

ORIGINAL ARTICLE

Design and synthesis of a zero-photoelastic birefringence polymer with a high glass-transition temperature by a random copolymerization method

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We designed and synthesized a zero-photoelastic birefringence polymer that had a high glass-transition temperature (T_g) by introducing *trans*-stilbene units into the side chains of the copolymer by a random copolymerization method. The concentration of the *trans*-stilbene units required to compensate for photoelastic birefringence in the random copolymer was lower than that required in a polymer prepared by an anisotropic molecule dopant method, because the presence of an anisotropic moiety in the side chain of the polymer has a greater effect than an anisotropic molecule doped in the polymer. Furthermore, the polymer with *trans*-stilbene units in side chains showed a higher T_g than the polymer containing an anisotropic dopant. We conclude that the introduction of an anisotropic molecule of a similar or larger size to *trans*-stilbene into the side chain gives a polymer with a high T_g . *Polymer Journal* (2011) 43, 306–312; doi:10.1038/pj.2010.136; published online 12 January 2011

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INTRODUCTION

Polymeric materials are currently used in a variety of optical devices, such as optical films for liquid crystal displays (LCDs),^{1–3} optical disks⁴ and lenses.⁵ Display devices are key infrastructural elements in multimedia systems. As one of several kinds of flat-panel display that are available, LCDs are widely used in a range of applications, including computer monitors, televisions, instrument panels, mobile telephones and aircraft cockpit displays. In comparison with glass, polymers have the advantages of being more easily processed, more easily handled, lower in cost and lighter in weight. However, polymeric materials tend to exhibit birefringence, which restricts their use in optical devices that handle polarized light. Birefringence occurs when a polymer is elastically deformed below its glass-transition temperature (T_g), that is when it is in an elastic deformation region. This type of birefringence has been named as ‘photoelastic birefringence.’ It has been confirmed that photoelastic birefringence depends mainly on the orientation of the side chains of the polymer, whereas the main chains have little effect.⁶ When a polarizing plate in an LCD contracts, stress is applied to the polymer film causing birefringence. This photoelastic birefringence results in light leakage when the LCD is in its ‘black’ state, thereby impairing the quality of the image, particularly its contrast. A polymer that does not generate photoelastic birefringence, even when stressed during use of an LCD, and which thereby prevents light leakage is therefore desirable. Photoelastic birefringence is also

observed in phase-difference films, which are used to increase the viewing angles of LCDs. Koike and co-workers proposed two methods for compensating for this birefringence (Figure 1): the anisotropic molecule dopant method^{7–9} and the random copolymerization method.^{10–13}

In the anisotropic molecule dopant method, the polymer is doped with a molecule that has an anisotropic polarizability and a rod-like form. The anisotropic dopant molecule must have an anisotropic form, such as a rod-like shape, so that it is oriented when the polymer is under stress, and it must show anisotropy in its polarizability to exhibit a birefringence that is opposite in direction of that of the polymer matrix. Generally, this method has the advantage of easy processing, as birefringence can be eliminated simply by doping the polymer with anisotropically polarizable molecule. However, doping with an anisotropic molecule results in a decrease in the T_g of the polymer matrix.⁸

In the random copolymerization method, monomers with negative and positive birefringences, which form polymers with negative and positive birefringence, respectively, are randomly copolymerized. As a result, the birefringence is canceled out when the monomers are present in a specific ratio. The resulting polymer, which is known as a ‘zero-photoelastic birefringence polymer’ exhibits no photoelastic birefringence under stress.¹¹ One example of such a polymer is a 92:8 (w/w) copolymer of methyl methacrylate (MMA) and benzyl

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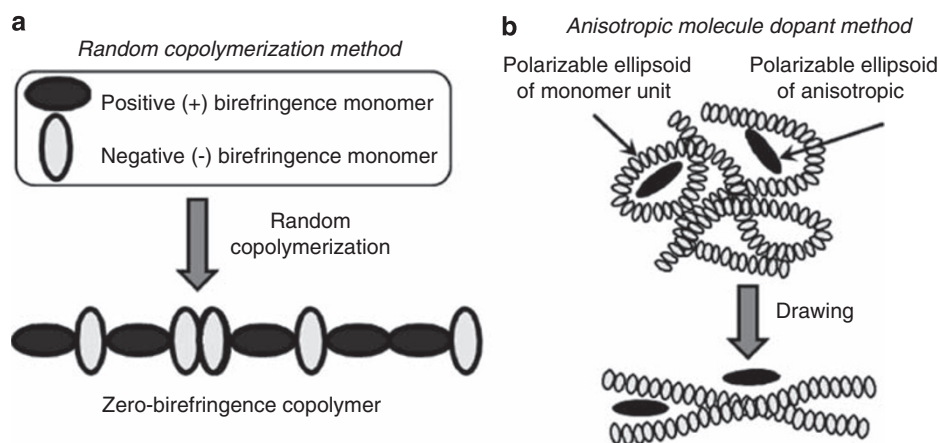


Figure 1 Methods for compensating for birefringence of polymers. (a) Anisotropic molecule dopant method; (b) random copolymerization method.

