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ORIGINAL ARTICLE

Mechanism of generation of birefringence in poly(methyl methacrylate/styrene)

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The relationship between the intrinsic birefringence and the composition ratio and between the photoelastic coefficient and the composition ratio in poly(methyl methacrylate (MMA)/styrene (St)) was investigated. A linear relationship was observed between the orientational birefringence and the composition ratio but not between the photoelastic coefficient and the composition ratio. The influence of the compositional distribution on the birefringence was investigated, and the results suggested that the compositional distribution of poly(MMA/St) minimally affects birefringence. We also analyzed the mechanism by which birefringence is generated in poly(MMA/St) by focusing on changes in St conformation. The results of this analysis suggested that the conformational changes in St units are different for orientational and photoelastic birefringence generation.
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INTRODUCTION

Optical polymers have recently been applied to lenses, optical disks, functional films for liquid-crystal displays and various other optical devices because of their ease of processing, light-weight and high transparency. However, polymers can create a serious problem by exhibiting birefringence when produced by injection molding, extrusion and drawing. Birefringence degrades the performance of optical devices that require the polarization state of incident light to be maintained; therefore, birefringence needs to be eliminated.

Birefringence comes from the anisotropic structure of a material.[1] Polarized light is separated into two waves when it enters a birefringent material. The refractive indices for these differently polarized waves are different; hence, retardation occurs between these two waves when the light exits the material.

Inoue et al.[2] propose that birefringence is described by a two-component function: one describing the behavior in the glass region and the other in the rubber zone. In the glass-to-rubber transition region, both of the components contribute to the birefringence; therefore, birefringence depends on both temperature and draw conditions.

In our laboratory, we mainly study the birefringence mechanisms prevalent above and below the glass-transition temperature (T_g) that are observed in typical thermoplastic optical devices: orientational birefringence and photoelastic birefringence. Orientational birefrin-

gence (Δn_{or}) is caused by the orientation of the polymer chains above T_g and is defined as

$$\Delta n_{or} = n_{\parallel} - n_{\perp} \qquad (1)$$

$$= \Delta n^0 \times f \qquad (2)$$

where $n_{\parallel}$ and $n_{\perp}$ are, respectively, the refractive indices for polarized light in the parallel and perpendicular directions to the drawing (tensile stress) direction, Δn^0 is the intrinsic birefringence and f is the orientation function. By this definition, $\Delta n > 0$ is positive birefringence, whereas $\Delta n < 0$ is negative birefringence.

The other mechanism, photoelastic birefringence (Δn_{ph}) is caused by the elastic deformation of polymers below T_g and is defined[3] as

$$\Delta n_{ph} = C \times \sigma \qquad (3)$$

where C is the photoelastic coefficient of the material and σ is the stress. The sign of the photoelastic birefringence is defined in the same way as that of the orientational birefringence. The generation mechanism of birefringence has been analyzed and reported.[2,4,5] It is known that the mechanism changes depending on the temperature and draw conditions.

In the previous study, the two types of polymer birefringence were simultaneously compensated by the random copolymerization of monomers having opposite anisotropic polarizability.[6–8] A zero zero-birefringence polymer, which exhibits neither orientational

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nor photoelastic birefringence hence the name 'zero zero', was designed using three different monomers: methyl methacrylate (MMA), 2,2,2-trifluoroethyl methacrylate and benzyl methacrylate. The composition of the zero zero-birefringence polymer was calculated by using the linear relationship between the birefringence of the constituent polymer and the composition ratio.[7,8] The linear relationship was previously shown for methacrylate copolymers. However, in other polymers, the relationship has not been confirmed.

Monomer reactivity ratios are important in a radical copolymerization because monomers copolymerize in accordance with these ratios. For a perfectly random copolymerization of two kinds of monomers, the reactivity ratios of both monomers must be equal to a value of one ($r_1=r_2=1$). Otherwise, the monomers do not copolymerize randomly, and the resultant copolymers have a compositional distribution.[9] The relationship between the compositional distribution of copolymers and their birefringence has not been clarified.

The purpose of this research is to investigate the relationship between the intrinsic birefringence and the composition ratio and between the photoelastic coefficient and the composition ratio in poly(MMA/styrene (St)). We chose this pair because it does not copolymerize at random (the monomer reactivity ratios are as follows: $r_1=0.46$ and $r_2=0.52$ (M_1=MMA, M_2=St)).[10] The influence of the compositional distribution on the birefringence is investigated. We also analyze the mechanism by which birefringence is generated in poly(MMA/St) by focusing on the conformational change of St.

