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NOTE

Novel Refractive Index Increase Material Based on Polystyrenes with Pendant Bicyclo Orthoester Groups upon Photoirradiation

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Introduction

Most of the thin films containing photoreactive groups show changes in the value of refractive index (n_D) after photoirradiation. Materials showing such changes can be utilized in write–read recording, switching devices, optical waveguides, memories, and holographic image recording.[1–4] The value of n_D of thin films is dependent upon density (ρ, g/cm^3), molecular weight (M), and molar refraction (R, cm^3/mol), in accordance with the Lorentz–Lorenz equation.[5]

$$n_D = \sqrt{(M+2\rho R)/(M-\rho R)} \qquad (1)$$

There are many reports on photofunctional thin films in which the value of n_D decreases after photoirradiation as a result of photochemical reactions of norbornadiene,[6–8] azobenzene,[8–10] anthracene,[8,11–13] cinnamate,[8,13,14] chalcone,[8,13,14] and nitrone.[15–20] These photoreactive groups showed changes of π-electron system after photoirradiation, with decreased R values.

On the other hand, in some cases the n_D of thin films increases after photoirradiation. Toussaere et al.[21] reported that photochemical isomerization of thiocyanate moieties resulted in Δn_D of about +0.03. Horie et al.[22] examined thin films doped with phenylazide and observed Δn_D after photoirradiation of +0.0161. Sakurai et al.[23] reported that n_D of thin film doped with *N*-acetyl-α-dehydroarylalanine naphthyl ester increased by about +0.02 after photoirradiation. Very recently, Kern et al.[24,25] recently examined the photo-Fries rearrangement of polymer and found Δn_D values in the range between +0.042 and +0.070. However, these materials released low-molecular-weight materials or gases after photoirradiation; this would present a serious problem in practical application in the optoelectronic industry.

Endo et al. reported the ring-opening polymerization of bicyclo orthoester,[26–28] spiro orthocarbonate,[29–31] and spiro orthoester[32,33] compounds and found that the volume was increased after the polymerization.[34,35] In this polymerization system, cyclic ether bonds are converted to ester bonds during the ring-opening polymerization. It is well-known that the value of molar refraction of ester groups is larger than that of ether groups. Therefore, we speculated that thin films of polymers with pendant bicyclo orthoester, spiro orthocarbonate, or spiro orthoester groups might show an increase in the value of n_D without release of any compounds after photoirradiation.

In this paper, we present a detailed study of the changes of refractive index of thin films of polystyrenes with pendant bicyclo orthoester groups upon photoirradiation.

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO) *N*,*N*-dimethylformamide (DMF), styrene (ST), and 3-chloromethyl-3-ethyloxetane were dried over with CaH_2 and purified by distillation before use. The commercial grade 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), α,α′-azobis(isobutyronitrile) (AIBN), bis({[4-(2-hydroxy) ethoxy]diphenylsulfoniophenyl} hexafluorophosphate) sulfide (sp-150), trifluoroboron ethyl ether complex ($BF_3 \cdot Et_2O$), and 2-methyl-1-(4-methylthiophenyl) -2-morpholinopropan-1-one (Irgacure 907) were used without purification. 4-Vinylbenzoic acid was synthesized according the previous method.[35]

Measurements. Infrared (IR) spectra were measured on a Thermo Electron model NICOLET 380 spectrometer. The ^{1}H NMR spectra were recorded on JEOL model JNM α-500 (500 MHz for ^{1}H NMR) instruments in DMSO-d_6 using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a Tosoh model HLC-8120 GPC equipped with refractive index and ultraviolet detectors using TSK gel columns (eluent THF, calibrated with narrow molecular weight polystyrene standards). The T_gs of the polymers were measured on a Seiko Instruments differential scanning calorimeter (DSC) model EXSTAR6000/DSC6200 at a heating rate of 10 °C/min under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analyzer (TGA) Model EXSTAR6000/TG/DTA6200 at a heating rate of 10 °C/min under nitrogen. The refractive index of thin films spin-coated at about 0.1 μm thickness on silicon wafers was measured by ellipsometry at 0.6328 μm with a Gaertener Scientific Co. model L116C ellipsometer. The rate of photochemical reaction of the bicyclo ortho ester groups was measured by real-time IR (RT-IR) spectroscopy (BIO RAD model Excalibur FTS3000MX spectrometers).

