Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Second Harmonic Generation of Side Chain Polymer Liquid Crystals Possessing Asymmetric Carbon without Poling Treatment

T. Sasaki [a] , Y. Ishikawa [a] , T. Yoshimi [a] , R. Kai [a] , H. Kato [b] & M. Matsuda [b]

[a] Department of Applied Chemistry, Faculty of Engineering, Oita University Dannoharu, Oita, 870-11, Japan

[b] Institute for Chemical Reaction Science, Tohoku University Katahira, Aoba-ku, Sendai, 980-77, Japan

Version of record first published: 04 Oct 2006

To cite this article: T. Sasaki, Y. Ishikawa, T. Yoshimi, R. Kai, H. Kato & M. Matsuda (1998): Second Harmonic Generation of Side Chain Polymer Liquid Crystals Possessing Asymmetric Carbon without Poling Treatment, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 309:1, 157-165

To link to this article: http://dx.doi.org/10.1080/10587259808045526

Mol. Cryst. Liq. Cryst., 1998, Vol. 309, pp. 157–165
Reprints available directly from the publisher
Photocopying permitted by license only

Second Harmonic Generation of Side Chain Polymer Liquid Crystals Possessing Asymmetric Carbon without Poling Treatment

TAKEO SASAKI[a,*], YUICHI ISHIKAWA[a], TAKESHI YOSHIMI[a], RYUTARO KAI[a], HIRONOBU KATO[b] and MINORU MATSUDA[b]

[a]*Department of Applied Chemistry, Faculty of Engineering, Oita University Dannoharu, Oita 870-11 Japan;*
[b]*Institute for Chemical Reaction Science, Tohoku University Katahira, Aoba-ku, Sendai 980-77 Japan*

(Received 25 April 1997; In final form 7 July 1997)

Side-chain polymer liquid crystals that possess mesogenic donor-π-acceptor chromophores (azobenzene and stilbene derivatives) and a chiral unit were synthesized, and the efficiencies of the second harmonic generation (SHG) of these polymers were investigated. It was found that these polymers exhibited SHG susceptibility without the application of high voltage.

Keywords: Polymer liquid cyrstal; chiral unit; nonlinear optical effect; second harmonic generation; hyperpolarizability

INTRODUCTION

During the last ten years, studies on the development of high performance nonlinear optical (NLO) organic materials have become vigorous. Especially studies on organic polymer materials have gained much interest [1]. Second order NLO polymers possess very useful functions, such as second harmonic generation (SHG) and the Pockels effect. Polymers having donor-π-acceptor chromophores are used for the second order NLO materials. The second

*To whom correspondence should be addressed.

order NLO effect appears only in noncentrosymmetric materials. To obtain large second-order NLO susceptibility, usually a high voltage is applied to the polymer film [1–4]. The donor-π-acceptor chromophores tend to align in one direction during this process. These poled polymers are thermodynamically unstable, and the NLO properties decrease as a function of time [5]. Thus, materials in which the poled structure is thermodynamically stable are necessary. Studies on the NLO properties of ferroelectric liquid crystals (FLCs) have been reported [6–8]. FLCs show a phase of very low symmetry in their surface-stabilized state and exhibit SHG susceptibility. However, the dipole moment of an FLC molecule is usually perpendicular to the molecular long axis; it is disadvantageous to obtain large hyperpolarizability. In this study, we synthesized a series of liquid crystalline NLO polymers in which each chromophore possesses a dipole moment and a chiral carbon on a molecular long axis and investigated their SHG susceptibility.