EXPERIMENTAL PROCEDURE
Preparation of polymer samples and film samples
We selected MMA (99.8%, Mitsubishi Gas Chemical Company, Tokyo, Japan) and St (99.9%, Sigma-Aldrich, Tokyo, Japan) as monomers, the structures of which are illustrated in Figure 1. MMA and St were distilled under reduced
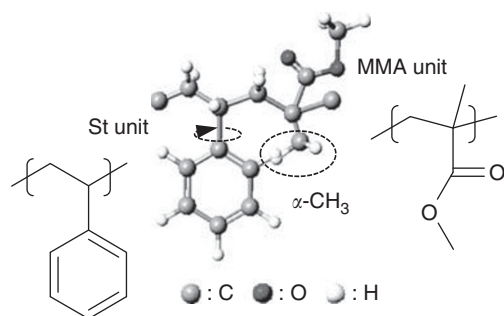

Figure 1 Molecular structure of poly(methyl methacrylate (MMA)/styrene (St)). A full color version of this figure is available at *Polymer Journal* online.

pressure before use. To change the copolymer compositional distribution, ~100 and ~10% conversion samples were prepared by bulk polymerization. Mixtures of MMA/St (100/0, 80.6/19.4, 51.0/49.0, 47.1/54.9, 20.6/79.4, 0/100 (mol/mol)) were prepared for the ~100% conversion samples. Tertiary-butyl peroxy-2-ethylhexanoate (98%, NOF, Tokyo, Japan) as an initiator and *n*-butyl mercaptan (95%, Wako Pure Chemical Industries, Osaka, Japan) as a chain transfer agent were added to the monomer mixtures at ratios of 0.3 and 0.2 wt. %, respectively. The mixtures were injected into glass tubes (16.5×165.0 mm), which were then set in a water bath at 70 °C for 24 h for polymerization. The obtained bulk polymers were heat-treated at 90 °C for 24 h to finalize the polymerization. The resulting polymers were dissolved in dichloromethane and then poured into methanol to precipitate the polymers and remove any remaining monomers. The pure polymers were dried at 90 °C for 24 h under reduced pressure. Meanwhile, mixtures of MMA/St (100/0, 80.6/19.4, 51/49, 47.1/54.9, 20.6/79.4, 0/100 (mol/mol)) were prepared for the ~10% conversion samples. The mixtures were injected into glass tubes (16.5×165.0 mm). We terminated the polymerization at ~10% conversion by rapid cooling and then poured the samples into methanol. The conditions for polymerization are shown in Table 1. The obtained polymers were dried at 90 °C for 24 h under reduced pressure. The composition of all obtained polymers was determined by ^{1}H-NMR analysis. To measure the orientational birefringence, photoelastic birefringence and infrared (IR) dichroism, polymer films were prepared. The polymers were dissolved in dichloromethane, and the obtained polymer solution was spread on a glass plate using a knife coater. The film thickness was adjusted to 20–50 μm. The films were dried at room temperature for 4 h and at 90 °C for 24 h under reduced pressure to eliminate the solvent. The films were then cut into dumbbell-shaped specimens.

Measurement of orientational birefringence
The obtained films were uniaxially drawn at above T_g (15–20 °C higher than T_g) with a universal tensile testing machine (Tensilon RTC-1210A, A&D Company Ltd., Tokyo, Japan). The draw ratio was from 1.25 to 2.0, and the draw speed was from 10 mm min^{-1} to 40 mm min^{-1}. The orientational birefringence Δn_{or} of the uniaxially heat-drawn films was calculated by dividing the optical retardation of the film by the film thickness. Retardation was measured at a wavelength of 633 nm by a birefringence evaluation system (ABR-10A, Uniopt Co., Ltd., Shizuoka, Japan) using optical heterodyne interferometry.[11] The experimental equipment is described in Figure 2a. This system consists of a rotating half-wave plate, a rotating linear polarizer, a photodiode, an electric phase meter, and a frequency-stabilized transverse Zeeman laser equipped with a two-frequency orthogonally polarized light source. The retardation and principal axis direction of the samples were measured by analyzing the phase difference between the obtained beat signal and the reference signal from the stabilized transverse Zeeman laser.