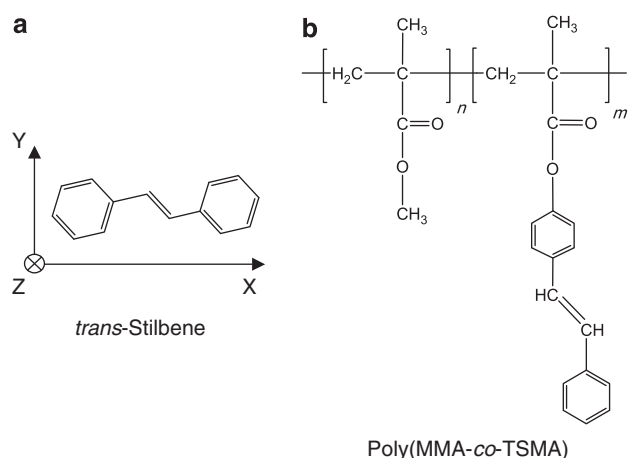


Figure 2 Molecular structures of (a) *trans*-stilbene and (b) poly(methyl methacrylate-*co*-*trans*-stilbene-4-yl methacrylate) (poly(MMA-*co*-TSMA)). MMA, methyl methacrylate; TSMA, *trans*-stilben-4-yl methacrylate.

methacrylate; however, the T_g of this polymer is 104 °C, which is lower than that of poly(methyl methacrylate) (PMMA) (T_g : 109 °C).¹³

Polymers that do not exhibit photoelastic birefringence during stress loading and which have a high T_g are required in many applications, for example, as polymer films for LCDs.^{14,15} The ideal monomer would be one that could be copolymerized with MMA, that would compensate for its photoelastic birefringence at a low concentration and that would produce a copolymer with a high T_g , because MMA is a mass-produced, commercially available monomer with low cost that demonstrated high-light transmittance and provides excellent resistance to both chemical and weather corrosions.¹⁶ Consequently, it is necessary to design a monomer that has a highly anisotropic polarizability.

We therefore designed and synthesized a zero-photoelastic birefringence polymer with a high T_g by incorporating a *trans*-stilbene unit in the side chain to give a monomer with the high polarizability anisotropy. We compared the effects of the *trans*-stilbene unit in compensating for photoelastic birefringence by the random copolymerization method and by the anisotropic molecular dopant method. We have also clarified the mechanism by which the *trans*-stilbene unit compensates for photoelastic birefringence. Moreover, we compared

the T_g values for of zero-photoelastic birefringence polymers produced by these two methods, and we clarified the effects on T_g of the presence of *trans*-stilbene unit in the side chain. In the anisotropic molecule dopant method, *trans*-stilbene (1,1'-(*E*)-ethene-1,2-diyl)benzene; Figure 2a) was chosen as an anisotropic molecule and was doped into PMMA. In the random copolymerization method, *trans*-stilben-4-yl methacrylate (TSMA; 4-((*E*)-2-phenylvinyl)phenyl 2-methylacrylate; Figure 2b), which contains a *trans*-stilbene unit in the side chain, was polymerized with MMA.

EXPERIMENTAL PROCEDURE

Preparation of TSMA monomer

TSMA was prepared by treating *trans*-4-hydroxystilbene (4-((*E*)-2-phenylvinyl)phenol) with 2-methacryloyl chloride in the presence of triethylamine in diethyl ether.^{17,18}

Trans-4-hydroxystilbene

A 1-l round-bottomed flask was charged with a mixture of 4-hydroxybenzaldehyde (122 g, 1 mol), phenylacetic acid (184 g, 1.35 mol) and piperidine (400 ml), and the mixture was refluxed for 6 h. The mixture was then cooled and poured onto crushed ice. The mixture was acidified to pH \approx 5 with concentrated hydrochloric acid diluted to 1:6 (v/v) with water to dissolve the piperidine, and the suspended product was intensively stirred to break up larger particles. The crude product was filtered off, washed successively with dilute hydrochloric acid and water, dried and dissolved in ethyl acetate. The solution was then dried over sodium sulfate and concentrated on a rotary evaporator. The residue was vacuum distilled and the resulting product was further purified by column chromatography (Silicagel (60–120 mesh), ethyl acetate–hexane (1:5 v/v)) to give pure *trans*-4-hydroxystilbene as a white solid; yield: 74.5 g (38%); m.p. 186–187 °C. ¹H NMR (300 MHz, CDCl₃): δ_H =7.63 (d, 2H), 7.46 (d, 2H), 7.40 (d, 2H), 7.22 (t, 1H), 7.21 (d, 2H), 7.01 (d, 1H), 6.88 (d, 1H). Anal. calcd for C₁₄H₁₂O: C, 85.73; H, 6.17. Found: C, 85.67; H, 6.25.

Trans-stilbene methacrylate

Triethylamine (30.3 g, 0.3 mol) was added to a solution of *trans*-4-hydroxystilbene (39.2 g, 0.2 mol) in diethyl ether (500 ml). A solution of methacryloyl chloride (26 g, 0.25 mol) in diethyl ether (150 ml) was then added dropwise with stirring at room temperature. The mixture was then stirred for 5 h, triethylamine hydrochloride was filtered off and the filtrate was washed successively with dilute hydrochloric acid (5 wt%), aqueous sodium carbonate (5 wt%) and water. The organic phase was dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration, the diethyl ether was evaporated on a rotary evaporator and the crude product was eluted with from silica gel (600–120 mesh) by using ethyl acetate–hexane (1:5 v/v). Recrystallization

from hexane gave a pure white product; yield: 36.3 g (68.5%); m.p. 157 °C. ^1H NMR (300 MHz, CDCl_3): $\delta_{\text{H}}=7.64$ (d, 2H), 7.46 (d, 2H), 7.40 (d, 2H), 7.22 (t, 1H), 7.20 (d, 2H), 7.01 (d, 1H), 6.88 (d, 1H), 6.30 (d, 1H), 5.92 (d, 1H), 2.03 (s, 3H). Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.23; H, 6.40. Found: C, 81.41; H, 6.37.

Preparation of polymer samples

Preparation of poly(MMA-co-TSMA) by random copolymerization. MMA (99.8%, Mitsubishi Gas Chemical Co., Tokyo, Japan) was distilled at 46–47 °C and 13.3 kPa to eliminate inhibitors and impurities. Copolymers with various weight ratios of MMA and TSMA were synthesized by solution polymerization in toluene at 90 °C under an inert atmosphere of nitrogen by using 0.15 wt% (on the weight of the monomer) of *tert*-butyl 2-ethylhexaneperoxoate (98%, NOF Corp., Tokyo, Japan) as an initiator. All polymers were precipitated in methanol for purification and dried at 90 °C for 48 h at reduced pressure (<1.33 Pa). To determine the reactivity ratio of the monomers experimentally, we needed to know the copolymer composition. The purified samples were dissolved in chloroform and analyzed by using ^1H NMR (JNM-LA400, JEOL Ltd, Tokyo, Japan). To investigate the infrared (IR) dichroism and birefringence of the polymers, films were prepared by dissolving poly(MMA-co-TSMA) in dichloromethane and spreading the polymer solution onto a glass plate with a knife coater. The sample films were dried at room temperature for 4 h and then at 90 °C under reduced pressure for 24 h to eliminate the solvent. The films were then cut into dumbbell-shaped specimens.