EXPERIMENTAL

Preparation of Samples

The SHG polymers used in this study are shown in Figure 1. Sulfonated stilbene and azobenzene with asymmetric carbon are incorporated as an

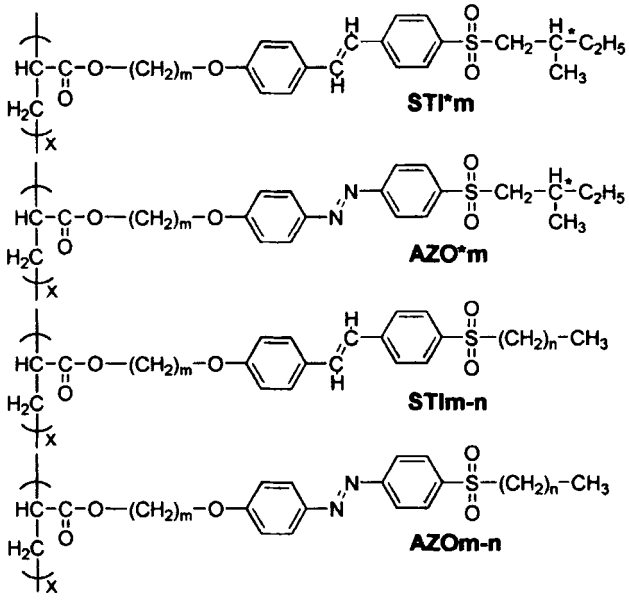


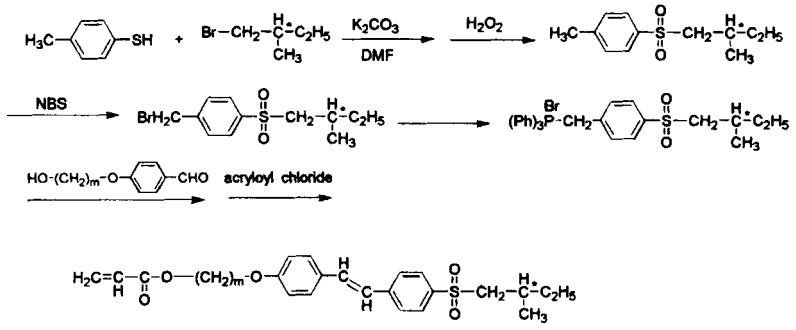
FIGURE 1 Structure of compounds used in this study.

NLO mesogen with different spacer chain lengths. Stilbene derivatives were synthesized via the Wittig reaction of phosphonium salt from 4-(2-methylbutyl)sulfonylbenzylbromide with 4-alkoxybenzaldehyde, and azobenzene derivatives were synthesized by the diazocoupling of 4-(2-methylbutyl)alkylsulfonylaniline with phenol. The synthetic routes of the monomers are shown in Scheme 1. The synthesis details of azobenzene-type monomers are described in a previous paper [9]. Synthesis of 4-(Acryloyloxy decyloxy)-4'-((2-methylbutyl)sulfonyl)stilbene (monomer STI*10) is described below as a representative case for the stilbene-type monomers.

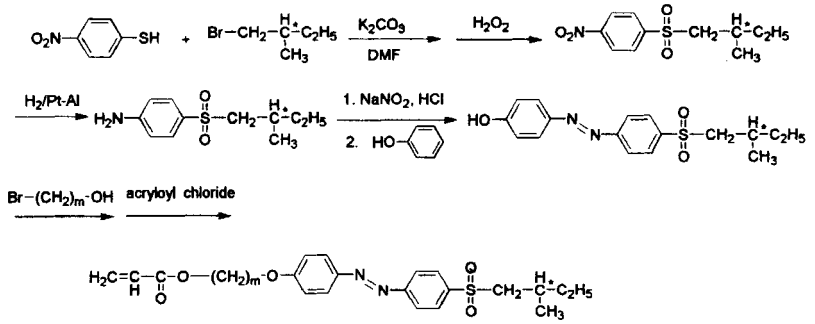
Synthesis of Stilbene Type Monomer STI*10

1) 4-(2-Methylbutyl) Sulfonyl Toluene

4-Methyl thiophenol (25 g, 0.16 mol) and 1-bromo-2-methylbutane (22 g, 0.18 mol) were dissolved in 200 mL of *N*, *N*-dimethylformamide (DMF); 0.5 g of



STI*m monomer



AZO*m monomer

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 the resulting solid was dissolved in 400 mL of methanol. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, 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 concentrated by evaporation, and 200 mL of water was added. The product was extracted by ethyl acetate and purified by recrystallization from methanol. Yield 76%. mp 48–49; ^{1}H NMR ($CDCl_3$) δ0.85 (*t*, CH_3), 1.05 (*m*, CH_3), 1.26 ~ 1.51 (*m*, —CH_2—), 2.00 (*m*, —C*H—), 2.45 (*s*, Ar—CH_3), 2.87 ~ 3.08 (*m*, SO_2CH_2), 7.35 and 7.78 (AA'BB'), 4H). Anal. Calcd. for $C_{12}H_{18}O_2S$ (226.34); C, 63.67; H, 8.01. Found: C, 63.67; H, 8.00.