Synthesis of (3-Ethyloxetan-3-yl)methyl 4-Vinylbenzoate (EOMVB). A mixture of 4-vinylbenzoic acid (1.48 g, 10 mmol), 3-chloromethyl-3-ethyloxetane (1.68 g, 12.5 mmol), and DBU (2.24 mL, 15 mmol) in DMSO (20 mL) was stirred at 50 °C for 24 h, and then ethyl acetate (150 mL) was added. The resulting solution was washed with 1.0 N hydrogen chloride solution once, saturated aqueous sodium hydrogen carbonate solution twice, and water three times. The organic phase was dried over with $MgSO_4$ and concentrated in a rotary evaporator. The residue was purified by silica gel column chromatography eluted with ethyl acetate/*n*-hexane (volume ratio 1/1), followed by concentration to obtain a colorless oil. Yield = 1.82 g (74%). IR (KRS, cm^{-1}): 2964 and 2875 (ν CH), 1718 (ν C=O of ester), 1608 (ν C=C of aromatic), 1403 (ν C=C of vinyl group), 1272 (ν C(O)–O of ester), and 1106 (ν C–O–C of oxetane). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 0.97 (t, J = 7.0, 3H, $-CH_3$), 1.85

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(q, $J = 7.5$, 2H, $-CH_2-CH_3$), 4.45 (s, 2H, $-OCHH_2-$), 4.49 and 4.60 (AB quartet, J = 6.5, 4H, $-OCHH_2-$ of oxetane), 5.39 (d, J = 10.0, 1H, H$-CH$=CH$-$), 5.87 (d, J = 17.5, 1H, H$-CH$=CH$-$), 6.76 (dd, J = 17.0, 11.0, 1H, CH_2=CH$-$), 7.47 (d, J = 8.0, 2H, aromatic H), 8.10 (d, J = 8.5, 2H, aromatic H). ^{13}C NMR (500 MHz, $CDCl_3$, TMS): 7.98 (CH_3), 36.34 ($-CH_2-$), 54.82 (quaternary C), 66.57 ($-O-CH_2-$ of ester), 76.60 ($-CH_2-$ of oxetane), 117.22 ($-CH=CH_2$), 126.34−141.81 (aromatic C and $-CH=CH_2$), 165.44 (⟩C=O).

Synthesis of 4-Ethyl-1-(4-vinylbenzoyl)-2,6,7-trioxabicyclo-[2.2.2]octane (BOES). The mixture of EOMVB (7.38 g, 30 mmol) and $BF_3\cdot Et_2O$ (0.426 g, 3.0 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h, and then triethylamine (0.5 mL, 3.6 mmol) was added. Ethyl ether was added to the resulting mixture and washed with water three times. The organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator to obtain a white solid. This product was purified by recrystallization from ethyl ether to give a while solid (BOES). Yield = 4.77 g (65%); melting point (mp) = 125−126 °C. IR (KRS, cm^{-1}): 2974 and 2887 (ν CH), 1629 (ν C=C of aromatic), 1461 (ν C=C of vinyl), 1335 and 1098 (ν C−O−C of cyclic ether). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): 0.80 (t, $J = 8.0$, 3H, $-CH_3$), 1.27 (q, $J = 8.0$, 2H, $-CH_2-CH_3$), 4.02 (s, 6H, $-OCHH_2-$), 5.29 (d, J = 11.0, 1H, H$-CH$=CH$-$), 5.85 (d, J = 17.0, 1H, H$-CH$=CH$-$), 6.73 (dd, J= 17.0, 11.0, 1H, CH_2=CH$-$), 7.47 (s, 4H, aromatic H). ^{13}C NMR (500 MHz, DMSO-d_6, TMS): 7.38 (CH_3), 21.61 ($-CH_2-$), 32.77 (quaternary C), 70.89 ($-O-CH_2-$), 106.74 ($-CH=CH_2$), 115.02 ($-C(O-)_3-$), 125.53−136.18 (aromatic C and $-CH=CH_2$). Anal. Calcd for $C_{15}H_{18}O_3$: C 73.15, H 7.37. Found: C 73.11, H 7.42.

