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Hyperpolarizabilities and Second Harmonic Generation of Side-Chain Polymer Liquid Crystals Possessing Alkylsulfone-Substituted Stilbene and Azobenzene Chromophores

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Side-chain polymer liquid crystals that possess mesogenic donor-π-acceptor chromophores (azobenzene and stilbene derivatives) were synthesized, and the efficiencies of second harmonic generation (SHG) were investigated. SHG susceptibility was found to be stabilized in liquid crystalline polymers. Hyperpolarizabilities (β) of chromophores of the polymers were also investigated by the hyper Rayleigh scattering method, and it was found that the β value of the polymers was nearly twice of that of the corresponding monomers. The magnitude of the β of polymers was affected by the length of the spacer unit that connects the chromophore (mesogen) to the polymer main chain.

Keywords: Polymer liquid crystal; nonlinear optical effect; second harmonic generation; hyperpolarizability

INTRODUCTION

Photonics is a technology in which photons are utilized in place of electrons in electronics. This has stimulated studies on nonlinear optical (NLO)

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materials. Many NLO polymers, especially the second harmonic generation (SHG) polymers, have been reported [1–4]; however, none of them has been put into practical use because of the instability of the SHG efficiency [1]. The instability of the SHG efficiency of polymer films comes predominantly from the thermodynamic relaxation of the alignment of NLO chromophores [5]. In order to stabilize the alignment of chromophores, the films are often cured by crosslinking. However, the crosslinking reaction itself disturbs the alignment of the chromophores. Thus, materials in which the alignment of chromophores is thermodynamically stable are required.

In liquid crystals, rod-shaped units like stilbene or azobenzene are aligned into a specific direction spontaneously; this is considered to be advantageous for improving the stability of the ordered structure of NLO chromophores. The structures of stilbenes and azobenzenes are suitable for both the NLO chromophore and liquid crystalline unit (mesogen). Several studies on the SHG properties of liquid crystalline polymers have been reported [6–9]. It was reported that the SHG susceptibility was enhanced in the liquid crystalline phase [7]. However, the liquid crystalline SHG chromophores used in the previous work were nitrated or cyanidated biphenyl and stilbene, so that the molecular design was somewhat restricted. In this study, side-chain polymer liquid crystals possessing stilbene and azobenzene chromophores with a sulfone substituent were synthesized and their SHG properties were investigated. The characteristic of these polymers is that they can possess flexible chains at the both ends of the chromophore. That structure is considered to be advantageous for the stabilization of the alignment of the chromophores.

EXPERIMENTAL

Preparation of Samples

The SHG polymers used in this study are shown in Figure 1. Stilbene and azobenzene with a sulfone substituent are incorporated as NLO mesogens with different spacer chain lengths. The monomers were synthesized according to Scheme 1. The stilbene derivatives were synthesized via the Wittig reaction of a phosphonium salt of 4-alkylsulfonylbenzylbromide with 4-alkoxybenzaldehyde, and the azobenzene derivatives were synthesized by diazo coupling of 4-alkylsulfonylaniline with phenol. Synthesis of a stilbene type monomer is described elsewhere [10–13]. Synthesis of 4-(acryloyloxyoctyloxy)-4′-propylsulfonyl azobenzene (monomer AZO8-2) is described below as a representative case for the azobenzene monomers.