Preparation of PMMA doped with *trans*-stilbene by the anisotropic molecule dopant method. MMA (99.8%, Mitsubishi Gas Chemical Co.) was distilled at 46–47 °C and 13.3 kPa to eliminate inhibitors and impurities. A mixture of *tert*-butyl 2-ethylhexaneperoxoate (98%, NOF Corp.) as an initiator and butane-1-thiol (95%, Wako Pure Chemical Industries Ltd, Osaka, Japan) as a chain-transfer agent was added to the MMA in amounts of 0.4 wt% and 0.1 wt%, respectively. The mixtures were injected into cylindrical glass tubes and then polymerized at 70 °C for 24 h. The resulting bulk polymer samples were heat treated at 90 °C for 24 h. The polymer was precipitated in methanol for purification and dried at 90 °C for 48 h at reduced pressure (<1.33 Pa). To prepare film samples, mixtures of PMMA and *trans*-stilbene (98%, Wako Pure Chemical Industries Ltd) were dissolved in dichloromethane, and the solution was spread onto a glass plate with a knife coater. The sample films were dried at room temperature for 4 h and then at 90 °C at reduced pressure for 24 h to eliminate the solvent. The films were finally cut into dumbbell-shaped specimens.

Measurement of the photoelastic birefringence

The photoelastic birefringence (Δn_{ph}) generated in a stressed material is defined as follows:

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

where C is the photoelastic coefficient of the material and σ is the stress.¹⁹ The sign of photoelastic birefringence is defined as $\Delta n = n_{\parallel} - n_{\perp}$, where n_{\parallel} and n_{\perp} are the refractive indices for light polarized in the directions parallel and perpendicular, respectively, to the direction of drawing (tensile stress). The shape of a typical sample is shown in Figure 3a and the experimental setup is shown in Figure 3b. The photoelastic birefringence of each film sample was measured at various levels of uniaxial tensile stress (about 1% strain) at room temperature by optical heterodyne interferometry at a wavelength of 633 nm using a birefringence measurement system (ABR-10, UNIOPT Corporation, Ltd., Shizuoka, Japan).²⁰

IR measurements

To analyze the motion of the polymer molecules during the generation of photoelastic birefringence, we measured the IR dichroism of the polymer film in an elastically deformed state.⁹ The experimental setup is shown in Figure 4. The sample film was fixed and then uniaxially drawn at room temperature by using actuators. The absorbance of the drawn film was measured at 400–4000 cm^{-1} by using a Fourier-transform IR spectrometer (7000e FT-IR, Varian Inc., Santa Clara, CA, USA). We measured the absorbance of IR light polarized in the directions parallel and perpendicular to the drawing direction. We selected a wavelength

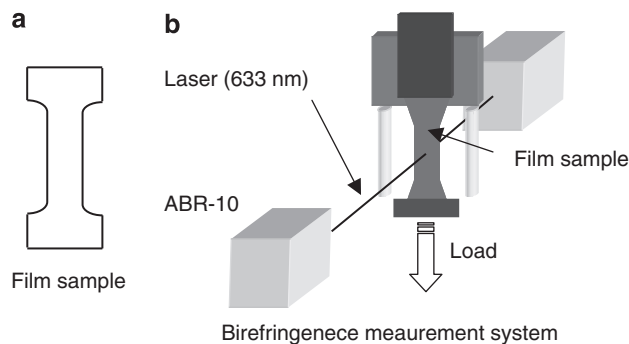


Figure 3 Schematic representation of the system for measuring photoelastic birefringence. (a) Film sample. (b) Birefringence measurement system.

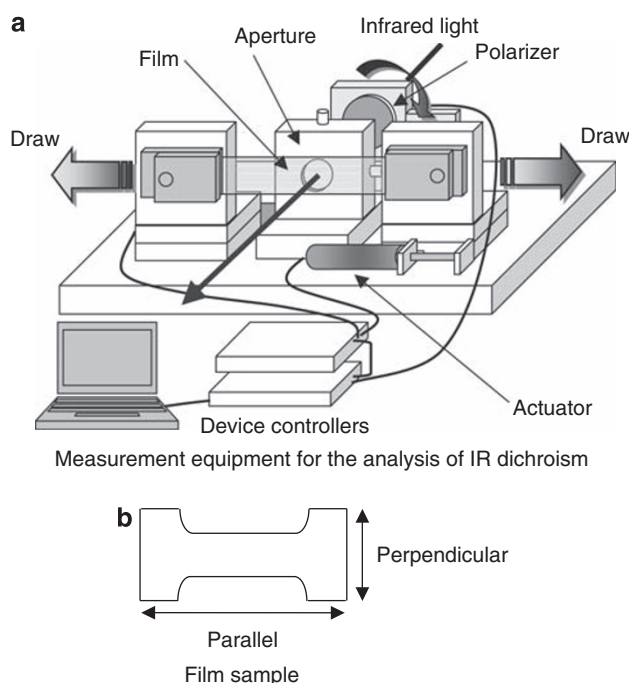


Figure 4 Schematic representation of equipment for the measurement of the IR dichroism of elastically deformed polymer films. (a) Measurement equipment for the analysis of infrared dichroism. (b) Film sample.