Measurement of photoelastic birefringence
As shown in Figure 2b, the retardation was measured at a wavelength of 633 nm during the application of stress to the sample films. The measurement was carried out at room temperature (25 °C), which is lower than the sample T_g by 60–80 °C. The draw ratio is equivalent to a strain of less than ~1%, which is in

Table 1 Polymerization conditions for samples at ~10% conversion ratio (polymerization temperature: 70 °C) and results of polymerization

MMA/St (mol/mol) in feed	Polymerization time (min)	Tertiary-butyl peroxy-2-ethylhex-anoate (wt. %)	n-butyl mercaptan (wt. %)	At ~10% conversion		At ~100% conversion	
				Conversion ratio (%)	MMA/St (mol/mol) in copolymer	Conversion ratio (%)	MMA/St (mol/mol) in copolymer
100/0	40	0.3	0.2	9.1	100/0		100/0
80.6/19.4	120	0.1	—	7.5	72.9/27.1		79.7/20.3
47.1/52.9	195	0.1	—	8.4	47.5/52.5	Approximately 100	46.9/53.1
20.6/79.4	240	0.1	—	10.2	24.7/75.3		20.8/79.2
0/100	195	0.1	—	8.3	0/100		0/100

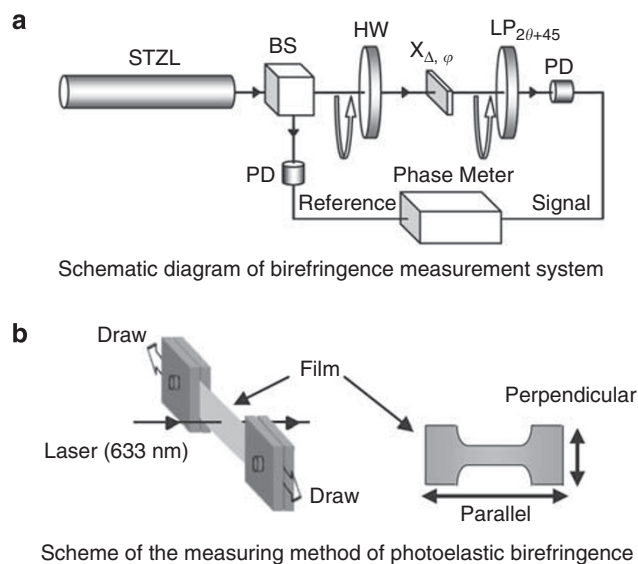Abbreviations: MMA, methyl methacrylate; St, styrene.

Figure 2 (a) Schematic diagram of birefringence measurement system. STZL: stabilized transverse Zeeman laser; BS, beam splitter; HW$_\theta$, half-wave plate that is set at the azimuthal angle θ; X$_{\Delta,\varphi}$, measurement sample with a phase difference Δ at azimuthal angle φ; LP$_{2\theta+45}$, linear polarizer with the azimuthal angle $\theta+45$; PD, photodiode. (b) Scheme of the measuring method of photoelastic birefringence.
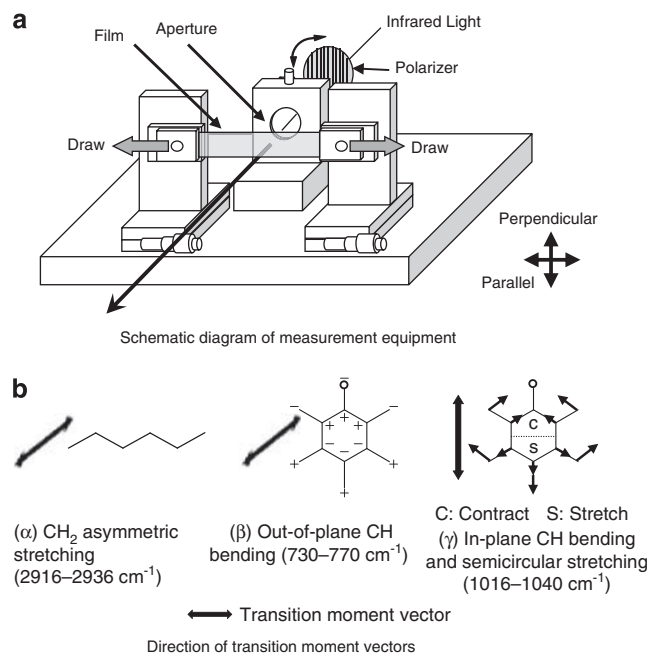

Figure 3 (a) Schematic diagram of measurement equipment for infrared dichroism of elastically deformed polymer films and (b) direction of transition moment vectors in each absorbance.

the elastic range. Birefringence measurement equipment (ABR-10A, Uniopt Co., Ltd.) was used. The photoelastic birefringence Δn_{ph} was calculated by dividing the optical retardation of the film by the film thickness.