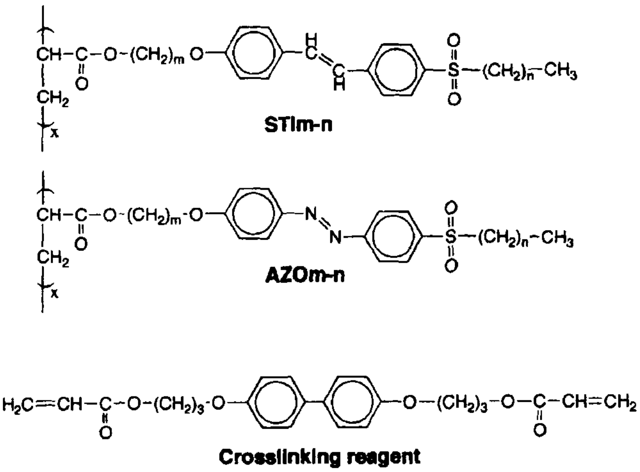
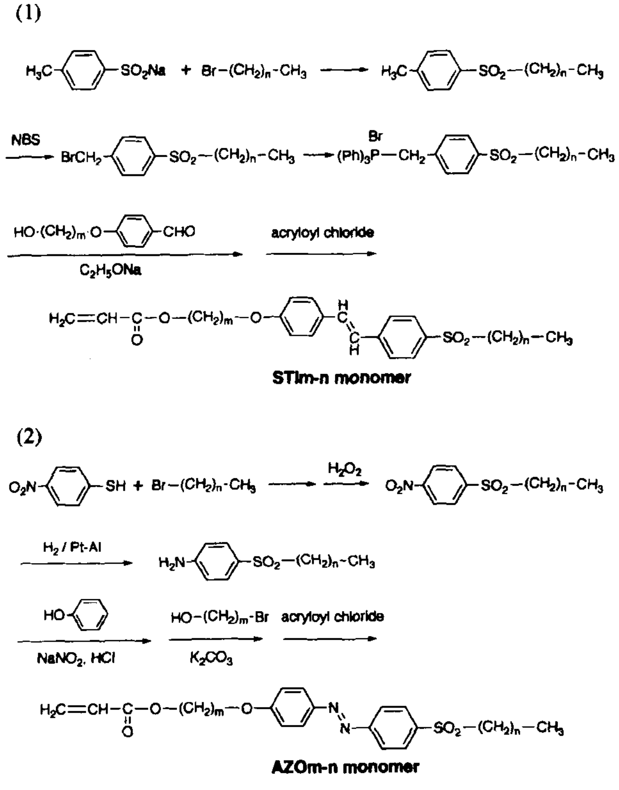


FIGURE 1 Structures of polymers used in this study.



SCHEME 1

Synthesis of Azobenzene Type Monomer AZO8-2

1) 4-Propylsulfonyl nitrobenzene

4-Nitrothiophenol (25 g, 0.16 mol) and 1-bromopropane (22 g, 0.18 mol) were dissolved in 200 mL of *N*,*N*-dimethylformamide (DMF), and 0.5 g of potassium iodide and 40 g of potassium carbonate were added. The mixture was stirred vigorously at 60°C for 3 h. After the solution was cooled to ambient temperature, 400 mL of water was added to the solution, and the sulfide was extracted with diethylether. After the diethylether solution was dried over sodium sulfoxide, the solvent was evaporated and resulting solid was dissolved in 400 mL of methanol. Sodium tungstate dihydrate ($Na_2WO_4 \cdot H_2O$, 0.6 g) in 30 mL of water was added to the solution. The solution was stirred and heated to 40°C, and 50 mL of 30% H_2O_2 was added dropwise over 2 h. The solution was then heated to 80°C, 25 mL of H_2O_2 was added and the mixture was refluxed for 2 h. The solution was cooled to ambient temperature and slightly yellow crystals were obtained by filtration. The product was purified by recrystallization from methanol-water (3:1). Yield 61%. mp 111–112°C; ^{1}H NMR ($CDCl_3$) δ 0.97 (*t*, CH_3), 1.71 (*m*, CH_2), 3.44 (*t*, SO_2CH_2), 8.17 and 8.46 (AA'BB', 4H). Anal. Calcd. for $C_9H_{11}O_4NS$ (229.26): C, 47.15; H, 4.84. Found: C, 47.15; H, 4.87.

2) 4-Propylsulfonyl aminobenzene

4-Propylsulfonyl nitrobenzene (15 g 0.065 mol) was dissolved in 300 mL of methanol, and 1.0 g of Pt–Al catalyst (5% Pt on alumina) was suspended under N_2 atmosphere. The flask was flashed with hydrogen and stirred at ambient temperature for 48 h. After the Pt–Al was removed by filtration, the solvent was evaporated and the product was purified by column chromatography on silica gel (eluent, dichloromethane). Yield 77%. mp 80–81°C; ^{1}HNMR ($CDCl_3$) δ 0.97 (*t*, CH_3), 1.71 (*m*, CH_2), 3.01 (*t*, SO_2CH_2), 4.32 (*s*, BH_2), 6.69 and 7.62 (AA'BB', 4H).