2) 4-(2-Methyl butyl) Sulfonyl Benzylidene Bromide

4-(2-Methylbutyl) sulfonyl toluene (15 g, 0.065 mol) was dissolved in 300 mL of benzene, and a small amount of AIBN was added. The solution was refluxed for 24 h. After the solution was concentrated by evaporation, precipitated succinimide was removed by filtration. The solvent was evaporated and the product was purified by column chromatography on silica gel (eluent, dichloromethane). Yield 50%; ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, CH_3), 1.05 (*m*, CH_3), 1.26 ~ 1.51 (*m*, —CH_2—), 2.00 (*m*, —C*H—), 3.04 ~ 3.10 (*m*, SO_2CH_2), 4.51 (*s*, Ar—CH_2—Br), 7.59 and 7.89 (AA'BB', 4H).

3) 4-(2-Methyl butyl) Sulfonyl Benzylidene Triphenylphosphonium Bromide

4(2-Methylbutyl) sulfonyl benzylidene bromide (10 g, 0.050 mol) and triphenylphosphine (10 g, 0.050 mol) were dissolved in 200 mL of benzene and refluxed for 5 h. The solution was cooled to ambient temperature and the resultant precipitate of phosphonium salt was obtained by filtration. Yield 80%. ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, CH_3), 1.05 (*m*, CH_3), 1.26 ~ 1.51 (*m*, —CH_2—CH_3), 2.00 (*m*, —C*H—), 2.85 ~ 3.04 (*m*, SO_2CH_2), 5.75 (*s*, Ar—CH_2—P), 7.38 and 7.75 (AA'BB', 4H), 7.64 ~ 7.82 (*m*, P-Ar).

4) 4-(10-Hydroxy decyloxy)benzaldehyde

p-Hydroxybenzaldehyde (8.0 g, 0.065 mol) and 1-bromo-10-decanol (15 g, 0.063 mol) were dissolved in DMF, and potassium carbonate and 1 g of sodium iodide were added. The solution was stirred vigorously by a mechanical stirrer at 80°C for 30 h. 300 ml of water was added and the product was extracted by ethyl acetate and washed by an aqueous solution of 10% potassium hydrate and pure water. The solution was dried on sodium sulfate and the solvent was evaporated. The product was purified by recrystallization from a 1:1 mixture of hexane/ethyl acetate. Yield 70%. ^{1}H NMR ($CDCl_3$) δ 1.88 ~ 1.15 (*m*, —CH_2—), 3.66 (*t*, —CH_2—OH), 4.05 (Ar—O—CH_2—), 6.99 and 7.83 (*d*, AA′BB′, 4H), 9.88 (*s*, Ar-CHO).

5) 4-(10-Hydroxy decyloxy)-4′-((2-methylbutyl)sulfonyl)stilbene

4-(2-Methylbutyl)sulfonyl benzylidene triphenylphosphonium bromide (25 g, 0.044 mol) was dissolved in 120 mL of dry methanol and sodium methoxide was added for 10 min. After the addition of sodium methoxide, the solution was stirred for 5 min; 4-(10-hydroxy decyloxy)benzaldehyde (11 g, 0.040 mol) in 40 ml of dry methanol was added dropwise for 10 min. After the solution was stirred for 1 h, the resultant precipitate was collected and purified by recrystallization from methanol. To isolate the trans isomer from the cis isomer, the recrystallization was repeated three times [10]. Yield 20%; ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, CH_3), 1.05 (*m*, CH_3), 1.26 ~ 1.51 (*m*, —CH_2—), 2.00 (*m*, —C*H—), 2.90 ~ 3.10 (*m*, SO_2CH_2), 3.67 (*t*, —CH_2—OH), 3.99 (Ar—O—CH_2—), 6.91 (*d*, Ar, 2H), 6.98 ~ 7.24 (*m*, —CH_2=CH_2—), 7.47 (*d*, Ar, 2H), 7.63 and 7.85 (*d*, AA′BB′, 4H)