Measurement of IR dichroism

To analyze the conformational changes in the polymer molecules during the generation of orientational and photoelastic birefringence, we measured the IR dichroism of polymer films that were uniaxially heat drawn and had elastic deformation of less than ~1% (the strain induced by the draw ratio is of less than ~1%) using polarized Fourier-transform infrared spectroscopy.[12–14] The measurement was carried out at room temperature (25 °C), which is 60–80 °C lower than T_g. The experimental equipment is described in Figure 3a. For the analysis of the conformational change during the generation of orientational birefringence, the heat-drawn film was used. The drawing direction of the film was set parallel to the parallel direction of the equipment. For the analysis of the conformational change during the generation of photoelastic birefringence, a sample film was fixed and then uniaxially drawn by actuators at room temperature. The absorbance of the films was measured within the spectral range of 400 to 4000 cm^{-1} using a Fourier-transform-IR spectrometer (7000e FT-IR, Varian Inc., Tokyo, Japan). We selected the CH$_2$ asymmetric stretching at 2916–2936 cm^{-1}, the out-of-plane CH bending of the benzene ring at 730–770 cm^{-1}, and the in-plane CH bending mixed with the semicircular stretching of the benzene ring at 1016–1040 cm^{-1} as the characteristic bands of poly(MMA/St).[15,16] The direction of the transition moment vectors in each absorbance is shown in Figure 3b. The absorption peak of the CH$_2$ asymmetric stretching was measured for analysis of the motion of the main polymer chain. Additionally, the absorption peak of the out-of-plane CH bending and the in-plane bending mixed with the semicircular stretching of the benzene ring was measured for analysis of the motion of the side chain of St units in copolymers. The dichroic ratio, D, is defined by $D=A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbance for linearly polarized IR light in the directions parallel and perpendicular to the drawing direction, respectively. $A_{\parallel}$ and $A_{\perp}$ of the heat-drawn films were measured. The orientation function, f, is related to the dichroic ratio D as

$$f = \frac{D-1}{D+2} \cdot \frac{2\,\cot^2\alpha + 2}{2\,\cot^2\alpha - 1} \tag{4}$$

where α is the angle between the transition moment vector of the absorbing group and the long axis of the molecule. We used $\alpha=90°$ for the CH$_2$ asymmetric stretching.

RESULTS AND DISCUSSION

Compositional distribution in copolymers at ~10 and ~100% conversion

Table 1 shows the results of the compositional ratio measurement in copolymers at ~10 and ~100% conversion. Figure 4a shows the relationship between the composition ratio and the conversion in poly(MMA/St) with a ratio of MMA/St of 80.6/19.4 (mol/mol), calculated using the Mayo-Lewis equation,[17] which is

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]} \tag{5}$$

where $d[M_1]$ and $d[M_2]$ are the instantaneous compositions of monomer M_1 and monomer M_2 in the copolymer, $[M_1]$ and $[M_2]$ are the concentrations of M_1 and M_2 in the system at a given time, and r_1 and r_2 are the monomer reactivity ratios of M_1 and M_2, respectively. It was confirmed that the composition ratio varies according to the degree of conversion. Figures 4b and c shows the compositional distribution at ~10 and ~100% conversion for poly(MMA/St)=80.6/19.4 (mol/mol). The compositional distribution at ~100% conversion ranged from 72 to 99 (MMA composition (mol %)). However, the compositional distribution at ~10% conversion ranged from 72 to 73 (MMA composition (mol%)). At ~10% conversion for poly(MMA/St)=80.6/19.4 (mol/mol), the values of the composition ratio measured by ^{1}H-NMR and the values calculated by the Mayo–Lewis equation (Figure 4c) were similar. It was confirmed that ~10% conversion copolymers were controlled, as defined by their narrow compositional distribution.
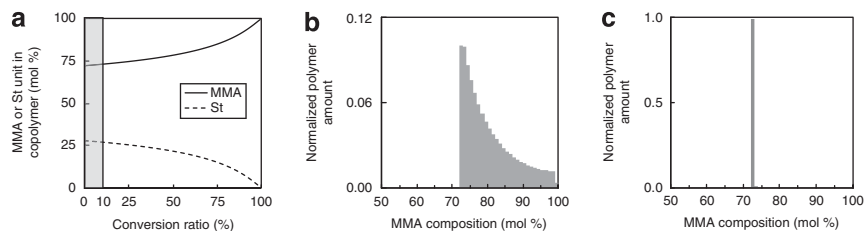
Figure 4 Compositional distribution of poly(methyl methacrylate (MMA)/styrene (St)=80.6/19.4 (mol/mol)) calculated using the Mayo–Lewis equation; (**a**) copolymer composition ratio against conversion ratio, (**b**) compositional distribution at approximately 100% conversion and (**c**) composition distributional at approximately 10% conversion.
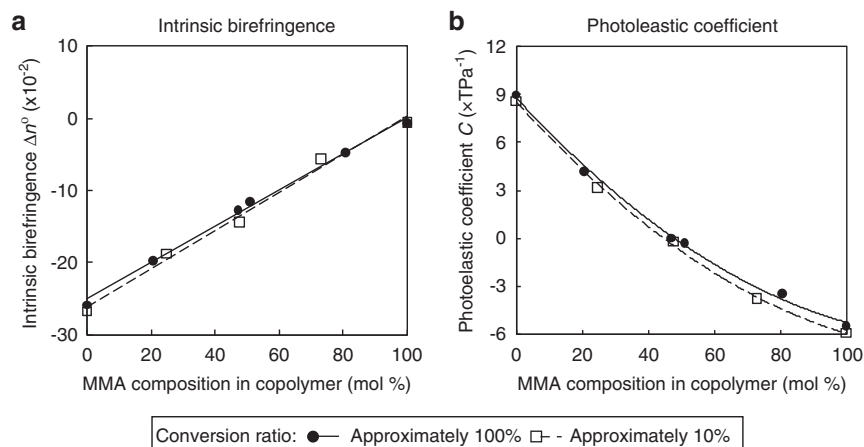