3) 4-Hydroxy-4'-propylsulfonyl azobenzene

4-Propylsulfonyl aminobenzene (10 g, 0.050 mol) was dissolved in 200 mL of a 1:1 mixture of acetone and 1N HCl. The solution was cooled to 0°C and 3.8 g (0.055 mol) of sodium nitrite in 100 mL of water was added slowly. The resulting diazonium solution was added dropwise to an aqueous solution of phenol (4.7 g, 0.050 mol) and sodium hydroxide (4.0 g, 0.10 mol) at 0°C. After stirring for 2 h, the solution was brought to ambient temperature and neutralized with HCl, and the resulting precipitate was collected by filtration. The product was purified by column chromatography on silica gel (eluent, dichloromethane). Yield 68%. ^{1}H NMR ($CDCl_3$) δ 0.97 (*t*, CH_3), 1.71 (*m*, CH_2), 3.01 (*t*, SO_2CH_2), 5.77 (*s*, OH), 7.01 and 7.93 (AA'BB', 4H), 0.83 (AA'BB', 4H).

4) 4-(8-Hydroxyoctyloxy)-4'-propylsulfonyl azobenzene

4-Hydroxy-4'-propylsulfonyl azobenzene (5.0 g, 0.016 mol) and 3.5 g (0.017 mol) of 8-bromooctanol were dissolved in 100 mL of DMSO, and 10 g of sodium carbonate was added and the mixture was vigorously stirred at 60°C for 32 h. The solution was poured into 500 mL of water, and the resulting precipitate was collected by filtration. The product was purified by column chromatography on silica gel (eluent, dichloromethane), followed by recrystallization from methanol. Yield 72%. mp 116–117°C; ^{1}H NMR ($CDCl_3$) δ 1.01 (*t*, CH_3), 1.20–1.90 (*m*, CH_2, 14H), 3.11 (*t*, SO_2CH_2), 3.67 (*t*, CH_2OH), 4.15 (*t*, OCH_2), 7.01 and 7.94 (AA'BB', 4H), 8.03 (AA'BB', 4H).

5) 4-(Acryloyloxyoctyloxy)-4'-propylsulfonyl azobenzene (AZO8-2 monomer)

4-(8-Hydroxyoctyloxy)-4'-propylsulfonyl azobenze (5.0 g, 0.012 mol) and 3 mL of pyridine were dissolved in 100 mL of dichloromethane; 1.26 g (0.014 mol) of acrylic chloride in 50 mL of dichloromethane was added dropwise and stirred for 12 h. The solution was washed with aqueous solution of saturated sodium bicarbonate and dried over sodium sulfate. After the solvent was evaporated, the product was purified by column chromatography on silica gel (eluent, dichloromethane), followed by recrystallization from 2-propanol. Yield 52%. mp 95–96°C; ^{1}H NMR ($CDCl_3$) δ 1.01 (*t*, CH_3), 1.20–1.90 (*m*, CH_2, 14H), 3.11 (*t*, SO_2CH_2), 4.05 and 4.15 (*t*, OCH_2), 5.60–6.43 ($CH_2=CH$), 7.01 and 7.94 (AA'BB', 4H), 8.03 (AA'BB', H). Anal. Calcd. for $C_{26}H_{34}O_5N_2S$ (486.63): C, 64.17; H, 7.04. Found: C, 64.15; H, 7.05.

Polymerization

Thermal radical polymerization of STI*m*-*n* and AZO*m*-*n* was carried out in a 10 wt% benzene solution with azobis (isobutylonitrile) (AIBN, 3 mol%) as an initiator. All solutions were degassed by a freeze-pump-thaw cycle and heated at 70°C for 20 h. The resulting polymers were purified by repeated reprecipitations from chloroform solution into methanol.

