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NONLINEAR OPTICAL PROPERTIES OF MOLECULAR TWINS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Three different series of twin nonlinear optic (NLO) molecules were studied, in which the two NLO chromophores are linked by a central flexible polymethylene spacer. The first series, which had two azobenzene chromophores (Azo-twins), was designed to also exhibit liquid crystallinity. Most of the members of this series exhibited a nematic mesophase. The second series had two 4-nitrophenol units as chromophores (PNP-twins), while the third one was based on 4-alkylsulfonyl-4'-alkoxy azobenzene chromophores (Sulfazo-twins). These twin NLO systems exhibited interesting odd-even oscillations in their second harmonic generation (SHG) efficiencies in the powder form. When the spacer had an odd number of methylene groups, they exhibited significantly higher powder SHG efficiency than their even counterparts, with the even ones most often exhibiting no detectable SH signal. Preliminary single crystal X-ray diffraction studies performed on the PNP-twin series showed that while the even members possess a molecular center of symmetry and pack centro-symmetrically, the odd ones do not, leading to the observed alternation. The orientational-disordering dynamics of two of the twin series – the PNP and the Sulfazo-twin series, doped in a poly(methyl methacrylate) matrix, was also studied by monitoring the SH-signal decay in electric field poled samples. Interestingly, the maximum attainable SH signal, $\chi^{(2)}$, in the

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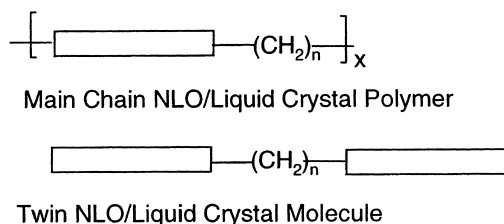
poled samples also showed an odd-even oscillation with the odd ones again exhibiting a higher value of $\chi^{(2)}$. The temporal stability of the SHG intensity at 70°C, after the removal of the applied corona, was also studied and the relaxation of the chromophores was found to follow a biexponential decay. The slower relaxation component exhibits a spacer length dependence, which suggests the interplay of two factors in governing the temporal stability in such polymer doped twin systems, one is the conformational discomfort experienced by the spacer in adopting a U-shaped geometry, and the other the electrostatic repulsion when two aligned dipoles lie very close to each other.

Key Words: Molecular twin; Nonlinear optics; Liquid crystals; Temporal stability

INTRODUCTION

Molecular twins having two chromophores/mesogens linked by a central flexible spacer serve as excellent models for main chain liquid crystalline polymers and main chain nonlinear optical (NLO) polymers (Scheme 1).

In the context of main chain liquid crystalline polymers, it has been shown that the spacer segment plays an important role in governing the phase transition temperatures and also entropies associated with these transitions [1-3]. In model dimeric liquid crystals, the flexible spacer modifies their properties, in that the odd spacers have lower phase transition temperatures, clearing and melting enthalpies/entropies compared to the even ones [4-6]. This is due to the preferred extended all-trans conformation of the polymethylene spacer that leads to the even twins adopting a collinear arrangement of the mesogens, while the odd twins have their mesogens biaxially disposed [7-10]. It was anticipated that this difference in crystal packing between the odd and even members would also be reflected in the second harmonic generation (SHG) efficiencies in the solid state for twin NLO molecules. In the context of main chain NLO polymers, this difference in packing between odd and even spacers could also lead to a difference in the extent of alignment during poling, and also in governing their temporal stability following the removal of the electric field. A study of these properties of twin NLO molecules doped in a suitable polymer matrix, would serve as models for the intrinsically more complex main chain NLO polymers, wherein the analysis is compli-

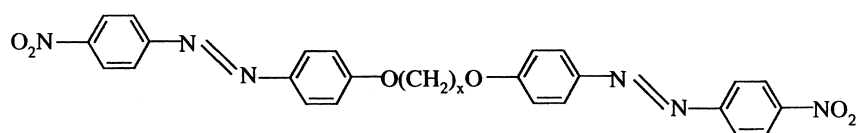


Scheme 1.

cated by their heterogeneity. Thus, studies of twin NLO chromophores are useful not only as conceptual intermediates in the monomer \rightarrow oligomer \rightarrow polymer progression but also as interesting systems in their own right.

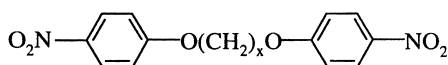
Three different homologous series of twin NLO chromophores were synthesized. The first series, the Azo-twins (Scheme 2), has two 4-nitro-4'-alkoxy azobenzene units linked by a spacer of length varying from 1-12 methylene units.