Figure 5 (**a**) Intrinsic birefringence Δn° and (**b**) photoelastic coefficient C of poly(methyl methacrylate (MMA)/styrene) against MMA composition in copolymer.
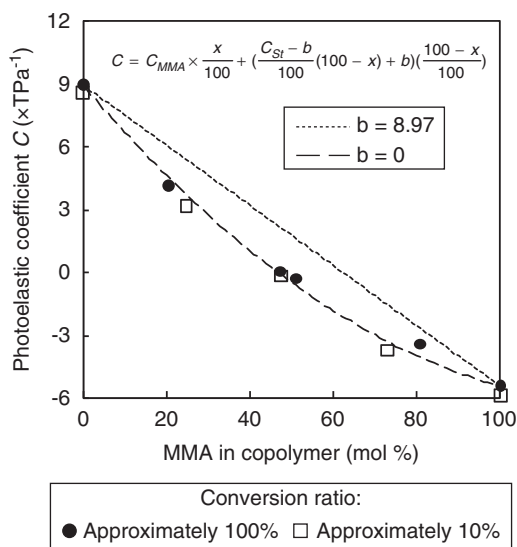

Figure 6 Calculated approximate curves and photoelastic coefficient C of poly(methyl methacrylate (MMA)/styrene).

Table 2 Effect of St units on photoelastic birefringence in copolymers against St (mol %) for two b values

	$C'_{St}(y)/C_{St}(y)$	
St in copolymer y (mol %)	b=0	b=8.97
100	1	1
80	0.80	1
50	0.50	1
20	0.20	1
1	0.01	1

Abbreviation: St, styrene.

line shows the approximate line of $\sim$100% conversion copolymers, and the broken line shows that of $\sim$10% conversion copolymers. These lines were obtained by the least-squares method. As shown in Figure 5a, there is a linear relationship between the intrinsic birefringence and the composition ratio in the copolymers at both $\sim$10 and $\sim$100% conversion. It was determined that this amount of compositional distribution has minimal effect on the orientational birefringence.

Orientational birefringence in copolymers at $\sim$10 and $\sim$100% conversion

From the results of the measured orientational birefringence and the IR measurements, the intrinsic birefringence of the copolymers was determined. Figure 5a shows the results of the intrinsic birefringence as a function of the composition ratio of the copolymers. The solid