Measurements

NMR spectra were obtained with a Bruker MSL300 spectrometer. Number average molecular weights (Mn) of the polymers were determined by gel permeation chromatography (GPC; Toyo Soda HLC-802A, column, G5000H6 + G4000H8 + G3000H8; eluent, tetrahydrofuran); glass transition temperatures (Tg) and phase transition temperatures were determined by a differential scanning calorimeter (DSC; Rigaku 8240B) and by microscopic observation (Olympus BH2 polarizing microscope with thermocontroller), respectively. Sample films for the observation of liquid crystalline behavior were prepared by casting of the chloroform solutions of each polymer onto glass plates. After drying at room temperature, the samples were heated in vacuo at 60°C for several hours and annealed at 90°C. UV/vis spectra were measured with a Hitachi U-3500 spectrophotomer.

The hyperpolarizabilities of polymers were evaluated by the hyper Rayleigh scattering (HRS) method [14–16]. By the HRS method, the magnitude of β is measured without application of high voltage (alignment of chromophores is not necessary in this method). Thus, the β value of polymers is evaluated without considering the mobility of the chromophores. Figure 2 shows the experimental setup for the measurement of hyper

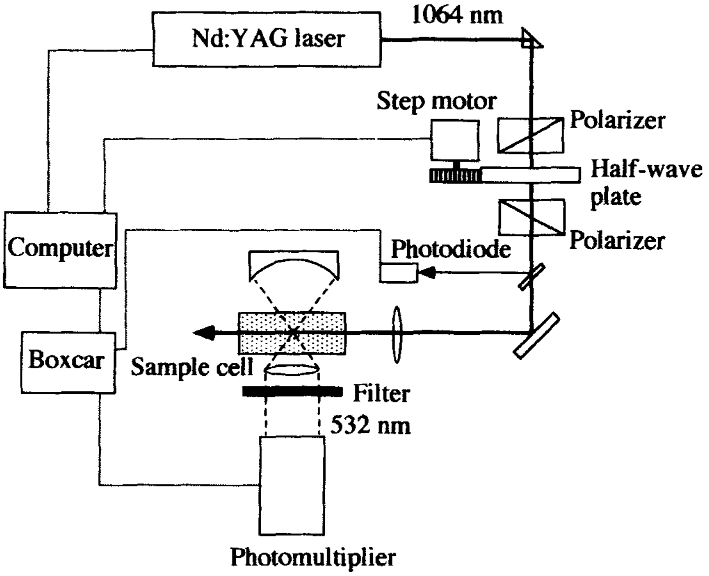


FIGURE 2 Schematic illustration of experimental set-up used for the measurement of hyper Rayleigh scattering.

Rayleigh scattering. The 1064 nm pulse from a Nd: YAG laser (Spectron HL-21; pulse width, 6 ns fwhm) was irradiated on a chloroform solution of the sample, and the scattered 532 nm light (hyper Rayleigh scattered light) intensity was monitored by a photomultiplier. The 532 nm scattered light intensity ($I_{2\omega}$) was measured as a function of the intensity of the incident 1064 nm beam (I_ω). The I_ω vs. $I_{2\omega}$ plot was fitted with $I_{2\omega} = A \cdot I_\omega{}^2$. The factor A was plotted against the concentration (cm^{-3}) of the chromophores (N_1) and fitted with $A = a \cdot N_1 + b$. The hyperpolarizability β was then obtained by the following equation [15]

$$|\beta_1| = |\beta_2| \cdot \sqrt{a \cdot N_2 / b}$$

where N_2 is the concentration of the solvent, and β_1 and β_2 are the hyperpolarizabilities of the solute and the solvent, respectively. $|\beta_2| = 0.492 \times 10^{-30}$ esu was adopted for the value of chloroform [15].

SHG measurements were performed on the sample films. A chloroform solution of the polymer (10 wt%) was spin-coated on an ITO-glass substrate and dried to form a thin film (0.3–0.7 μm thickness). The film was exposed to a high voltage using a wire corona electrode (13 kV at the needle point) for 10 minutes at 3–5°C higher than the glass transition temperature. The film was then simultaneously cooled to ambient temperature. SHG intensities were measured by the Maker fringe method (Tokyo Instruments NL-100 nonlinear optics evaluation system). The 1064 nm Nd:YAG laser was used as a fundamental source. The sample film was rotated by a step motor which was controlled by a computer. The generated 532 nm signals were detected by a photomultiplier and integrated with a boxcar averager.