of 696 cm^{-1} for observing the ring out-of-plane deformation of the benzene rings of *trans*-stilbene^{21–24} in PMMA doped with *trans*-stilbene. In the case of poly(MMA-co-TSMA), we selected a wavelength of 693 cm^{-1} to observe the ring out-of-plane deformations of the monosubstituted and 1,4-disubstituted benzene rings of TSMA.^{25–27} The dichroic ratio D is defined as $D = A_{\parallel} / A_{\perp}$, where A_{\parallel} and A_{\perp} are the absorbances for linearly polarized IR light in the directions parallel and perpendicular to the drawing direction, respectively. The orientation function f is related to the dichroic ratio D by the following equation:

$$f = \frac{D - 1}{D + 2} \cdot \frac{2 \cot^2 \alpha + 2}{2 \cot^2 \alpha - 1} \quad (2)$$

where α is the angle between the transition moment vector of the absorbing group and the long axis of the molecule.^{28,29} We assumed that $\alpha = 0$, because the *trans*-stilbene is a planar rod-like molecule and the transition moment vector of the absorbing group is perpendicular to the plane of the benzene rings of *trans*-stilbene.

Other measurements

The stress–strain curves of the sample films were investigated at room temperature to confirm that they exhibited elastic behavior. The stress–strain curves of the samples were measured at a strain rate of 0.5 mm min^{-1} by using a universal tensile testing machine (Tensilon RTC-1210A, A&D Co., Ltd, Tokyo, Japan) at room temperature.

The values of the glass-transition temperature (T_g) of the purified polymers were measured by differential scanning calorimetry (DSC-60, Shimadzu Corp., Kyoto, Japan). All polymer samples were heated from room temperature to around 160°C in air, then cooled to -20°C and reheated to 160°C at a scanning rate of $10^\circ\text{C min}^{-1}$. The T_g was measured during the second heating scan.

The polarizability was calculated by means of a semi-empirical molecular orbital calculation program (SCIGRESS, Fujitsu Ltd., Kanagawa, Japan). The moderate neglect of differential overlap (MNDO Hamiltonian) was adopted with AM1.^{30,31} First, the molecular geometry was optimized, and then the electronic polarizability was calculated. The polarizability anisotropy $\Delta\alpha$ was calculated from the following equation:

$$\Delta\alpha = \alpha_{XX} - (\alpha_{YY} + \alpha_{ZZ})/2 \quad (3)$$

where α_{XX} , α_{YY} and α_{ZZ} are the polarizabilities along the X, Y and Z axes, respectively.⁷ The X, Y and Z axes are aligned to the principal axes of polarizability tensor.

RESULTS

The photoelastic coefficients and glass-transition temperatures of the polymers

Figure 5a is a plot of the photoelastic birefringence of the poly(MMA-co-TSMA) samples against the stress, and Figure 5b is a similar plot for PMMA samples doped with *trans*-stilbene. The photoelastic birefringences of poly(MMA-co-TSMA) and of PMMA doped with *trans*-stilbene decreased and shifted from the negative side to the positive side as the concentration of *trans*-stilbene moieties increased. The slope of a straight-line approximation corresponds to the photoelastic coefficient C of the samples. Figure 6 shows plots of the photoelastic coefficients of poly(MMA-co-TSMA) and of PMMA doped with *trans*-stilbene against the concentration of *trans*-stilbene moieties (mol%). We calculated the concentration of *trans*-stilbene unit that is required to eliminate the photoelastic coefficient. As Table 1 shows, the photoelastic coefficient of poly(MMA-co-TSMA) became zero on

introducing 0.8 mol% of *trans*-stilbene moieties, and that of PMMA doped with *trans*-stilbene became zero on addition of 1.7 mol% of *trans*-stilbene. The T_g of polymers of these compositions is shown in

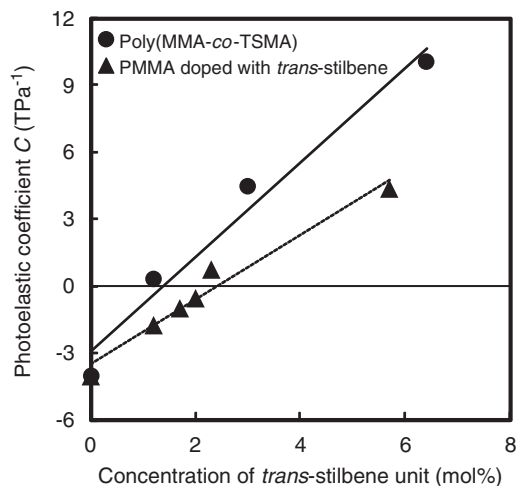


Figure 6 Plots of the photoelastic coefficients of poly(MMA-co-TSMA) and of poly(methyl methacrylate) doped with *trans*-stilbene against the concentration of *trans*-stilbene units (mol%). MMA, methyl methacrylate; TSMA, *trans*-stilben-4-yl methacrylate.

Table 1 Concentration of the *trans*-stilbene units in the PMMA doped with *trans*-stilbene and in the poly(MMA-co-TSMA) required to eliminate the birefringence, and the glass-transition temperature of each polymer sample

Polymer	Zero-birefringence composition ^a (mol%)	Glass-transition temperature (T_g) ^c C
Poly(MMA-co-TSMA)	0.8	125
PMMA+ <i>trans</i> -stilbene	1.7	84
PMMA	—	109

Abbreviations: MMA, methyl methacrylate; PMMA, poly(methyl methacrylate); TSMA, *trans*-stilben-4-yl methacrylate.

^amol%: molar ratio of *trans*-stilbene to methyl methacrylate.