It was seen that most of the members of this series exhibited a nematic mesophase. Their liquid crystalline transition temperatures exhibited the expected odd-even oscillation with spacer length, n . More importantly, their powder SHG efficiencies also showed an odd-even oscillation with the odd ones having higher values than the even ones [11]. But their poor solubility made the SHG relaxation studies of these molecules in doped polymer matrix difficult. Therefore, a second series, PNP- n , based on *p*-nitro phenol, was synthesized, which had the expected higher solubility. Like the Azo-twins, the PNP- n twins also showed an odd-even oscillation in their powder SHG efficiency [12]. Preliminary single crystal X-ray diffraction studies carried out on several members of this series confirmed that the even members, in general, had a centrosymmetric packing, whereas the odd ones went into non-centrosymmetric space groups [13]. The improved solubility in common organic solvents rendered the PNP-series amenable to SHG relaxation studies, when doped in a polymer matrix. The third twin series - the Sulfazo-twins, was designed with the expectation of having a larger β value, as well as higher solubility. Here, we compare the behavior of these three series of twin chromophores with greater emphasis on the new Sulfazo-twins.



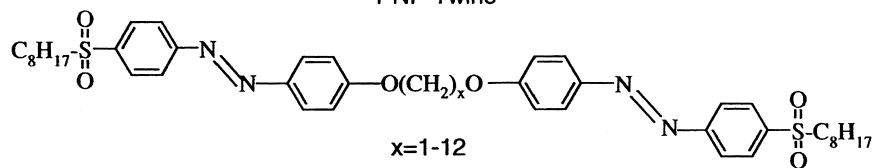
$x=1-12$

Azo Twins



$x=1-12$

PNP Twins



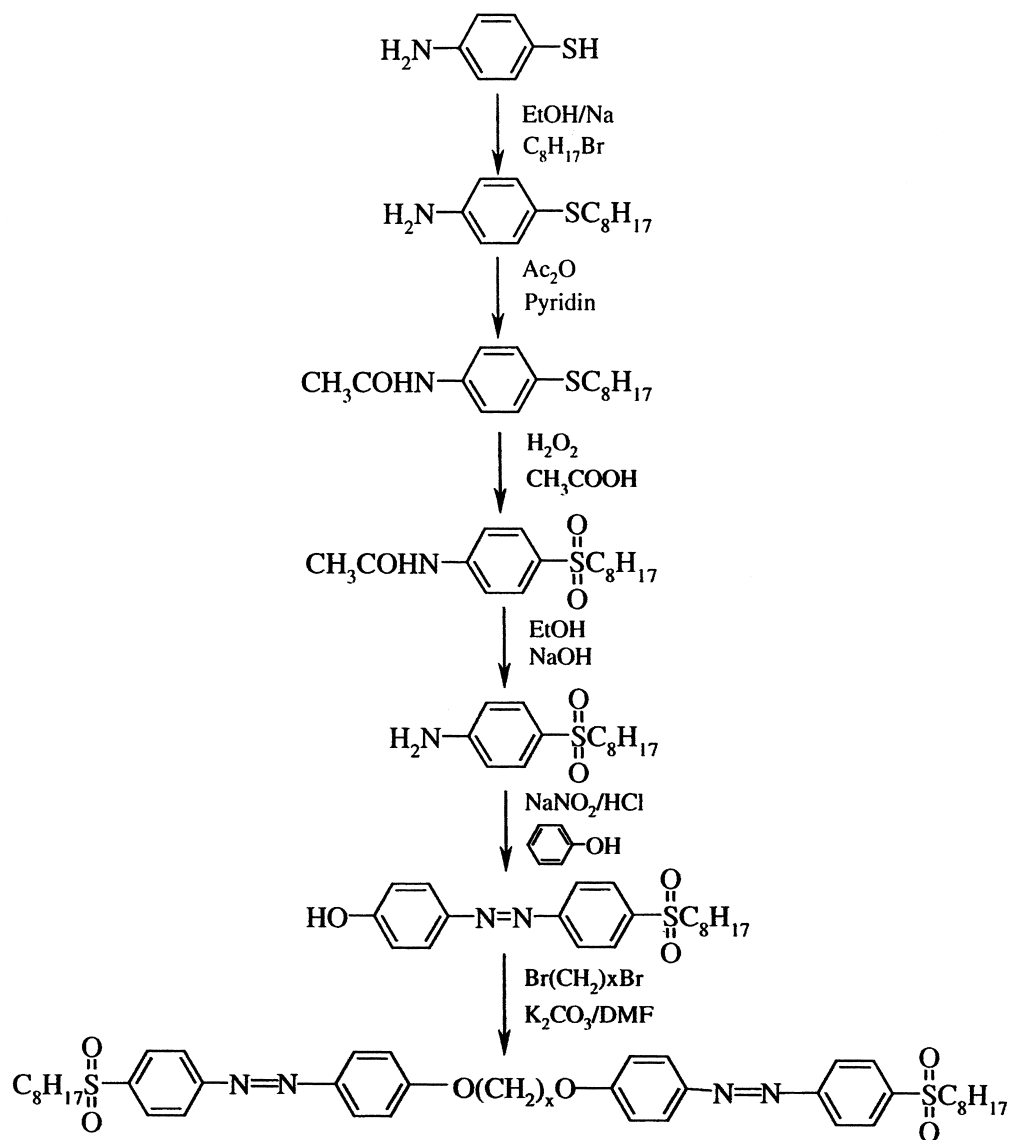
$x=1-12$

Sulfazo Twins

Scheme 2.