Photoelastic birefringence in copolymers at $\sim$10 and $\sim$100% conversion

From equation (3), the photoelastic coefficient of the copolymers was determined. Figure 5b shows the results of the photoelastic coefficient as a function of the composition ratio of the copolymers. The solid curve shows the approximate line of $\sim$100% conversion copolymers, and the broken curve shows that of $\sim$10% conversion copolymers.
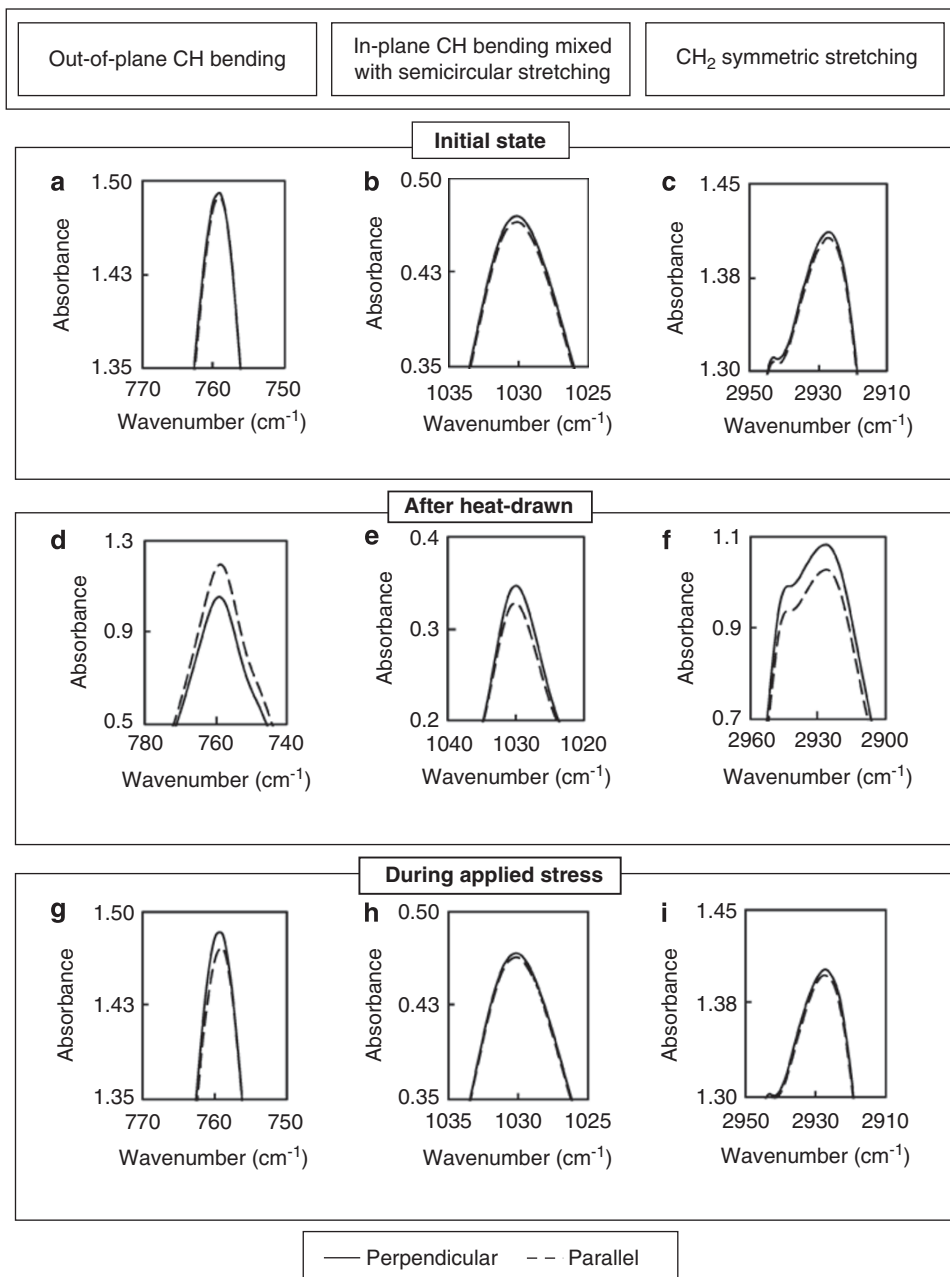
Figure 7 Infrared spectra of poly(methyl methacrylate/styrene=24.7/75.3 (mol/mol)) films against wavenumber (cm^{-1}); out-of-plane CH bending of the benzene ring (**a**) in the initial state, (**d**) after heat-drawn and (**g**) during applied stress; in-plane CH bending mixed with semicircular stretching of the benzene ring (**b**) in the initial state, (**e**) after heat-drawn and (**h**) during applied stress; CH$_2$ asymmetric stretching (**c**) in the initial state, (**f**) after heat-drawn and (**i**) during applied stress.

These curves were fitted by the least-squares method. As shown in Figure 5b, a linear relationship was not observed between the photoelastic coefficient and the composition ratio in the polymers at either ~ 10 or $\sim 100\%$ conversion. It was suggested that this amount of compositional distribution has only a minimal effect on the photoelastic birefringence, similar to the behavior of the orientational birefringence.