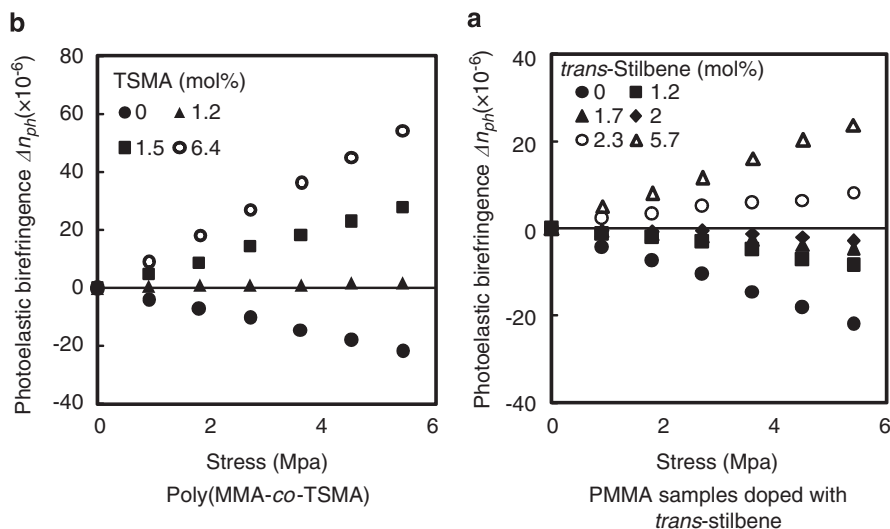


Figure 5 Plots of the photoelastic birefringence of the samples at a wavelength of 633 nm against the stress for (a) poly(MMA-co-TSMA) and (b) poly(methyl methacrylate) samples doped with *trans*-stilbene.

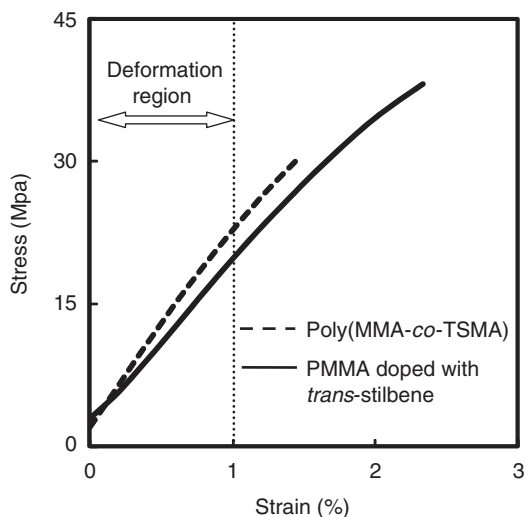


Figure 7 Stress–strain curves of films of poly(MMA-*co*-TSMA) and of poly(methyl methacrylate) doped with *trans*-stilbene. The thickness of the films was 10 μm . MMA, methyl methacrylate; TSMA, *trans*-stilben-4-yl methacrylate.

Table 1. The T_g of PMMA doped with *trans*-stilbene (1.7 mol%) was 84 $^{\circ}\text{C}$, whereas that of poly(MMA-*co*-TSMA) containing 0.8 mol% of *trans*-stilbene moieties was 125 $^{\circ}\text{C}$. These results show that the polymer that we obtained by introducing *trans*-stilbene units into the side chains by random copolymerization had a higher glass-transition temperature than the polymer that we prepared by doping with an anisotropic molecule.

Analysis of the effects of *trans*-stilbene units in compensating for photoelastic birefringence

The stress–strain curves of poly(MMA-*co*-TSMA) and PMMA doped with *trans*-stilbene films are shown in Figure 7. The thickness of the films was 10 μm in both cases. We decided to draw the films uniaxially to an elongation ratio of 1% at room temperature to analyze the IR dichroism of the films, because the deformation of each film was almost elastic when the strain was within about 1%, because of the linear curve of the film. The composition of the poly(MMA-*co*-TSMA) copolymer was analyzed by means of ^1H NMR spectroscopy, and it was found that the concentration of *trans*-stilbene units was 6.4 mol%. The composition of PMMA doped with *trans*-stilbene was similarly analyzed, and it was shown to contain 5.4 mol% of *trans*-stilbene. The IR dichroism of the poly(MMA-*co*-TSMA) film and the *trans*-stilbene-doped PMMA film were measured to investigate the motions of the molecule during the generation of photoelastic birefringence by the application of tensile stress. Figure 8 shows the absorption of the ring out-of-plane deformation of the benzene rings of *trans*-stilbene in poly(MMA-*co*-TSMA) (a) before stress loading and (b) during stress loading. The solid lines show the IR absorption spectra in the direction perpendicular to the drawing direction, and the broken lines show the absorbance of the light polarized in the parallel direction. The thickness of the sample was 12 μm . As can be seen in Figure 8a, the ring out-of-plane absorbance (693 cm^{-1}) in the parallel direction before stress loading is almost the same as that in the perpendicular direction. Figure 8b shows that the absorbance of the ring out-of-plane in the perpendicular direction during stress loading is larger than that in the parallel direction, suggesting that the benzene rings of the *trans*-stilbene were oriented in the direction perpendicular to the drawing direction during stress loading.

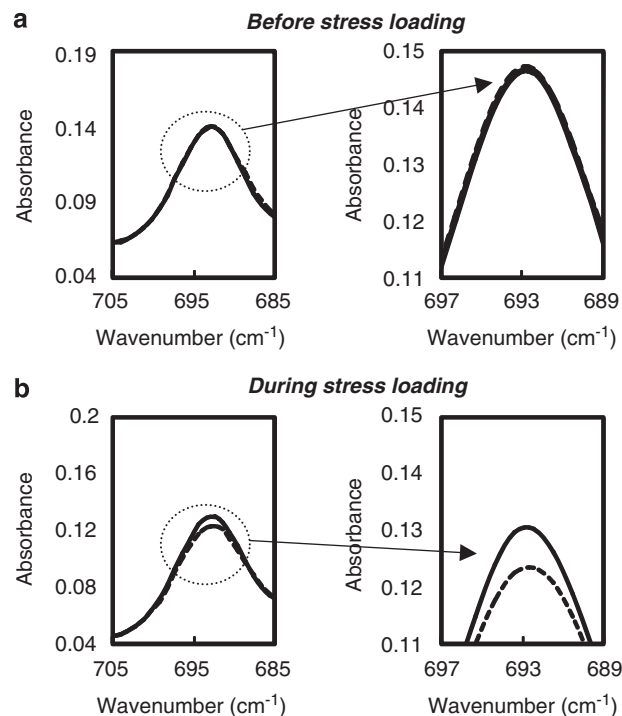


Figure 8 Infrared absorption spectra of a 12- μm -thick film of poly(MMA-*co*-TSMA) (6.4 mol% *trans*-stilbene) (a) before stress loading and (b) during stress loading. The out-of-plane deformation of the benzene ring of *trans*-stilbene was observed at 693 cm^{-1} . MMA, methyl methacrylate; TSMA, *trans*-stilben-4-yl methacrylate.