RESULTS AND DISCUSSION

The Azo-twins and the PNP-twins were readily synthesized by coupling 4-hydroxy-4'-nitroazobenzene and 4-nitrophenol, respectively, with the appropriate α,ω -dibromoalkanes, the details of which were presented elsewhere [11, 12]. The synthesis of the new Sulfazo-twins is given in Scheme 3. The azo-dye was synthesized using a series of standard transformations starting from 4-mercaptoaniline, and was then coupled with the appropriate α,ω -dibromoalkanes in presence of a



Scheme 3.

phase transfer catalyst to obtain the Sulfazo-twins. The Azo-twins are denoted as A-n, the PNP-twins as PNP-n and the Sulfazo-twins as S-n, where $n = 1-12$. The structures of all the Sulfazo-twins were confirmed by their ^1H NMR spectra. In their UV-visible spectra, all of them had a prominent peak around 363 nm ($\epsilon = 4.3$ to $5.4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) with a tail extending to 500 nm, except for S-1, which had a slightly blue-shifted λ_{max} . These data for members of all the three series are compared in Table 1. In general, it is seen that the two chromophores are electronically isolated in all the twins, except for the case where a single carbon atom links them.

Powder SHG Measurements

The recrystallized samples were powdered, sieved ($<100 \mu\text{m}$), and taken in a glass capillary. The fundamental of a Q-switched Nd:YAG laser (1064 nm, 10 Hz, 8 ns) was used as incident light. The second harmonic signal (532 nm) was collected and measured using a previously described setup [11]. A similar measurement was carried out for a standard sieved sample of urea, and the SHG efficiencies are taken as the ratio ($I_{2\omega(\text{sample})}/I_{2\omega(\text{urea})}$). A plot of this ratio as a function of spacer length “n” for the Azo-twins [11] and the PNP-n [12] series is shown in Figure 1.

Both these twins exhibited an odd-even oscillation of the SHG efficiency with the odd ones having high values and the even ones showing almost no measurable SH signal in the powder form. Similar measurements for the Sulfazo-series in the usual manner were difficult due to the highly static nature of the powdered samples. However, an attempt was made to measure the solid state SHG

Table 1. UV-Visible Data of the Three Twin Series

Spacer length (n)	Azo Series A-n		PNP Series PNP-n		Sulfazo Series S-n	
	λ_{max} (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	λ_{max} (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	λ_{max} (nm)	ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)
1	365	49557	295	18500	352	51120
2	377	52339	307	19500	360	48570
3	376	38116	309	19330	361	47970
4	379	46122	310	19750	363	45590
5	379	52273	311	19760	364	45730
6	380	43184	311	19850	363	50300
7	380	52407	311	20300	363	43330
8	380	50067	311	19880	363	54290
9	379	38204	312	18990	364	50430
10	379	52884	312	19600	363	53270
11	379	47057	312	20100	364	51410
12	380	49862	312	17400	363	54190

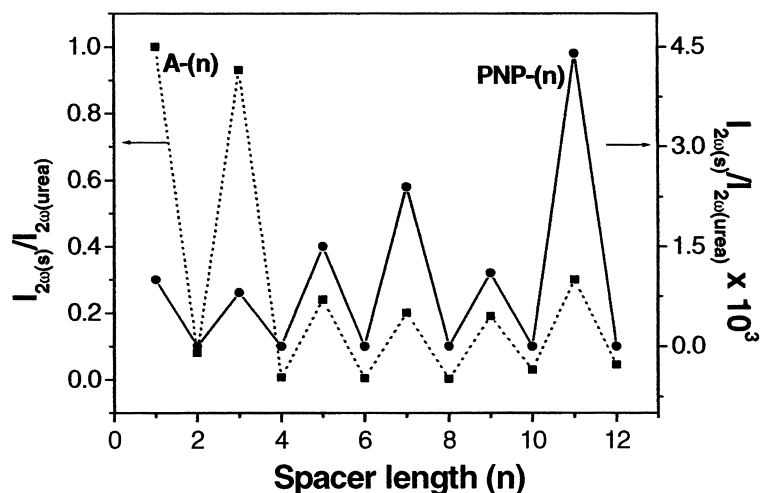


Figure 1. Plot of powder SHG efficiencies of the A-n twins taken as the ratio $[I_{2\omega(s)}/I_{2\omega(urea)}]$ vs. spacer length (n) and for the PNP-n twins as the ratio $[I_{2\omega(s)}/I_{2\omega(urea)}] \times 10^3$ vs. the spacer length (n).

efficiency by powdering the sample using an inert medium like petroleum ether, and then filtering the suspension followed by drying. The dry powder was then taken up as a thin coating on to silicon grease coated glass capillaries. A sample of the standard urea was also prepared in a similar fashion. Thus, a similar cylindrical geometry of the sample was attained without having to fill the powders into capillaries. For purpose of comparison, the PNP-n twin series also was similarly coated on glass capillaries. The experimental setup was the same as that used for measuring the powder SHG efficiency of the other two series, and the SHG efficiencies were taken as the ratio of $I_{2\omega(\text{sample})}/I_{2\omega(\text{urea})}$. Figure 2 shows the plot of the SHG efficiencies of the PNP-n series, measured both with the sample inside and outside the capillary.