RESULTS AND DISCUSSION

Properties of Polymers

The absorption spectra of the monomers are shown in Figure 3. The absorption maxima of the STI*m*-*n* were around 350 nm and they have no absorbance at 532 nm, which is the second harmonic wavelength of the fundamental laser used in this study. Thus, there was no need to consider the effects of absorption and fluorescence in the SHG measurements. On the other hand, the absorption maxima of AZO*m*-*n* were around 430 nm, and they slightly absorbed 532 nm light so that the SHG intensity of AZO*m*-*n* would be resonantly enhanced under the experimental conditions.

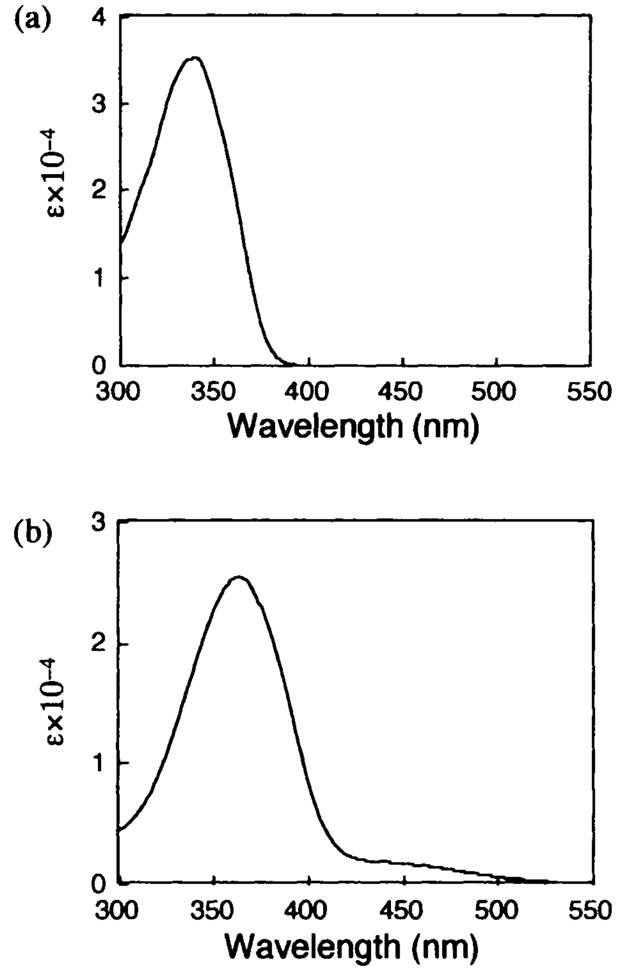


FIGURE 3 Absorption spectra of STI10-5 monomer (a) and AZO8-2 monomer (b) in chloroform.

Liquid crystalline behavior was observed under a polarizing microscope. Some of the monomers and the polymers showed a liquid crystal phase. The phase transition temperatures are listed in Tables I and II. It was found that the azobenzene monomers were more likely to form a liquid crystal phase compared to the stilbene monomers. Among the polymers, AZO8-2 exhibited the stablest liquid crystal phase. Schlieren texture was observed in this polymer, and the phase transition entropy was determined to be 6.66 J/mol/K by DSC. The phase was attributed to a nematic phase. However, in STI10-5, birefringence was observed only partially. The longer spacer

TABLE I Thermodynamic Properties of Monomers and Polymers of STI*m*-*n*

m	*n*	*phase transition temperature of monomer (°C)*[a]					*phase transition temperature of polymer (°C)*[a]					*Mn*	*Mw*/*Mn*	ΔH_{SI} (*kJ/mol*)	ΔS_{SI} (*J/molK*)
10	5	*C*	110	*Sm*	120	*I*	*g*	47	*N*[b]	124	*I*	7000	2.1	0.14	0.35
9	5	*C*	110	*I*			*g*	52	*I*			10000	2.5		
8	5	*C*	104	*I*			*g*	55	*I*			10000	2.5		
7	5	*C*	104	*I*			*g*	59	*I*			19000	3.5		
6	5	*C*	100	*I*			*g*	61	*I*			18000	8.2		
10	3	*C*	106	*I*			*g*	58	*I*			8000	1.7		
8	4	*C*	90	*I*			*g*	50	*I*			6000	1.6		