6) 4-(Acryloyloxy decyloxy)-4′-((2-methylbutyl)sulfonyl)stilbene (STI *10 monomer)

4-(10-Hydroxy decyloxy)-4′-((2-methylbutyl)sulfonyl)stilbene (3 g, 0.0062 mol) and 1.2 g of triethylamine were dissolved in 50 mL of dry dichloromethane and stirred at 0°C. 0.85 g of acrylchloride (0.0094 mol) in 20 mL of dry dichloromethane was added dropwise for 20 h. After the solution was stirred for 10 h, it was washed with a saturated aqueous solution of sodium hydrocarbonate and pure water. The solution was dried over sodium sulfate and the solvent was evaporated. The product was purified by column chromatography on silica gel (eluent, dichloromethane) followed by recrystallization

from methanol. Yield 70%. mp 90°C. ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, 3H, —CH_3), 1.06 (*d*, 3H, —CH_3), 1.15 ~ 1.85 (*m*, 20H, —CH_2—), 2.02 (*m*, 1H, —C*H—), 2.90 ~ 3.12 (*m*, 2H, —SO_2—CH_2—), 3.99 (*t*, 2H, —Ar—O—CH_2—), 4.15 (*t*, 2H, —$COOCH_2$—), 5.80 ~ 6.42 (*m*, 3H, —CH=CH_2), 6.91 (*d*, 2H, ArH), 6.96 ~ 7.22 (*m*, 2H, —Ar—CH=CH—Ar—), 7.47 (*d*, 2H, ArH), 7.62 (*d*, 2H, ArH), 7.85 (*d*, 2H, ArH). Anal. Calcd. for $C_{32}H_{44}O_5S$ (540.76): C, 71.08; H, 8.20. Found: C, 71.1; H, 8.23.

The ^{1}H NMR data of AZO*10 monomer is as follows:

AZO*10: ($CDCl_3$) δ 0.85 (*t*, 3H, —CH_2—CH_3), 1.06 (*d*, 3H, —CH_3), 1.15 ~ 1.85 (*m*, 20H,—CH_2—), 2.02 (*m*, 1H, —C*H—), 2.90 ~ 3.12 (*m*, 2H, —SO_2—CH_2—), 3.99 (*t*, 2H, —Ar—O—CH_2—), 4.15 (*t*, 2H, —$COOCH_2$—), 5.80 ~ 6.42 (*m*, 3H, —CH=CH_2), 6.91 (*d*, 2H, ArH), 6.96 ~ 7.22 (*m*, 2H, —Ar—CH=CH—Ar—), 7.47 (*d*, 2H, ArH), 7.62 (*d*, 2H, ArH), 7.85 (*d*, 2H, ArH).

Polymerization

Thermal radical polymerization STI*m and AZO*m were carried out in a 10 wt% benzene solution with azobis(isobutyronitrile) AIBN, 3 mol%) as an initiator. The resulting polymers were purified by repeated reprecipitation 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 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 spectrophotometer.

SHG measurements were performed on the sample films. A chloroform solution of the polymer (10 wt%) was cast on a glass substrate and dried to form a thin film (~ 10 μm thickness). After drying at room temperature, the

samples were heated under vacuum at 60°C for several hours and annealed at 80°C to exhibit the liquid crystalline phase. SHG intensities were measured by the Maker fringe method [11, 12] (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

The liquid crystalline behaviors of the polymers were observed under a polarizing microscope. In these polymers, STI*10, STI*11, and AZO*8 exhibited the liquid crystal phase. These polymers did not form a large domain, so that the liquid crystal phase was not classified directly from the microscopic observation. The phase transition temperatures were measured by DSC, and the results are listed in Table I. In these polymers, only one peak was observed above *Tg*. The phase transition enthalpies were estimated from DSC to be ~ 2 kJ/mol. The phase can be attributed to the nematic phase. The effect of the flexible chain length (*m*) on the thermal stability of the liquid crystal phase can be seen in Table I. The liquid crystal phase was observed in polymers with a spacer chain longer than $m = 8$. The behaviors were similar to those of the achiral polymers AZO*m-n* and STI*m-n* previously reported [9].