The full line represents the SHG efficiencies measured with the powdered and sieved sample inside the glass capillaries and the dotted one represents the SHG efficiencies with the sample coated on the outside of the glass capillaries using silicon grease. As seen from the figure, there is a reasonable agreement between the two methods except for a few points, in particular PNP-11. Hence, the Sulfazo-series was similarly examined. Most members of the Sulfazo-series, did not show any measurable SHG efficiency except for samples S-7 and S-11, which gave an $I_{2\omega(\text{sample})}/I_{2\omega(\text{urea})}$ ratio of 4.9×10^{-3} and 1.6×10^{-3} , respectively. None of the even members gave any SH signal. Although, in effect, the Sulfazo-series did not lend itself to a thorough powder-SHG analysis, these measurements are generally in concurrence with the expectation that the odd members should exhibit higher SHG efficiencies: in that only the odd members, S-7 and S-11 exhibited any SH signal. Based on this, and similar unequivocal observations in both the Azo-n and PNP-n series, it may be concluded that the odd-even oscillation of SHG efficiencies in the solid state of such twin chromophores appears to be a universal feature similar to the odd-even oscillation of transition temperatures

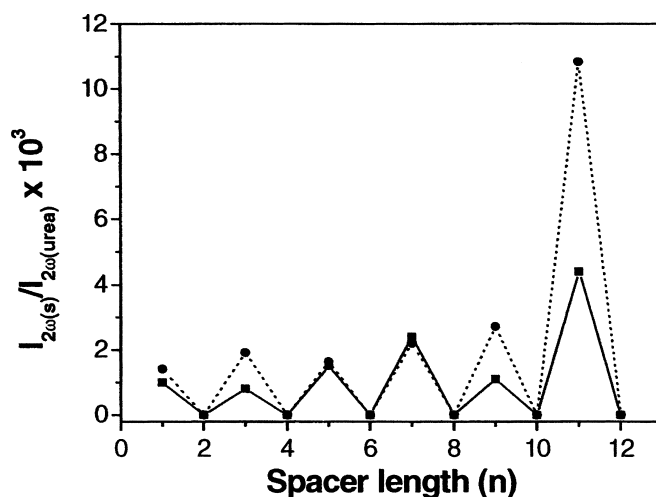


Figure 2. Powder SHG efficiencies of PNP-(n) vs. n, (dotted line represents the values when the sample was taken as a thin coating on the outside surface of glass capillaries and straight line represents the values when the sample was taken inside the capillary).

with spacer length observed in the case of twin liquid crystal molecules. As with twin liquid crystals, the odd-even oscillation of SHG efficiency arises from the difference in crystal packing between the odd and even members.

Single Crystal X-Ray Analysis [13]

The good solubility of the PNP-n twins made it possible to grow quality crystals suitable for single crystal analysis. Preliminary single crystal X-ray analysis was carried out for most of the members of the series, except PNP-3, PNP-8, and PNP-12, for which good quality crystals could not be obtained. All the even members showed centrosymmetric packing while the odd ones were non-centrosymmetric. The molecular center of symmetry coincides with the crystal center of symmetry in the even series, which ensured that the even membered twins do not exhibit second harmonic behavior. In all the odd members, the dipolar axes of the two chromophores were biaxial and the molecules did not possess a center of symmetry forcing them to pack in a non-centrosymmetric lattice, thereby causing the material to exhibit non-zero SHG values. Unfortunately, it was not possible to grow good quality crystals of the Azo- and Sulfazo-twins, and therefore, no single crystal X-ray diffraction studies were possible.

SHG Measurements of Films

For SHG measurements of the doped polymer films, the fundamental of a Q-switched Nd:YAG (1064 nm, 10 Hz, 8 ns) was employed. SH intensities were obtained relative to Y-cut quartz. A corona poling process was adopted to align the

NLO chromophores. The corona discharge was generated at the tip of a stainless steel needle biased with 5 KV DC voltage across an 8 mm air gap. The corona current was limited to 1-2 μA using a 10 M Ω resistor connected in series. *In situ* poling was performed with the film placed at an angle of 45° with respect to the fundamental beam [14].