[a] *C*, crystal; *Sm*, smectic phase; *N*, nematic phase; *I*, isotropic; *g*, glass.
[b] Birefringence was observed only partially under polarizing microscope.

length ($m > 9$) was required for the STI*m*-*n* polymer to exhibit the liquid crystal phase. The short tail length was favorable for AZO*m*-*n* polymers to exhibit the liquid crystal phase but the long spacer ($m > 8$) destabilized the liquid crystal phase. The effect of the length of the spacer and tail on the liquid crystalline behavior of the AZO*m*-*n* and STI*m*-*n* polymers cannot be explained simply from the present data. The phase diagram of the crosslinking reagent/STI10-5 polymer is shown in Figure 4. The phase transition temperatures of the STI10-5 polymer varied according to the amount of the crosslinking reagent introduced into the polymer. No aggregation of the

TABLE II Thermodynamic Properties of Monomers and Polymers of AZO*m*-*n*

m	*n*	*phase transition temperature of monomer (°C)*[a]					*Mn*	*Mw/Mn*	ΔH_{SI} (*kJ/mol*)	ΔS_{SI} (*J/molK*)
10	2	*C*	97	*Sm*	99	*I*	3600	1.3		
9	2	*C*	89	*Sm*	94	*I*	3400	1.3	0.8	2.16
8	2	*C*	95	*Sm*	99	*I*	3100	1.2	2.52	6.66
10	5	*C*	104	*Sm*	108	*I*	4000	1.4		
9	5	*C*	101	*Sm*	102	*I*	3500	1.3		
8	5	*C*	90	*I*			3100	1.6		

[a] *C*, Crystal; *Sm*, smectic phase; *N*, nematic phase; *I*, isotropic.

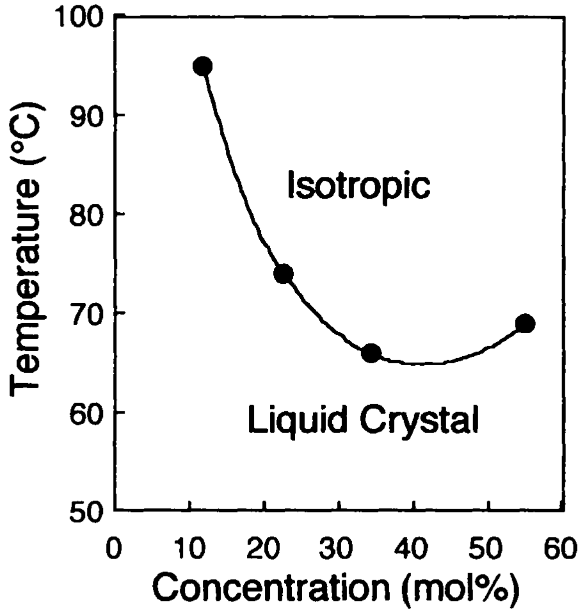


FIGURE 4 Phase diagram of crosslinking reagent/STI10-5.

crosslinking reagent was observed under a microscope. The phase diagram of the crosslinking reagent/STI10-3 is shown in Figure 5. Although polymer STI10-3 itself did not exhibit a liquid crystal phase, the mixture of 10 mol% of the crosslinking reagent/STI10-3 showed an obvious fan-shaped texture. The behavior must be caused by the plasticization and anisotropic interactions between the mesogenic crosslinker and the mesogenic NLO chromophores. All the other STI*m*-*n* polymers doped with 10 mol% of the crosslinking reagent also exhibited the liquid crystal phase. The crosslinking reaction took place with 0.5 mol% of AIBN as an initiator at 70°C.