Nonlinear relationship observed between photoelastic coefficient and composition ratio

As shown in Figure 5b, a linear relationship was not observed between the photoelastic coefficient and the composition ratio in

the copolymers at either degree of conversion. We hypothesize that the photoelastic birefringence generated by the poly(styrene) (PSt) units is suppressed by the effect of steric hindrance from the MMA units. The relational expression is given by equation (6):

$$C = C_{MMA} \times \frac{x}{100} + C'_{St}(y) \times \frac{y}{100} \tag{6}$$

$$C'_{St}(y) = ay + b \tag{7}$$

$$x + y = 100 \tag{8}$$

where x and y are, respectively, the mole fractions of MMA and St in poly(MMA/St), C_{MMA} and C are, respectively, the photoelastic coefficients of poly(MMA) and poly(MMA/St=x/y), C'_{St} (y) is the photoelastic coefficient of PSt in the copolymer, and a and b are constants. The photoelastic coefficient of PSt is assumed to change linearly with the composition ratio of MMA (St), as shown in equation (7). C_{St} is defined as the photoelastic coefficient of PSt, and when $y=100$, $a=(C_{St}-b)/100$, yielding the following equation:

$$C'_{St}(y) = \frac{C_{St} - b}{100}y + b = \frac{C_{St} - b}{100}(100 - x) + b \quad (9)$$

From equations (6), (8), and (9) we obtain:

$$C = C_{MMA} \times \frac{x}{100} + \left(\frac{C_{St} - b}{100}(100 - x) + b\right)\left(\frac{100 - x}{100}\right) \quad (10)$$

The functions corresponding to $b=0$ and 8.97 are shown in Figure 6 by broken and dotted lines. The function corresponding to $b=0$ is in good agreement with the plots. When $b=0$, equation (9) can be rewritten as

$$C'_{St}(y) = \frac{C_{St}}{100}(100 - x) \quad (11)$$

Table 2 shows C'_{St} (y) (the photoelastic coefficient of the St unit in the copolymer) as a function of C_{St} (photoelastic coefficient of PSt) for $b=0$ and for $b=8.97$. Equation (11) and Table 2 show that C'_{St} (y) (the photoelastic coefficient of the St unit in the copolymer) decreases linearly for $b=0$ when the composition ratio of MMA increases. It is suggested that the photoelastic coefficient of the St unit in the copolymer is suppressed by the MMA unit.

Analysis of generation mechanism of orientational birefringence in poly(MMA/St)

Figure 7 shows the IR spectrum of poly(MMA/St)=24.7/75.3 (mol/mol) films at several wavelengths. The absorbance of the CH_2 asymmetric stretching at 2916–2936 cm^{-1} (a, d, g), the out-of-plane CH bending of the benzene ring at 730–770 cm^{-1} (b, e, h) and the in-plane CH bending mixed with the semicircular stretching of the benzene ring at 1016–1040 cm^{-1} (c, f, i) are represented in the figure. The solid line shows the absorbance of polarized IR light in the perpendicular direction, and the broken line shows the absorbance of the polarized light in the parallel direction. The spectrum of the initial-state film is shown in Figures 7a–c. In this case, the absorbance is almost the same in both the parallel and perpendicular directions at the wavelength used. The spectra of the heat-drawn films are shown in Figures 7d–f, in which it can be seen that the absorbance of both the CH_2 asymmetric stretching and the in-plane CH bending mixed with the semicircular stretching of the benzene ring in the perpendicular direction are larger than that in the parallel direction. In contrast, the absorbance of the out-of-plane CH bending of the benzene ring in the parallel direction is larger than that in the perpendicular direction. These results show that the main chain is oriented in the drawing direction after the film is heat drawn. It is suggested that the conformation of the St units during the generation of orientational birefringence in poly(MMA/St) changes as shown in Figure 8a.

Analysis of generation mechanism of photoelastic birefringence in poly(MMA/St)

The stress-strain curves of poly(MMA), poly(MMA/St)=24.7/75.3 (mol/mol) and PSt films are shown in Figure 9. The deformation of each film was nearly elastic when the strain was within ~0.7%.