The reported $\chi^{(2)}$ values are normalized with respect to the sample thickness, as well as the number density to allow comparisons to be made between films doped with different twin chromophores. The number densities (N) of the chromophore in the films were calculated as follows:

$$N = wN'\rho/M \quad (1)$$

where w is the weight fraction of each sample in PMMA, N' is the Avogadro number, M is the molecular weight, and ρ is the density of PMMA [15]. In a typical poling experiment, the film was heated to 100°C (15°C above T_g) for the PNP-n twins or 112°C (8°C above T_g) for the S-n twins and allowed to equilibrate at that temperature for 15 minutes, after which a voltage of 5 KV was applied for 10 minutes. The temperature was then reduced to the desired temperature (25°C/70°C) with the field still on. The field was switched off after the temperature stabilized for 5 minutes, and the SHG efficiency was measured either *in situ* for the relaxation studies (at 70°C) or independently for the maximum attainable value at 25°C.

Maximum SHG in Poled Films

Typically, films were prepared by spin coating a chloroform solution containing the appropriate NLO twin (10 wt% PNP twin or 7.5 wt% Sulfazo twin) and PMMA onto a soda-lime glass substrate (2.5 × 2.5 cm² and 0.2 cm thickness) and poling was done using a setup described previously [12]. Homogeneous film samples of S-1, S-2, and S-4 of the Sulfazo series could not be prepared in 7.5 wt% because of their limited solubility, and hence, films of S-1 and S-4 were prepared in 2.5 wt%, whereas S-2 film could be prepared only in 1.25 wt%. Films were then dried at 70°C for 36 hours in a hot-air oven to remove any residual solvent. The film thickness was measured with a profilometer (Taylor-Hobson, Talysurf series). Typical film thickness varied from 2.2 to 5.0 μm for the PNP-series, and from 1.6 to 2.8 μm for the Sulfazo-series. The T_g 's of two PMMA-doped samples, with PNP-1 and PNP-11 (two extreme members of the PNP series), were measured and found to be nearly the same: 84 and 86°C, respectively. Hence, the poling for the PNP series was carried out at 100 °C, around 15°C above the expected T_g . Similarly, the T_g of PMMA doped with S-11 at 10 wt% was found to be 104° C. Therefore, the poling for this series was carried out at 112°C. The very poor solubility of the Azo-twins made it difficult to dope them in a suitable polymer matrix for similar relaxation studies. The poling setup was first standardized using a pure sample of disperse red (DR-1). The $\chi^{(2)}$ values were calculated using the equation [16, 17]:

$$\chi^{(2)}_{(\text{film})} = (2/\pi) \chi^{(2)}_{(\text{Quartz})} \{ [I_f (n_f)^3 (l_c)^2] / [I_Q (n_Q)^3 (l_f)^2] \}^{1/2} \quad (2)$$

where I_f and I_Q are the SH intensities of the film and that of y-cut quartz, n_f and n_Q are the refractive indices of film and quartz, l_f and l_c are the film thickness and coherence length of quartz, respectively. $\chi^{(2)}_{(\text{Quartz})}$ is taken as 1 pm/V, l_c as 20.6 μm , n_Q as 1.4605 and n_f as 1.49. In addition, the $\chi^{(2)}_{(\text{film})}$ obtained using Equation 2 was normalized with respect to both thickness of film as well as the chromophore number density. The normalized values of $\chi^{(2)}_{(\text{film})}$ thus obtained for the S-n series are listed in Table 2. The plot of $\chi^{(2)}_{(\text{film})}$ vs. spacer length n for both the series are given in Figure 3.

Both the series show an odd-even variation; the even ones also exhibiting a finite, although smaller value compared to their odd counterparts. Interestingly, in

Table 2. Measured Voltage, Film Thickness, Number Density, SHG Coefficient, and the Slow and Fast Relaxation Time Constants for the Sulfazo Twin Series

Sample	L_{film}^a (μm)	N^b ($10^{19}/\text{cm}^3$)	$\chi^{(2)c}$ (pm/V)	τ_2^d (min)	τ_1^d (min)
S-1	2.5			259.8	2.5
(2.50%)	2.4	2.3	—		
S-2	—			150.9	4.3
(1.25%)	2.6	1.1	—		
S-3	2.0			121.7	5.0
	1.8	6.3	2.69		
S-4	1.8			189.1	1.7
(2.50%)	2.4	2.2	—		
S-5	2.2			167.4	4.8
	2.5	6.1	1.63		
S-6	2.5			142.6	2.3
	2.8	6.0	1.59		
S-7	2.7			168.4	3.1
	1.8	5.9	3.03		
S-8	1.7			172.7	4.0
	1.8	5.8	2.96		
S-9	1.8			182.2	5.7
	1.7	5.7	2.99		
S-10	1.6			174.6	5.3
	2.0	5.6	1.72		
S-11	1.8			200.5	2.0
	2.4	5.5	3.76		
S-12	1.7			123.6	6.8
1.8	5.5	1.57			

^aFilm thickness measured using Profilometer for two different films of each sample (average error bar is ca. 2%).

^bNumber density of doped film calculated using Equation 1.

^cSecond-order susceptibility of doped film poled at 112°C and measured at 25°C. Values normalized with respect to film thickness and number density.