Radical Polymerization of BOES. *Typical Procedure*. BOES (0.492 g, 2.0 mmol), AIBN (0.01 g, 3 mol %), and solvent (2.0 mL) were charged into a polymerization tube. The tube was cooled, degassed, sealed off, and heated at 60 °C for 20 h, and then tetrahydrofuran (2.0 mL) was added. The resulting mixture was poured into a large amount of ethyl ether to precipitate a polymer. The polymer was isolated by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45 μm) and then dried *in vacuo* at room temperature for 12 h. Yield = 0.39 g (79%). M_n = 6600, M_w/M_n = 1.37. IR (KRS, cm^{-1}): 2926 and 2877 (ν CH), 1616 (ν C=C of aromatic), 1340 and 1100 (ν C−O−C of cyclic ether). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 0.86 (broad s, 3H, $-CH_3$), 1.27 (broad s, 4H, $-CH_2-CH_3 + -CH_2-$CH⟨), 3.61 (broad s, 1H, $-CH_2-CH$⟨), 4.05 (broad s, 6H, $-OCHH_2-$), 6.64 and 7.43 (broad s, 4H, aromatic H).

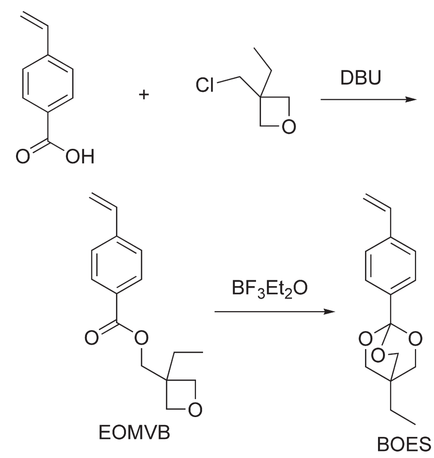
Photochemical Reaction of Thin Films of Polymers with Pendant BOES Groups. A typical procedure for the photochemical reaction is as follows: A solution of a polymer (19 mg) and SP-150 (1 mg) as a photoacid generator in $CHCl_3$ (1.0 mL) was cast on a KBr plate and dried *in vacuo* at room temperature to obtain a film. The resulting film was irradiated with a 250 W high-pressure mercury lamp (6.0 mW/cm^2 at 254 nm) through a monochromator (Jasco model CT-10). The decrease of the peak at 1100 cm^{-1} assignable to cyclic ether was followed with an RT-IR spectrophotometer.

Refractive Index (n_D) Change of CD Derivatives upon Photoirradiation. $CHCl_3$ solutions of polymers and SP-150 were prepared and spin-coated on a silicon wafer and then dried *in vacuo* at room temperature. The n_D's of the thin films (about 0.1 μm thick) before and after photoirradiation were determined by ellipsometry.

Results and Discussion

Synthesis of Monomer Containing Bicyclo Orthoester Groups. The styrene derivative containing the oxetanyl group (3-ethyloxetan-3-yl)methyl 4-vinylbenzoate (EOMVB) was synthesized by the reaction of 4-vinylbenzoic acid and 3-chloromethyl-3-ethyloxetane, using DBU in NMP. The cationic isomerization of EOMVB in the presence of boron trifluoride ethyl ether as a catalyst in CH_2Cl_2 was examined with reference to previous reports[37-40] and afforded the corresponding 4-ethyl-1-(4-vinylbenzoyl)-2,6,7-trioxabicyclo[2.2.2]octane (BOES) (Scheme 1). The structure of BOES was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy as well as elemental analysis.