Table 2 Dichroic ratio (D) and orientation function (f) of the out-of-plane deformation of the benzene ring of *trans*-stilbene before stress loading and during stress loading. Δf is the difference between the orientation function before stress loading (f_B) and during stress loading (f_D). (a) Poly(MMA-*co*-TSMA) and (b) PMMA doped with *trans*-stilbene at a wavenumber of 696 cm^{-1}

	Before stress loading	During stress loading
(a) Poly(MMA- <i>co</i> -TSMA)		
D	1.004	0.936
f	$f_B: -0.002$	$f_D: 0.043$
$\Delta f = f_D - f_B$		0.046
(b) PMMA doped with <i>trans</i> -stilbene		
D	1.002	0.985
f	$f_B: -0.001$	$f_D: 0.010$
$\Delta f = f_D - f_B$		0.012

Abbreviations: MMA, methyl methacrylate; PMMA, poly(methyl methacrylate); TSMA, *trans*-stilben-4-yl methacrylate.

Table 2 lists the dichroic ratio D and the orientation function before stress loading (f_B) and during stress loading (f_D) of *trans*-stilbene in (a) poly(MMA-*co*-TSMA) and (b) PMMA doped with *trans*-stilbene, as calculated by using Equation (2). The value of f_B was almost zero before stress loading, showing that the *trans*-stilbene units in the undrawn film were not oriented. During stress loading, the value of f_D of the oriented film was more than zero, showing that the *trans*-stilbene units were oriented in the direction perpendicular to the draw direction. We therefore confirmed that the *trans*-stilbene units were

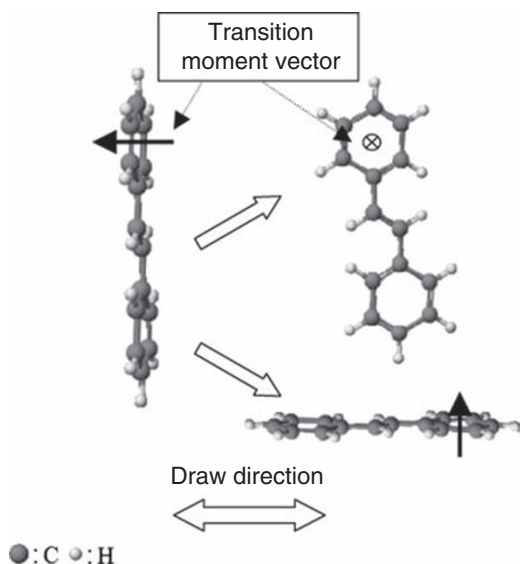


Figure 9 Estimated motion of *trans*-stilbene units in uniaxially stressed poly(methyl methacrylate).⁹

highly oriented during stress loading. As can be seen in Table 2b, the *trans*-stilbene molecules in PMMA are not oriented before stress loading and during stress loading they become oriented in the direction perpendicular to the draw direction. We have therefore confirmed that *trans*-stilbene was moved elastically by the load stress. The motion of *trans*-stilbene units in poly(MMA-*co*-TSMA) is virtually identical to that of *trans*-stilbene molecules in PMMA as described in ref. 9. The two types of motions of *trans*-stilbene unit were estimated, as shown in Figure 9. The transition moment vector is perpendicular to the benzene ring and the polarizability of the benzene ring is higher in the direction perpendicular to the transition moment vector. Both of the motions steer the transition moment vector in the direction perpendicular to the draw direction.

DISCUSSION

We found that the *trans*-stilbene moiety had an effect of 2.1 times greater in compensating for the photoelastic birefringence in poly(MMA-*co*-TSMA) than that in PMMA doped with *trans*-stilbene. The introduction of *trans*-stilbene unit into the side chains of the polymer therefore enhanced the compensatory effect in photoelastic birefringence.

In general, any factor that affects segmental mobility will affect the T_g . This includes factors that influence the nature of the moving segment, chain stiffness or steric hindrance, as well as those that affect the free volume that is available for segmental motion. As a general rule, any structural feature that reduces chain mobility or free volume will increase the T_g .³² It has been observed that the size and flexibility of side groups can alter the T_g of polymers.^{33,34} As a result, a high- T_g polymer was obtained by introducing *trans*-stilbene units into the side chain, because the *trans*-stilbene units inhibit the motions of the molecular chains and reduce chain mobility. We estimated that high- T_g polymer could be obtained by introducing anisotropic molecule having a rod-like form of a size that is similar to or larger than that of *trans*-stilbene into the side chain.