^dCharacteristic relaxation times from equation 2 from films poled at 112°C and relaxation studied at 70°C.

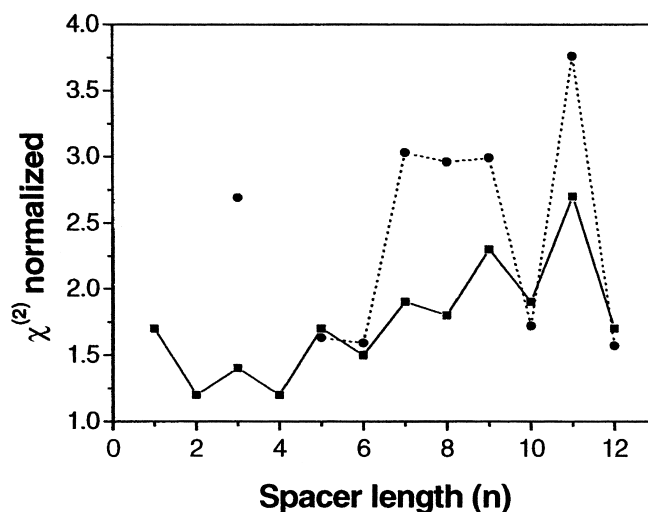


Figure 3. Plot of the maximum attainable SHG ($\chi^{(2)}$) vs. spacer length (n) in doped films at 25°C. (Straight line is for PNP- n and dotted line is for S- n).

both the Sulfazo- and PNP-series, the twin with a 11-carbon spacer exhibited the highest $\chi^{(2)}$ values. The fact that the even twins also exhibit a significant SH signal in the doped systems, unlike that in the crystalline form, is expected as in the former case, the molecules are forced to align (noncentrosymmetrically) in the direction of the applied field during poling and are not constrained by packing considerations. However, it does appear that the even ones experience greater discomfort in arriving at such a geometry, in which the dipoles are oriented parallel to each other, resulting in their lower SHG coefficients. This suggests that the flexible spacer plays an active role in determining the maximum attainable SHG efficiency.

SHG Relaxation Studies

In order to understand the role of the spacer in governing the temporal stability of the twin chromophoric molecules, the decay of the SH signal in poled films was monitored. The poling was done *in situ* with the film placed at an angle of 45° with respect to the incident laser beam. After 10 minutes of poling at 100°C (for PNP- n twins) and 112°C (for S- n twins), the temperature was lowered to 70°C, with the field still on. Once the SH signal stabilized, the field was turned off and the SH signal was monitored as a function of time. A few typical relaxation profiles of the SH signal for the S- n series are shown in Figure 4.

The studies of the relaxation behavior of PNP-twins were reported earlier [12] The relaxation data were fitted to a biexponential equation (Equation 3) [17-19].

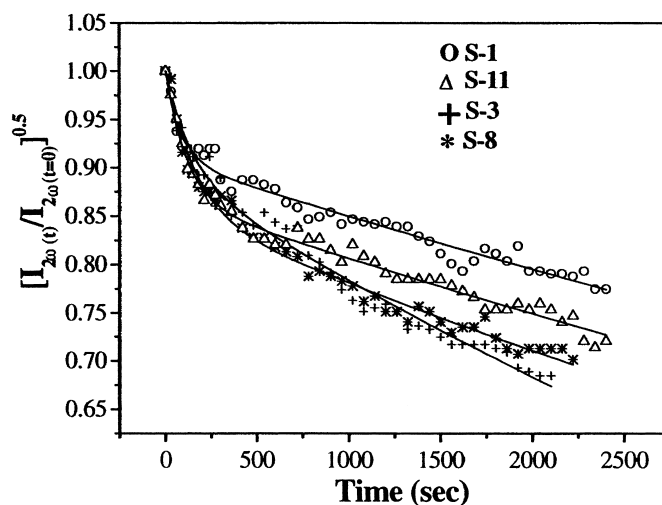


Figure 4. Typical relaxation profile of the SHG signal $[I_{2\omega(t)} / I_{2\omega(t=0)}]^{0.5}$ versus time.

$$[I_{2\omega(t)} / I_{2\omega(t=0)}]^{1/2} = a (\exp^{-t/\tau_1}) + (1-a) (\exp^{-t/\tau_2}) \quad (3)$$

$I_{2\omega(t)}$ is the SHG intensity at any given time and $I_{2\omega(t=0)}$ is that at the start of the relaxation measurement, at which point the poling voltage was turned off. τ_1 and τ_2 are the characteristic relaxation times for the fast and slow components of the decay, respectively. The τ_1 has been assigned to surface charge effects and τ_2 represents the chromophore reorientation dynamics [20, 21]. For comparison, the plot of τ_2 vs. the spacer length, n , for the Sulfazo-series, along with that for the PNP-series is shown in Figure 5.