Scheme 1



Synthesis of Polymers with Pendant Bicyclo Orthoester Groups. The radical polymerization of BOES was carried out, using AIBN as an initiator in DMF at 60 °C for 20 h, to afford a polymer with M_n = 12 000, M_w/M_n = 1.96 in 73% yield. The obtained polymer was partly insoluble in common organic solvents. Its structure was confirmed by IR spectroscopy (Figure 1). New peaks at 3500 and 1714 cm^{-1} were assignable to hydroxyl groups and carbonyl groups, respectively (Figure 1B). This means that ring-opening reaction of the bicyclo orthoester moiety occurred to form ester groups as cross-linking bonds, at least in part, during the radical polymerization, as shown in Scheme 2. When this radical polymerization was carried out for 3 h, a polymer was obtained in 18% yield and was confirmed by IR spectroscopy to contain cross-links.

Next, this radical polymerization was examined in toluene by the same method to afford the corresponding polymer with M_n = 6600 and M_w/M_n = 1.37 in 79% yield. Its structure was confirmed by ^{1}H NMR and IR spectroscopy. Figure 2 depicts the ^{1}H NMR spectrum of the obtained polymer along with that of BOES. The spectrum of the polymer shows the signals of methylene protons and methine protons, which were produced by the radical polymerization of BOES, at 0.86−1.27 ppm. IR spectroscopy also showed that the radical polymerization proceeded without ring-opening of the bicyclo orthoester groups (Figure 1C). Consequently, the polymer with pendant bicyclo orthoester groups [poly(BOES)] was successfully synthesized in high yield. A small amount of water in DMF might have caused ring-opening reaction of the bicyclo ortho ester moieties, and therefore toluene is a more appropriate medium for the radical polymerization of BOES.

The radical copolymerization of BOES and ST was also carried out by the same method in toluene to afford the corresponding copolymers poly(BOES$_m$-*co*-ST$_n$) (m:n = 69:31, 51:49, and 32:68) with M_n = 7300−9600, M_w/M_n = 1.48−1.64 in 58−72% yields. These results are summarized in Table 1. It was observed that yields of copolymers poly(BOES$_m$-*co*-ST$_n$) decreased with increasing comonomer composition ratios of ST. This result might be cause from that the solubility of poly(BOES$_m$-*co*-ST$_n$) were good in common organic solvents. We examined certain organic solvents to separate the synthesized copolymers. As the result, *n*-hexane is most suitable medium to precipitate the polymers.

The thermal properties of the obtained polymers were determined by DSC and TGA: $T_g = 158-225$ °C, $T_d^{i} = 271-284$ °C, $T_d^{5\%} = 328-345$ °C, and $T_d^{10\%} = 352-371$ °C (Table 1). It was found that poly(BOES$_m$-*co*-ST$_n$)] had high thermal stability, and their T_g's increased with increasing unit ratio of BOES, presumably due to the bulky structure of BOES.

Photochemical Ring-Opening Reaction of Thin Films of Poly(BOES) and Poly(BOES$_m$-*co*-ST$_n$). The photochemical reaction of thin films of poly(BOES) and poly(BOES$_m$-*co*-ST$_n$) was examined using SP-150 as a photocationic initiator. Solutions of polymers in chloroform were coated on KBr plates and dried *in vacuo* at room temperature for 12 h. The resulting thin films were irradiated with a 250 W high-pressure mercury lamp. Figure 1C,D illustrates the IR spectra of the thin films before and after photoirradiation. Before the photoirradiation, a peak at around 1100 cm^{-1} was assignable to stretching vibration of cyclic ether groups of bicyclo ortho ester groups. After photoirradiation, two new