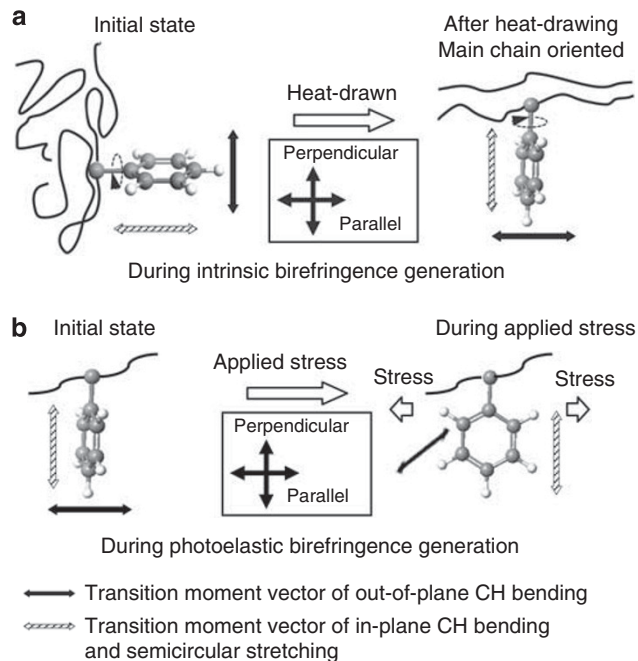**Figure 8** Conformational change in benzene ring during generation of (**a**) orientational birefringence and (**b**) photoelastic birefringence.
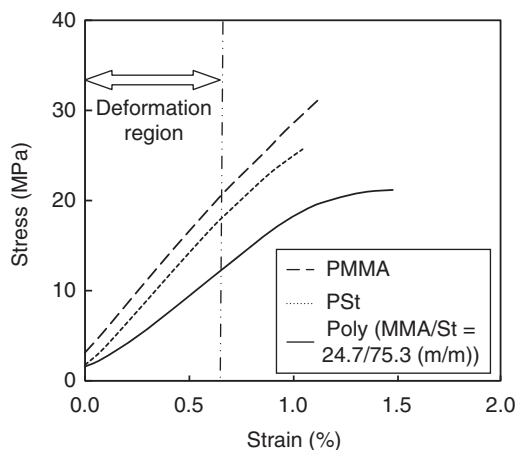

Figure 9 Stress-strain curves of poly(methyl methacrylate) (PMMA), poly(methyl methacrylate (MMA)/styrene (St)=24.7/75.3 (mol/mol)) and PSt films. Sample thickness is approximately 23 μm.

Figures 7g–i shows the absorbance of the out-of-plane CH bending of the benzene ring, the in-plane bending mixed with the semicircular stretching of the benzene ring and the CH_2 asymmetric stretching, respectively, during the applied uniaxial tensile stress. As shown in Figures 7h and i, the absorbance is almost the same in both the parallel and perpendicular directions. However, as shown in Figure 7g, the absorbance of the out-of-plane CH bending in the perpendicular direction is larger than that in the parallel direction. Figures 7h and i shows that the main chain is minimally oriented, and Figure 7g shows that the surface of the benzene ring turns in the direction parallel to the oriented direction during the applied uniaxial tensile stress. It is suggested that the conformation of the St units during the generation of photoelastic birefringence in poly(MMA/St) changes as shown in Figure 8b.

Figure 8 shows that the conformational change in the St unit differs between orientational and photoelastic birefringence generation. The effect of the St unit on the photoelastic birefringence might be suppressed when its conformation changes as shown in Figure 8b because the α-CH₃ group of the MMA unit hinders the conformational change in the benzene ring of the St unit, as shown in Figure 1, when the St unit is adjacent to an MMA unit. The probability of the St unit being adjacent to an MMA unit increases with the increase in composition ratio of MMA. In equation (11), the relationship between the photoelastic coefficient of the St unit in the copolymer and the composition ratio of St is indicated.

We conclude that a nonlinear relationship is observed between the photoelastic coefficient and the composition ratio during applied stress because of the effect of steric hindrance from the MMA unit.

CONCLUSIONS

We analyzed the relationship between the intrinsic birefringence and the composition of poly(MMA/St) and between the photoelastic coefficient and the composition of poly(MMA/St). The influence of the compositional distribution in generating both types of birefringence was analyzed. It is suggested that the amount of compositional distribution minimally affects the birefringence. A linear relationship was observed between the orientational birefringence and the composition ratio but not between the photoelastic coefficient and the composition ratio. Through IR measurement, the conformational changes in the St unit were suggested and found to differ between orientational and photoelastic birefringence generation. We believe that during applied stress, the α-CH₃ group of the MMA unit hinders the rotation of the benzene ring of the St units that are adjacent to MMA units, leading to the nonlinear relationship that was observed between the photoelastic coefficient and the composition ratio. We conclude that the control of birefringence by copolymerization is effective, even if random copolymerization is not realized (the obtained copolymers have a compositional distribution) and that a linear relationship is not observed between the birefringence and the composition ratio.

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