The τ_1 and τ_2 values are the average of two measurements made on different films of the same sample at the same dye concentration. The error bar in Figure 5 reflects the intrinsic variability between two such measurements. The τ_2 vs. n plot for the PNP-series showed that the τ_2 value goes through a minimum for $n=3$ and then increases before leveling off after $n=5$. The Sulfazo-series also shows a similar spacer length dependence as that of the PNP- n series, in that a minimum around $n=3$ and a leveling off around $n=4$ is seen, although in this case an unusually small value for S-12 is noticed. The variation of τ_2 with n can be rationalized as originating from the competing forces that operate on the system upon the application of an electric field. One results in the orientation of the chromophores in the direction of the field, while the other drives the disordering process, due to electrostatic repulsion between the oriented dipoles. In the case of twins that are connected by very short spacer segments, the electrostatic repulsion between oriented dipoles dominates, resulting in a faster relaxation or smaller values of τ_2 for them. Beyond an optimum length of the spacer segment, this factor does not contribute significantly to the overall relaxation process and the value of τ_2 becomes

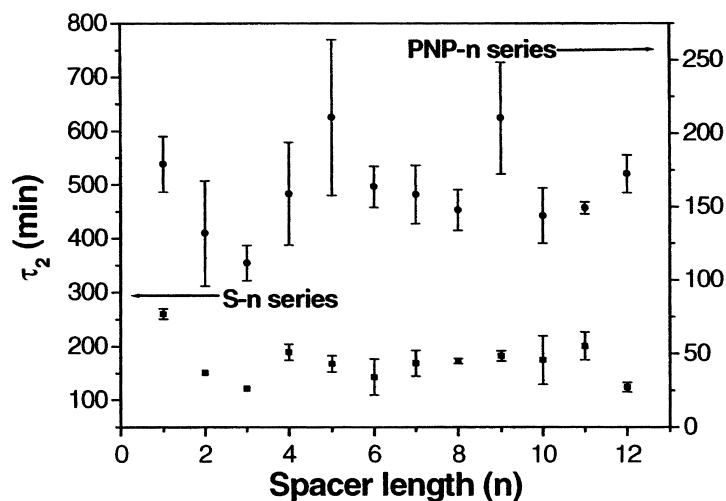


Figure 5. Plot of characteristic relaxation time τ_2 versus spacer length (n) for the new PNP- n series (O) and the Sulfazo series (■).

less sensitive to n . In the shortest spacer ($n=1$), the τ_2 -value is high both in the Sulfazo-series as well as the PNP-series. In this case, it appears that the lowest energy conformation is one where the chromophores are biaxially oriented with their dipoles adding cumulatively. Thus, despite their larger size and also larger β values, the general behavior of the Sulfazo-twins is similar to the PNP-twins.

In conclusion, studies on homologous series of twin chromophoric molecules have revealed several interesting features. One is the observation that when two NLO chromophores are linked by a spacer containing an odd number of methylene units they behave very differently than when they are linked by an even number of units, the odd members exhibit a significantly higher powder SHG efficiency than their even counterparts, with the even ones most often exhibiting no detectable SH signal. This behavior was shown to be a consequence of the manner in which such twin chromophores pack in the crystalline solid. Interestingly, the odd-even oscillation is also seen when the twin chromophores are molecularly dispersed in a polymer matrix and is subjected to electric field-induced poling, suggesting that it is not the packing constraints alone that govern such a behavior. Based on these observations, it may be reasonable to postulate that the spacer segment in main-chain NLO polymers do not merely serve the role of a connecting segment but may indeed play an active role in governing both the maximum attainable SHG value and also their temporal stability.

EXPERIMENTAL

^1H NMR spectra were recorded using a Bruker ACF, 200 MHz spectrometer, using tetramethylsilane (TMS) as the internal reference and CDCl_3 as the solvent.

The UV-visible spectra were recorded using a Hitachi U3400 instrument at a sample concentration of 10^{-5} M in CHCl_3 . DSC studies were done using a Rheometric Scientific DSC Plus instrument. The thermograms for the Sulfazo twins were recorded, both during the heating and cooling runs, using a heating/cooling rate of 10 deg/min. A slow purge of nitrogen gas (5 ml/min) was maintained to prevent any possible oxidative degradation. The reproducibility of the thermograms was confirmed by recording the second and third heating runs. Polarized light microscopic studies were carried out using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage. The glass transition temperature (T_g) of the doped polymer samples was measured using the DSC. The thickness of the spin-coated film was measured using a Taylor-Hobson step profilometer.

MATERIALS

The Sulfazo-twin series was synthesized starting from 4-mercaptoaniline and bomooctane, which were purchased from Aldrich Chemical Co. The α,ω -dibromoalkanes were either purchased from Aldrich Chemical Co. or prepared from the corresponding diols using red phosphorus and bromine [22]. All solvents were purified before use by standard methods [23]. The synthesis and purification of the Azo-twin and the PNP-twin series are reported elsewhere [11, 12].