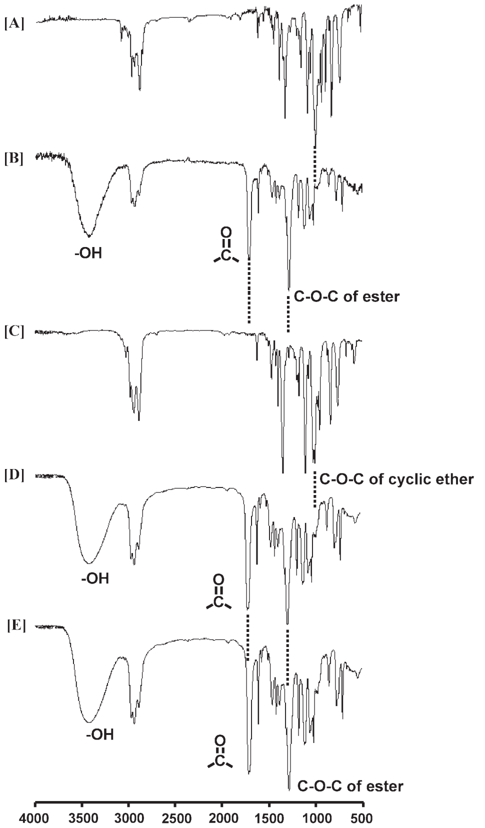


Figure 1. IR spectra of BOES, poly(BOES), and poly(BOES)cured: (A) BOES; (B) poly(BOES) obtained by the radical polymerization in DMF; (C) poly(BOES) obtained by the radical polymerization in toluene; (D) cured thin film obtained by the photoirradiation of poly(BOES) in the presence of PAG; (E) cured thin film obtained by the photoirradiation of poly(BOES) without PAG.

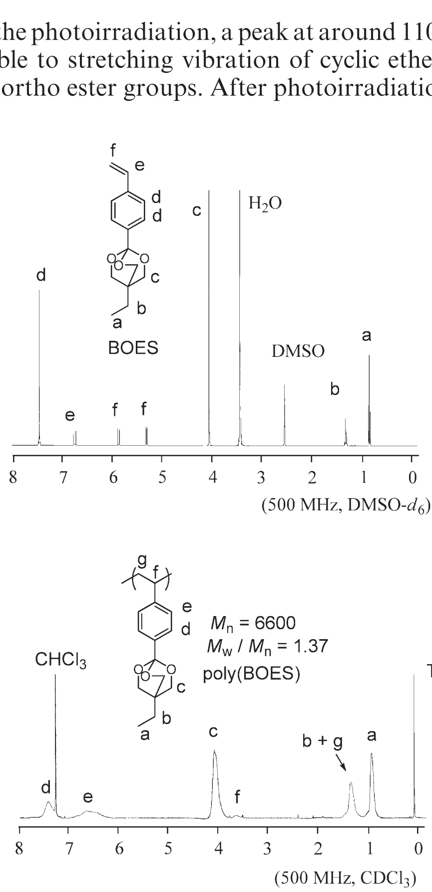


Figure 2. ^{1}H NMR spectra of BOES (500 MHz, DMSO-d_6) and poly(BOES) (M_n=6600, M_w/M_n=1.37, run 1 in Table 1) (500 MHz, CDCl$_3$).

Scheme 2

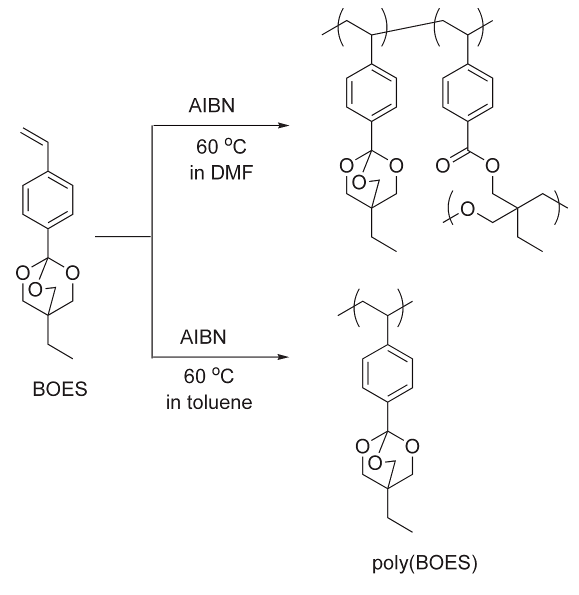
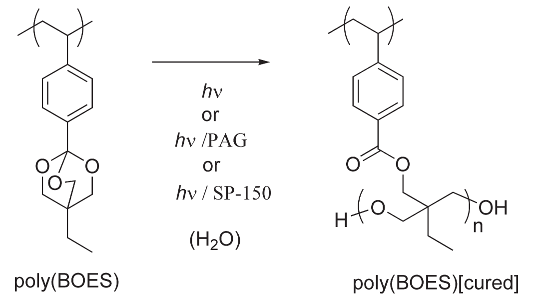