Birefringence can be formulated as the sum of the polarizability anisotropy and the orientation function of all the functional groups of a repeating unit of the polymer as follows:^{6,28}

$$\Delta n = \Delta\alpha_1 f_1 \phi_1 + \Delta\alpha_2 f_2 \phi_2 + \dots + \Delta\alpha_i f_i \phi_i. \quad (4)$$

Table 3 Polarizability anisotropies of the $\text{CH}_2=\text{O}$, CH_3OCH_3 and *trans*-stilbene calculated by using SCIGRESS

Anisotropic unit	Polarizability α (AU)			Polarizability anisotropy $\Delta\alpha$ (AU)
	α_{xx}	α_{yy}	α_{zz}	
$\text{CH}_2=\text{O}$	18.68	10.60	2.46	12.15
CH_3OCH_3	26.40	19.54	18.16	7.55
<i>trans</i> -Stilbene	260.59	142.32	20.52	179.17

Here, $\Delta\alpha_i$, f_i and ϕ_i are the polarizability anisotropy, the orientation function and the volume fraction of the i th functional group, respectively. It follows that functional groups with a high polarizability anisotropy will have a major effect on the birefringence. In poly(MMA-*co*-TSMA) and PMMA doped with *trans*-stilbene, the polarizability anisotropies of the C=O, C–O–C and *trans*-stilbene units are higher than those of other functional groups.^{6,8} The polarizability anisotropies of the C=O, C–O–C and *trans*-stilbene units were calculated by means of SCIGRESS (Table 3). However, it is difficult to calculate the polarizability anisotropy or polarizability tensor of a partial structure of molecule (C=O and C–O–C). We consider a small molecule that is roughly equivalent to the side chain structure. Actually, we used the following molecule structure; $\text{CH}_2=\text{O}$ instead of C=O bond and CH_3OCH_3 instead of C–O–C bond for calculating the polarizability anisotropy of C=O and C–O–C. Then, the polarizability anisotropy of the small molecule was calculated. The calculations are performed by using the MO-G method using the finite difference technique by SCIGRESS. In the case of *trans*-stilbene, the polarizability anisotropy of *trans*-stilbene molecule was calculated, because it is difficult to calculate the *trans*-stilbene unit in the side chain of TSMA. We calculated that the polarizability anisotropy of the *trans*-stilbene moiety is almost 17 times higher than those of the C=O and C–O–C groups. This method is not perfect for calculating the polarizability anisotropy of a side chain of molecule, but we think it is valid for comparing the polarizability anisotropy of *trans*-stilbene and those of C=O and C–O–C. Consequently, even if the volume fraction of *trans*-stilbene moiety is low, the motion of *trans*-stilbene units has a major impact on the photoelastic birefringence. Because the *trans*-stilbene unit had a 2.1 times greater effect in eliminating photoelastic birefringence in poly(MMA-*co*-TSMA) than that in PMMA doped with *trans*-stilbene, we assumed that the degree of orientation of *trans*-stilbene units in the poly(MMA-*co*-TSMA) was higher than that in PMMA doped with *trans*-stilbene. The results confirmed the hypothesis that, because the concentration of *trans*-stilbene unit in the poly(MMA/TSMA) was a maximum of 6.4 mol%, nearly all the *trans*-stilbene units are located adjacent to side chains of MMA units in a poly(MMA-*co*-TSMA) chain. We deduced that the motions of MMA units of a poly(MMA-*co*-TSMA) chain during the generation of photoelastic birefringence is similar to that in a PMMA chain, because the majority of repeating units in the poly(MMA-*co*-TSMA) chain are MMA units. Photoelastic birefringence is generated in PMMA when the side chains of the PMMA molecules are oriented and the main chain is barely oriented during stress loading.⁶ We estimated that the intramolecular interaction between the side chains of the MMA units and the *trans*-stilbene units in the poly(MMA-*co*-TSMA) is stronger than that between the PMMA chain and the *trans*-stilbene molecules in PMMA doped with *trans*-stilbene, because the *trans*-stilbene units of poly(MMA-*co*-TSMA) are thought to be closer to the main chain than are the *trans*-stilbene molecules in doped PMMA.

This discussion suggests that not only *trans*-stilbene units, but also the other anisotropic molecule structures with a rod-like form and high polarizability anisotropy, such as diphenylacetylene, *trans,trans*-1,4-diphenyl-1,3-butadiene or *trans*-chalcone⁸ units, in the side chain of the copolymer might have the same effect in compensating for photoelastic birefringence and producing a polymer with a high T_g .

CONCLUSIONS

We have demonstrated that a copolymer with zero photoelastic birefringence and a high T_g can be realized by introducing an anisotropic molecular structure with a rod-like form and a high polarizability anisotropy $\Delta\alpha$ into the side chains of the polymer.

We found that the concentration of anisotropic molecule required to compensate for photoelastic birefringence in the random copolymerization method is lower than that required in the anisotropic molecule dopant method, because an anisotropic moiety in the side chain of a copolymer has a greater effect than does an anisotropic molecule doped in the polymer. In addition, by introducing *trans*-stilbene units into the side chain of a MMA copolymer, we obtained a polymer with a higher glass-transition temperature than that of PMMA doped with *trans*-stilbene. We conclude that a polymer with a high T_g can be obtained by introducing anisotropic moieties of a size similar to *trans*-stilbene or larger into the side chain.