Hyperpolarizability of the Polymer

Hyperpolarizabilities (β) of the chromophores of monomers and polymers were measured by the hyper Rayleigh scattering method (HRS method). For the measurement of β, the EFISH (electric field-induced second harmonic generation) method is the most well known technique. In EFISH measurement, a large electric field is applied to a sample solution in order to align the chromophores to generate second harmonic light. The value of β is calculated from this SHG signal. However, in a polymer system, chromophores are

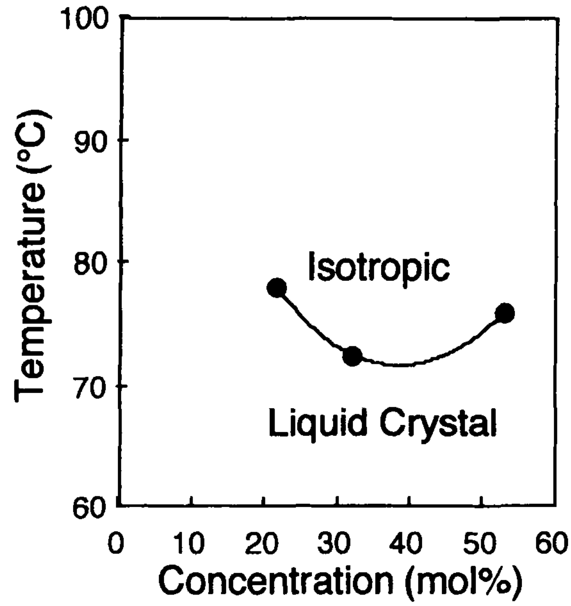


FIGURE 5 Phase diagram of crosslinking reagent/STI10-3.

attached to the polymer chain, so that the chromophores cannot align freely in accordance with the applied electric field. Thus, an exact value of β of a polymer cannot be obtained by EFISH measurement. The values of β of monomers and polymers of STI*m*-*n* measured by the HRS method are listed in Table III. The values of β of the polymers were found to be larger than those of the corresponding monomer. The origin of SHG is related to the vibration of the electron cloud of the chromophore, and thus SHG will be affected by electronic interactions between the chromophores. In a side-chain polymer, the chromophores are connected to the main chain of the polymer within a short distance so that the local concentration of chromophores becomes very high even in solution. This affects the local field factor on the chromophores and enhances the value of hyperpolarizability of the polymer. This mechanism of enhancement of the β value is supported by the fact that the magnitude of β was larger in the compound with shorter spacer length (STI7-3) as shown in Table III. The distance between chromophores is shorter in STI7-3 than STI10-3 so that interactions between chromophores in stronger in STI7-3 compared to those in STI10-3. Also, as seen in the values of STI7-3 and STI7-5, the tail length did not affect the β value. Thus, it may well be said that the higher local concentration of chromophores has affected the local field and caused the enhancement of the magnitude of β.

SHG Susceptibilities of Polymer Films

The effect of liquid crystallinity on SHG intensities was investigated using polymers without curing. The SHG intensities of polymers STI*m*-*n* and AZO*m*-*n* without a crosslinking reagent were measured within 20 minutes after poling treatment. The $\chi^{(2)}$ values of the polymers obtained by the Maker fringe measurement are listed in Table IV. The $\chi^{(2)}$ values were calculated according to the literature [4, 10, 7, 19] using the $\chi^{(2)}_{111}$ value of α-quartz (1.6×10^{-9} esu) as a reference. The $\chi^{(2)}$ values of the films were rather small considering the magnitude of the β values. The $\chi^{(2)}$ value of a poled

TABLE III Values of β Obtained by HRS Measurement

Abbreviation	*Mn*	*Mw/Mn*	*β(esu)*
STI10-3	monomer		22.4×10^{-30}
STI10-3	8000	1.7	37.7×10^{-30}
STI7-3	7000	1.5	40.9×10^{-30}
SIT7-5	19000	3.5	41.6×10^{-30}

TABLE IV Values of $\chi^{(2)}$ of Polymers without Curing Obtained by Maker Fringe Measurement