Table 1. Radical Copolymerization of BOES and ST^a

feed molar ratio BOES/ST	yield (%)	copolymer composition^d BOES/ST	M_n^e	M_w/M_n^e	T_g^f (°C)	$T_d^{i\,g}$ (°C)	$T_d^{5\%\,g}$ (°C)	$T_d^{10\%\,g}$ (°C)
100/0	79^b	100/0	6600	1.37	225	271	345	371
70/30	72^c	69/31	9600	1.64	215	273	328	356
50/50	68^c	51/49	9400	1.48	195	279	328	352
30/70	58^c	32/68	7300	1.58	158	284	334	360

[a] Conditions: total monomer = 1 mmol, initiator AIBN (3 mol %), in toluene (1.0 mL), 60 °C, for 20 h. [b] Insoluble part in ethyl ether. [c] Insoluble part in *n*-hexane. [d] Determined by ^{1}H NMR. [e] Estimated by GPC based on polystyrene standards in THF. [f] Measured by DSC. [g] Measured by TGA.

Scheme 3



broad peaks appeared around at 3500 and 1700 cm^{-1}, which were assignable to the stretching vibration of hydroxyl groups and carbonyl groups, respectively. This result shows that ester groups were produced by the ring-opening cationic polymerization of bicyclo ortho ester groups and the hydroxyl groups by the termination reaction of the ring-opening cationic polymerization, as shown in Scheme 3. The resulting thin film was insoluble in common organic solvents.

Furthermore, we examined the photoirradiation of thin films of poly(BOES) without PAG; again, the resulting film became insoluble in common organic solvents. Figure 1E depicts the IR spectra of the resulting thin film; this shows new peaks at 3500 and 1700 cm^{-1} in the same way as for the thin film including PAG. This means that ring-opening polymerization of bicyclo ortho ester groups occurred without PAG under photoirradiation. In this photochemical reaction of the thin film without PAG, the radical species might be produced as an intermediate. Thin film of poly(BOES) containing Irgacure907 as a photoradical initiator was prepared, and the effect of photoirradiation was examined. The same ring-opening polymerization proceeded to give the corresponding cross-linking film.

Next, the time course of the ring-opening reaction of thin films of poly(BOES) was examined by means of RT-IR spectroscopy (Figure 3). When thin film containing PAG was photoirradiated, the conversion reached 84% after 15 min. In the case of the thin films containing Irgacure907, the reaction reached 83% conversion after 45 min. This indicates that Irgacure907 might act as a photosensitizer.

However, the photochemical reaction occurred slowly in the case of thin films without PAG, and the conversion reached only 60% after 60 min. That is, ester groups of the cross-linking bonds are produced more smoothly in the film containing PAG, although the ring-opening polymerization of BOES groups proceeded without any additive and PAG.

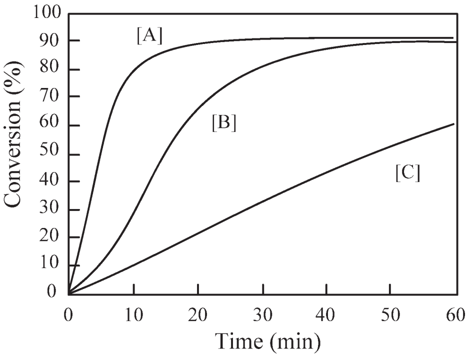


Figure 3. Time course of the ring-opening reaction of thin films of poly(BOES). (A) Thin film of poly(BOES) including SP-150. (B) Thin film of poly(BOES) including Irgacure 907. (C) Thin film of poly(BOES) without PAG or photoradical initiator.

