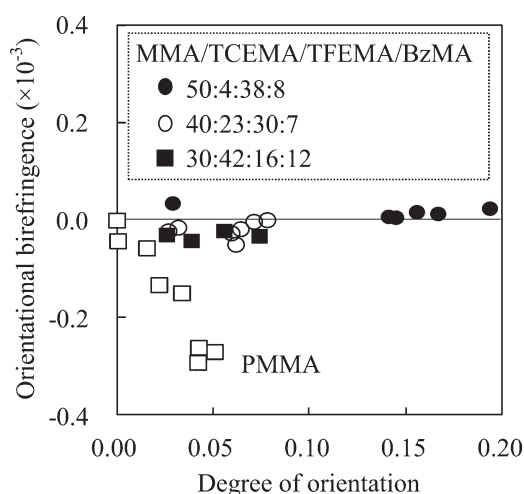

Figure 9. Orientational birefringence of poly(MMA/TCEMA/TFEMA/BzMA) and PMMA. MMA/TCEMA/TFEMA/BzMA composition ratios in feed were 50 : 4 : 38 : 8 (●), 40 : 23 : 30 : 7 (○), and 29 : 43 : 16 : 12 (■), wt %.
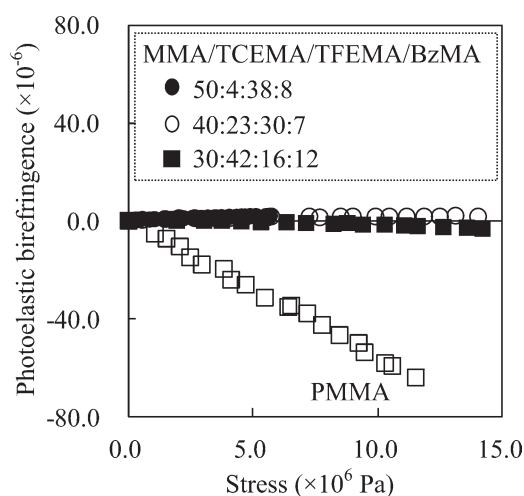

Figure 10. Photoelastic birefringence of poly(MMA/TCEMA/TFEMA/BzMA) and PMMA. MMA/TCEMA/TFEMA/BzMA composition ratios were 50 : 4 : 38 : 8 (●), 40 : 23 : 30 : 7 (○), and 29 : 43 : 16 : 12 (■), wt %.

[MMA/TFEMA/BzMA = 52 : 42 : 6 (wt %)] and its T_g was also fixed.[2,3] However, in the quaternary system we propose here, the T_g can be controlled while maintaining the zero–zero-birefringence property. This result shows that designing a quaternary copolymer has the advantage of permitting the selective synthesis of zero–zero-birefringence polymer with the most suitable characteristics in accordance with its intended application.

CONCLUSION

Binary copolymer films of MMA and TCEMA with various composition ratios were prepared and their birefringences were analyzed. Based on the measurement, the intrinsic birefringence and photoelastic coefficient were determined for the TCEMA homopolymer. By using the analysis results, a zero–zero-birefringence polymer was successfully synthesized by ternary copolymerization of MMA, TCEMA, and PFPhMA. By using TCEMA as a comonomer, this copolymer had much higher T_g compared with the zero–zero-birefringence polymer poly(MMA/TFEMA/BzMA) proposed in the previous research. Moreover, quaternary copolymers with three different compositions of MMA/TCEMA/TFEMA/BzMA (50 : 4 : 38 : 8, 40 : 23 : 27 : 10, and 29 : 43 : 16 : 12 wt %) were synthesized. These copolymers were confirmed to exhibit neither orientational nor photoelastic birefringence, regardless of their composition. T_g of these quaternary copolymers could be controlled while maintaining the zero–zero-birefringence property. We therefore showed that in a quaternary system of MMA, TCEMA, TFEMA, and BzMA, the best possible composition for a zero–zero-birefringence polymer can be found in accordance with its intended application.

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