Abbreviation	*Mn*	*poling temperture (°C)*	*$\chi^{(2)}$ (esu)*
SIT10-5	7000	50	1.1×10^{-9}
STI9-5	10000	55	0.5×10^{-9}
STI8-5	10000	60	0.6×10^{-9}
STI7-5	19000	63	0.6×10^{-9}
STI6-5	18000	65	0.5×10^{-9}
STI10-3	8000	63	0.7×10^{-9}
STI8-3	6000	55	0.5×10^{-9}
AZO10-2	3600	40	0.8×10^{-9}
AZO9-2	3400	50	1.7×10^{-9}
AZO8-2	3100	45	1.5×10^{-9}
AZO10-5	4000	38	0.9×10^{-9}
AZO9-5	3500	48	0.9×10^{-9}
AZO8-5	3100	45	0.8×10^{-9}

polymer is expressed by [1, 17]

$$\chi^{(2)} = Nf_{2\omega}f_{\omega}f_{\omega}\beta \ \mu E/5kT \tag{1}$$

where N is the number-density of NLO chromophores, f_ω and $f_{2\omega}$ are the Lorentz local field factors at the fundamental and SH wave frequency and $\mu E/5kT$ describes the strength of electric poling of the chromophores. The magnitude of the $\chi^{(2)}$ value is strongly affected by poling strength. It was considered that under the experimental conditions, thermal relaxation of the chromophores occurred during measurement. However, the $\chi^{(2)}$ values of the polymers which showed a liquid crystal phase were approximately twice as large as those of the other polymers. This indicates that the poled structure was much more stabilized in liquid crystalline polymers. The SHG intensities of AZO8-2 and AZO8-5 are plotted as a function of time in Figure 6. The SHG intensity of AZO8-2 was stabler than that of AZO8-5 even though the spacer length was the same and the molecular weight was almost the same in these polymers. Also, as seen in Table II, Tg was almost the same in these polymers. Thus, it was concluded that the stability of SHG susceptibility was enhanced in liquid crystalline polymers. Before the experiment, we expected that SHG susceptibility of a non-crosslinked polymer would completely disappear within a short period; however, the SHG susceptibility of the non-crosslinked liquid crystalline polymer was maintained over 10 days. The AZO8-2 polymer was cured by a thermal crosslinking reaction of 5 mol% doped crosslinking reagent with 0.5 mol% of

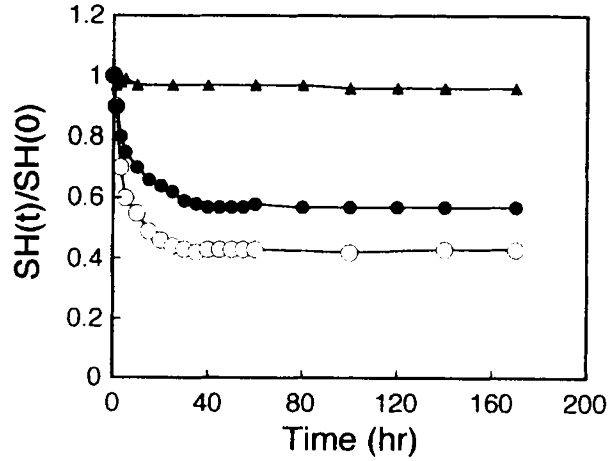


FIGURE 6 Normalized second harmonic intensity SH(*t*)/SH(0) as a function of time at room temperature.) (●) AZO8-2; (○) AZO8-5; (▲) AZO8-2 after curing.

AIBN as initiator. The crosslinking reaction took place at 70°C under corona poling treatment for 30 minutes. The stability of SHG susceptibility was enhanced, and little decay of SHG intensity was observed within 7 days. However, the magnitude of $\chi^{(2)}$ was considerably suppressed to 1/4 of that of the pure AZO8-2 polymer.

CONCLUSION

Side-chain polymers with two types of NLO chromophores were synthesized. Some of the polymers showed a liquid crystal phase. The hyperpolarizability of the polymer was found to be greater than that of the corresponding monomer. Interactions between chromophores existing within a short distance were concluded to have affected the local field factor and caused enhancement of the nonsymmetrical oscillation of π-electrons. The stability of the macroscopic SHG susceptibilities of the polymers was found to be higher in liquid crystalline polymers.

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