Table 2. Refractive Index Properties of Thin Films of Polymers[a]

run	thin film	n_{Db}[b]	n_{Da}[c]	Δn_D[d]
1	poly(BOES)	1.573	1.587	+0.014
2	poly(BOES) + Irgacure907	1.556	1.570	+0.014
3	poly(BOES) + PAG	1.585	1.608	+0.023
4	poly(BOES$_{69}$-*co*-ST$_{31}$) + PAG	1.553	1.571	+0.018
5	poly(BOES$_{51}$-*co*-ST$_{49}$) + PAG	1.557	1.573	+0.016
6	poly(BOES$_{32}$-*co*-ST$_{68}$) + PAG	1.566	1.577	+0.011

[a] Thin film was irradiated for 30 min. [b] n_{Db}: refractive index before photoirradiation. [c] n_{Da}: refractive index after photoirradiation. [d] $\Delta n_D = n_{Da} - n_{Db}$.

Refractive Index Characteristics of Thin Films of Poly(BOES) and Poly(BOES$_m$-*co*-ST$_n$). Thin films (0.1 μm) were prepared on silicon wafers by spin-coating of polymer solution, and the n_D's were measured by ellipsometry before and after photoirradiation. The values of n_{Db} (refractive index before photoirradiation), n_{Da} (refractive index after 30 min of photoirradiation), and Δn_D (the change of refractive index) are summarized in Table 2. When the film was prepared without photoradical initiator or PAG, Δn_D showed was +0.014 after photoirradiation for 45 min (run 1 in Table 2). In the case of thin films containing Irgacure907, Δn_D was +0.014 after 60 min of photoirradiation (run 2 in Table 2). Although the conversion of BOE moieties of thin film with Irgacure907 was higher than that of the film without any additive, the values of Δn_D's were the same. This might indicate that some effect might cause from Irgacure907 to decrease the n_D by the photoirradiation, i.e., the total value of Δn_D might become the same. Furthermore, we examined the refractive index change of the thin films containing PAG, and it was observed that Δn_D increased to +0.023 (run 3 in Table 2). In the same way, thin films of poly(BOES$_m$-*co*-ST$_n$) showed Δn_D values in the range between 0.011 and 0.018 (runs 4−6 in Table 2).

According to the Lorentz−Lorenz equation,[5] the values of Δn_D are dependent on the changes of molar refraction (R) and density (ρ) upon photoirradiation. In the case of the thin films of poly(BOES) and poly(BOES$_m$-*co*-ST$_n$), the value of R is increased by the change from ether bond to ester bond as a result of the ring-opening polymerization. However, the value of ρ should decrease because the volume of bicyclo ortho ester groups was increased, as mentioned in the Introduction.[34,35] The overall effect of these two factors caused the n_D's to increase without volume shrinkage upon photoirradiation.

In summary, thin films of polymer with pendant bicyclo ortho ester groups were prepared, and their photochemical reaction and refractive index changes were examined. Radical polymerization of the monomer containing bicyclo ortho ester groups (BOES) was carried out in toluene at 60 °C for 20 h to afford the corresponding polymer poly(BOES) in satisfactory yield. Similarly, radical copolymerization of BOES and ST gave the corresponding copolymers, poly(BOES$_m$-*co*-ST$_n$). When thin films of poly(BOES) and poly(BOES$_m$-*co*-ST$_n$) containing photoacid generator were photoirradiated, cationic ring-opening polymerization proceeded smoothly to give the corresponding cross-linked films quantitatively. The refractive index (n_D) increased by between +0.011 and +0.023 upon photoirradiation. Thin films of other polymers containing spiro orthocarbonate and spiro orthoester groups are under investigation as candidates for novel materials showing a refractive index increase upon photoirradiation.

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