The maximums of UV-vis absorption spectra of the STI**m* polymers were around 350 nm, and they have no absorbance the second harmonic wavelength (532 nm) of the fundamental laser used in this study. On the other hand, the absorption maximums of the AZO**m* polymers were

TABLE I Thermodynamic properties and the second-order nonlinear optical susceptibilities of polymers STI**m* and AZO**m* measured without poling treatment

Phase transition temperature (°C)[a]						*Mn*	*Mw/Mn*	ΔH_{NI} *(kJ/mol)*	ΔS_{NI} *(J/molk)*	d_{33} *(esu.)*
STI*11	g	48	N[b]	91	I	10000	1.86	0.18	0.52	2.1×10^{-10}
STI*10	g	48	N[b]	86	I	5500	1.81	0.17	0.47	1.6×10^{-10}
STI*9	g	52	I			7500	1.62			~ 0
STI*8	g	60	I			7800	1.83			~ 0
STI*6	g	73	I			8500	1.90			~ 0
AZO*8	g	45	N	91	I	3300	1.2	0.62	1.70	1.1×10^{-10}
AZO*6	g	41	I			4200	1.4			~ 0

[a]N, nematic phase; I, isotropic; g, glass.

around 430 nm, and they slightly absorbed 532 nm of light so that the SHG intensity of AZO**m* cannot be discussed simply. The hyperpolarizability of STI**m* was estimated experimentally to be 40×10^{-30} esu. by the hyper Rayleigh scattering method [9, 13].

SHG measurements were performed on cast films. The films were annealed at 85°C for 5 h to exhibit the liquid crystal phase. The SHG intensities of polymers STI* and AZO**m* without poling treatment were measured at room temperature. It was found that those *non-poling-treated* films exhibited SHG susceptibility. The SHG signal from the STI*10 film is shown in Figure 2. The maximum of the fringe pattern was at the incident beam angle perpendicular to the film surface. In a previous work, it was found that liquid crystalline polymer AZO*m-n* and STI*m-n* did not exhibit SHG susceptibility without poling treatment [9]. The SHG susceptibilities of AZO**m* and STI**m* were calculated according to Singer *et al.* using the d_{11} value of quartz (8.0×10^{-10} esu) as a reference [12]. The values of d_{33} of these films are also listed in Table I. As seen in this table, the achiral polymers STI*m-n* did not show any second-order susceptibility without poling treatment, films of chiral polymers STI*11 and STI*10 exhibited SHG susceptibility without poling. Chiral polymers which were not liquid crystals did not exhibit SHG susceptibly without poling. Thus, liquid crystallinity played an important role in exhibiting SHG susceptibility in those polymers. It was thought that the asymmetric structure of the phase was induced in the liquid crystal phase of those films. The exact classification of the phase was not identified because the birefringence of the films was very weak and no clear texture was observed. The chiral carbon probably induced the asymmetrical alignment of mesogens in the LC phase. The small domain of the asymmetrical liquid crystal phase must have been induced and exhibited the SHG susceptibility. Thus, the liquid crystalline polymers AZO**m* and STI**m* were SHG-active

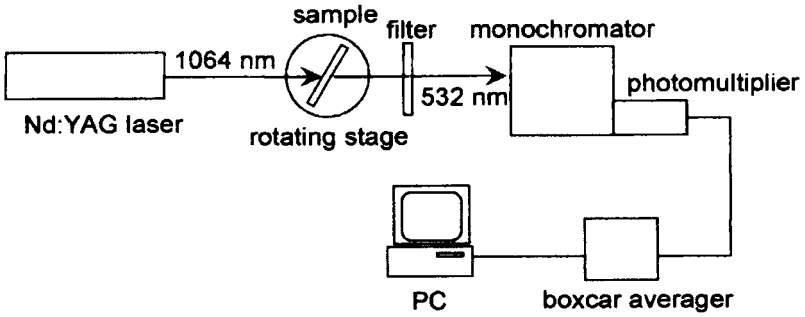


FIGURE 2 Schematic illustration of the set-up for Maker-fringe measurement.