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- Mori, H., Itoh, Y., Nishiura, Y., Nakamura, T. & Shinagawa, Y. Performance of a novel optical compensation film based on negative birefringence of discotic compound for wide-viewing-angle twisted-nematic liquid-crystal displays. *Jpn. J. Appl. Phys.* **36**, 143–147 (1997).
- Kawamoto, H. The history of liquid-crystal displays. *Proc. IEEE* **90**, 460–500 (2002).
- Hatalis, K. M., Kanichi, J. & Summers, J. C. Flat panel display materials 2. *Mater. Res. Soc. Symp. Proc.* **424**, 295–298 (1997).
- Bernacki, E. & Mansuripur, M. Investigation of substrate birefringence effects on optical-disk performance. *Appl. Opt.* **32**, 6547–6555 (1993).
- Koike, Y., Tanio, N., Nihei, E. & Ohtsuka, Y. Gradient-index polymer materials and their optical devices. *Polym. Eng. Sci.* **29**, 1200–1204 (1989).
- Shafiee, H., Tagaya, A. & Koike, Y. Mechanism of generation of photoelastic birefringence in methacrylate polymers for optical devices. *J. Polym. Sci. Part B Polym. Phys.* **48**, 2029–2037 (2010).
- Tagaya, A., Iwata, S., Kawanami, E., Tsukahara, H. & Koike, Y. Zero-birefringence polymer by the anisotropic molecule dope method. *Appl. Opt.* **40**, 3677–3683 (2001).
- Tagaya, A., Iwata, S., Kawanami, E., Tsukahara, H. & Koike, Y. Anisotropic molecule dopant method for synthesizing a zero-birefringence polymer. *Jpn. J. Appl. Phys.* **40**, 6117–6123 (2001).
- Ohkita, H., Ishibashi, K., Tanaka, R., Tagaya, A. & Koike, Y. Compensation of photoelastic birefringence of polymers by anisotropic molecules and analysis of compensation mechanism. *Jpn. J. Appl. Phys.* **44**, 3975–3982 (2005).
- Iwata, S., Tsukahara, Y., Nihei, E. & Koike, Y. Compensation for birefringence of oriented polymers by random copolymerization method. *Jpn. J. Appl. Phys.* **35**, 3896–3901 (1996).
- Iwata, S., Tsukahara, Y., Nihei, E. & Koike, Y. Transparent zero-birefringence copolymer and its optical properties. *Appl. Opt.* **36**, 4549–4555 (1997).
- Tagaya, A., Ohkita, H., Harada, T., Ishibashi, K. & Koike, Y. Zero-birefringence optical polymers. *Macromolecules* **39**, 3019–3023 (2006).
- Tagaya, A., Harada, T. & Koike, Y. Design of zero zero-birefringence polymers for injection molded products with low birefringence. *Seikei-Kakou* **21**, 426–435 (2009).
- Ohkita, H., Abe, Y., Kojima, H., Tagaya, A. & Koike, Y. Birefringence reduction method for optical polymers by the orientation-inhibition effect of silica particles. *Appl. Phys. Lett.* **84**, 3534–3536 (2004).
- Hatano, T., Yamanaka, S. & Arakawa, K. Polarizing plate, method for producing polarizing plate, and liquid crystal display device. US Patent 2010/0220267A1 (2010).
- Brydson, J. A. *Plastic Materials* 376 (Butterworth Scientific: London, UK, 1982).
- Tsai, F.-J., Torkelson, J. M. & Lewis, F. D. Photoresponsive behavior of methyl methacrylate/*trans*-4-stilbene methacrylate statistical copolymers in solution and the solid state. *Macromolecules* **23**, 1487–1493 (1990).
- Güsten, H. & Salzwedel, M. Die kernmagnetischen resonanzspektren substituierter *trans*-stilbene. *Tetrahedron* **23**, 173–185 (1967).
- Tsukiji, M., Kowa, H., Muraki, K., Umeda, N., Imoto, K., Kanasaki, M., Tahara, K., Morii, K. & Tajitsu, Y. Measurement system for very small photoelastic constant of polymer films. *Macromol. Symp.* **242**, 235–240 (2006).
- Umeda, N. & Kohwa, H. Measurement of the residual birefringence distribution in glass laser disk by transverse zeeman laser. *Electron. Commun. Jpn.* **74**(Part 2), 21–28 (1991).
- Dirlikov, S. K. & Koenig, J. L. Assignment of the carbon-hydrogen stretching and bending vibrations of poly(methyl methacrylate) by selective deuteration. *Appl. Spectrosc.* **33**, 555–561 (1979).
- Nyquist, R. A. *Interpreting Infrared, Raman, and Nuclear Magnetic Resonance Spectra* Vol. 2, 351 (Academic Press, San Diego, CA, 2001).
- Shimanouchi, T., Kakiuti, Y. & Gamo, I. Out-of-plane CH vibrations of benzene derivatives. *J. Chem. Phys.* **25**, 1245–1251 (1956).
- Margoshes, M. & Fassel, V. A. The infrared spectra of aromatic compounds: I. The out-of-plane C-H bending vibrations in the region 625–900 cm⁻¹. *Spectrochim. Acta* **7**, 14–24 (1955).
- Socrates, G. *Infrared Characteristic Group Frequencies; Tables and Charts* 2nd edn (Wiley, Chichester, 1994).
- Higuchi, S., Tsuyama, H., Tanaka, S. & Kamada, H. Some considerations on the out-of-plane vibration bands of Ph_nX type molecules in the 800–670 cm⁻¹ region in relation to the estimation of the twist angle θ of benzene rings from their intensities. *Spectrochim. Acta* **30**(Part A), 463–477 (1974).
- Whiffen, D. H. Infra-red summation bands of the out-of-plane C-H bending vibrations of substituted benzene compounds. *Spectrochim. Acta* **7**, 253–263 (1955).
- Saito, H. & Inoue, T. Chain orientation and intrinsic anisotropy in birefringence-free polymer blends. *J. Polym. Sci. Part B Polym. Phys.* **25**, 1629–1636 (1987).
- Jasse, B. & Koenig, J. L. Orientational measurements in polymers using vibrational spectroscopy. *J. Macromol. Sci. Rev. Macromol. Chem.* **17**, 61–135 (1979).
- Healy, E. F. & Holder, A. An evaluation of AM1 calculated vibrational frequencies. *J. Mol. Struct. (Theochem)* **281**, 141–156 (1993).
- Kurtz, H. A., Stewart, J. J. P. & Dieter, K. M. Calculation of the nonlinear optical properties of molecules. *J. Comput. Chem.* **11**, 82–87 (1990).
- Turi, E. A. *Thermal Characterization of Polymeric Materials* 2nd edn, Vol. 1, 507 (Academic Press, San Diego, CA, 1997).
- Rogers, S. & Mandelkern, L. Glass transitions of the poly-(n-alkyl methacrylates). *J. Phys. Chem.* **61**, 985–991 (1957).
- Yazdani-Peddrum, M., Soto, E., Tagle, L. H., Diaz, F. R., Gargallo, L. & Radiaè, D. Effect of the side chain structure on the glass transition temperatures of some poly(thiocarbonate)s. *Thermochim. Acta* **105**, 149–160 (1986).