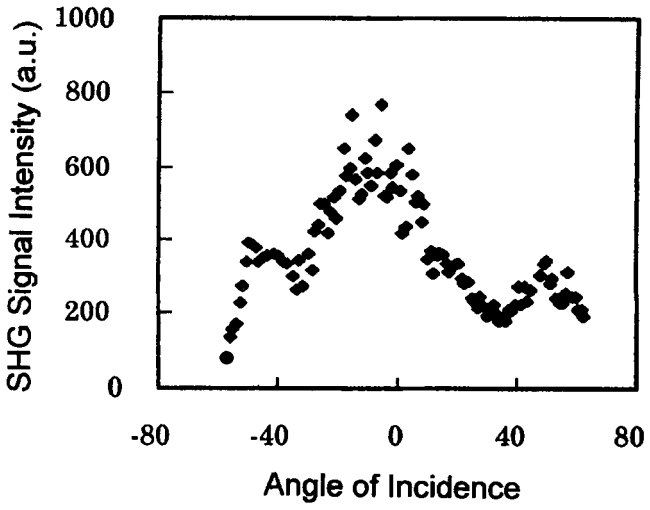


FIGURE 3 Maker fringe pattern observed in STI*11 film without poling treatment.

without an application of high voltage. The liquid crystalline SHG polymers which can be used without poling treatment will be useful for a wide variety of photonic applications.

References

[1] D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, **94**, 31 (1994).
[2] C. Xu, B. Wu, L. R. Dalton, P. M. Ranon, Y. Shi and W. H. Steier, *Macromolecules*, **25**, 6716 (1992).
[3] L. Yu, W. Chan and Z. Bao, *Macromolecules*, **25**, 5609 (1992).
[4] M. Chen, L. Yu, L. R. Dalton, Y. Shi and W. H. Steier, *Macromolecules*, **24**, 5421 (1991).
[5] G. A. Lindsay, R. A. Henry, J. M. Hoover, A. Knoesen and M. A. Mortazavi, *Macromolecules*, **25**, 4888 (1992).
[6] I.-C. Khoo, *Liquid Crystals: Physical Properties and Nonlinear Optical Phenomena*; John Wiley and Sons (1995).
[7] I. Benne, K. Semmler and H. Finkelmann, *Macromolecules*, **28**, 1854 (1995).
[8] H. Wang, M. Y. Jin, R. C. Jarnagin, T. J. Bunning, W. Adams, B. Cull, Y. Shi, S. Kumar and E. T. Samulski, *Nature*, **384**, 244 (1996).
[9] T. Sasaki, Y. Ishikawa, T. Yoshimi, K. Makiguchi and M. Matsuda, *Mol. Cryst., Liq. Cryst.*, (1997), in press.
[10] The cis isomer of STI*6 was thermally isomerized to the trans form by refluxing the chloroform solution, however, the cis isomer of STI*10 did not isomerized thermally to the trans isomer.
[11] W. N. Herman and L. M. Hayden, Polymers for Second Order Nonlinear Optics. In *Am. Chem. Soc. Advences in Chemistry Series 601*, G. A. Lindsay and K. D. Singer Eds, (*Am. Chem. Soc.*: Washington, D. C., 1995) Chapter 20.
[12] K. D. Singer, J. E. Sohn and S. J. Lalama, *Appl. Phys. Lett.*, **49**, 248 (1986).
[13] K. Clays, A. Persoons and L. D. Mayer, *Adv. Chem. Phys.*, **85**, 455 (1994).