4-Octylmercapto Aniline [24]

1.8 g (78.3 mmol) sodium metal was dissolved in 50 ml of absolute ethanol in a two-necked round-bottom flask. 10g (80.0 mmol) of 4-mercaptoaniline was added to this solution under nitrogen purge. The contents were refluxed for one hour under nitrogen atmosphere. 15.4 g (79.8 mmol) bromooctane was then added dropwise to the solution. The reaction was stopped after refluxing for around 4 hours. The ethanol was pumped off, water added and the solution was extracted with dichloromethane. The organic layer was washed with 5% NaHCO_3 , then water, and finally dried over anhydrous Na_2SO_4 . The low melting solid was purified by vacuum distillation using a solid distillation apparatus. It distilled at 0.1-0.2 mm Hg, temperature 140-150°C. Yield = 15.7 g (83%). ^1H NMR (CDCl_3): 7.2 ppm (d, 2H, Ar-H); 6.8 ppm (d, 2H, Ar-H); 3.7 ppm (s, 2H, $-\text{NH}_2$); 2.8 ppm (t, 2H, $-\text{S}-\text{CH}_2$); 2.2 ppm (s, 3H, $-\text{CO}-\text{CH}_3$); 1.6 ppm (m, 2H, $\text{S}-\text{CH}_2-\text{CH}_2$); 1.4 ppm (m, 10H, $\text{S}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_5$); 0.87 ppm (t, 3H, $-\text{CH}_2-\text{CH}_3$).

N-Acetyl-4-octylmercapto Aniline

4-Octylmercapto aniline was refluxed with 8 ml (84.6 mmol) acetic anhydride and 7ml (87 mmol) pyridine under nitrogen atmosphere. After 4 hours, the reaction was stopped, and the contents poured into ice water. The white crystalline

solid was filtered, washed with 5% HCl, then water and dried. It was recrystallized from methanol-water to get white crystals. Melting point = 74-76°C. Yield = 15.0 g (83%). $^1\text{H NMR}$ (CDCl_3): 7.4 ppm (d, 2H, Ar-H); 7.3 ppm (d, 2H, Ar-H); 7.1 ppm (s, 1H, -NH); 2.9 ppm (t, 2H, -S-CH₂); 2.2 ppm (s, 3H, -CO-CH₃); 1.6 ppm (m, 2H, S-CH₂-CH₂); 1.5 ppm (m, 10H, S-CH₂-CH₂- (CH₂)₅); 0.87 ppm (t, 3H, -CH₂-CH₃).

N-Acetyl-4-octylsulfonyl Aniline

The acetamide from the previous step was refluxed with 40 ml glacial acetic acid for an hour under nitrogen atmosphere and then 20 g (50%) H₂O₂ was added dropwise, and left to reflux overnight. The excess acetic acid was distilled off and then extracted using CH₂Cl₂. The organic layer was washed with water and dried over anhydrous Na₂SO₄. It was used as such without further purification for the next step.

4-Octylsulphonyl Aniline

The acetamide, from the previous step, was refluxed with 50 ml ethanol/water (25/25 v/v) containing 2.5 g (62.5 mmol, 10%) of NaOH under nitrogen atmosphere, for around 16 hours. Ethanol was removed using rotary evaporator and water added and extracted using diethyl ether. Ether was removed and the solid recrystallized from methanol/water. Melting point = 88-90°C. Yield = 12.4 g (84%). $^1\text{H NMR}$ (CDCl_3): 7.7 ppm (d, 2H, Ar-H); 6.7 ppm (d, 2H, Ar-H); 4.2 ppm (s, 2H, -NH₂); 3.0 ppm (t, 2H, SO₂-CH₂); 1.7 ppm (m, 2H, SO₂-CH₂-CH₂); 1.3 ppm (m, 10H, SO₂-CH₂-CH₂- (CH₂)₅); 0.86 ppm (t, 3H, -CH₃).

Sulfazo-Dye

To 9.5 g (35.2 mmol) of the amine in crushed ice was added 5.5 ml (53.0 mmol) concentrated HCl. 2.7 g (39.0 mmol) NaNO₂ in 10 ml water was cooled in ice and added dropwise to the amine in acid solution. It was left stirring using a mechanical stirrer for one hour at 5°C. This clear solution was then placed in a dropping funnel and added dropwise to a solution of 3.3 g (35.2 mmol) phenol in 5.6 g (140.8 mmol) NaOH dissolved in 50 ml water. During the entire addition, the temperature was maintained at 5°C. It was slowly brought to room temperature and left stirring overnight. Then, it was acidified under ice cold conditions using concentrated HCl. The solid obtained was filtered by suction and washed free of acid. It was purified by column chromatography using silica gel as the stationary phase and eluted using 20% ethyl acetate in pet ether. Melting point = 142°C. Yield = 7.9 g (60%). $^1\text{H NMR}$ (CDCl_3): 8.0 ppm (m, 4H, Ar-H); 7.9 ppm (d, 2H, Ar-H); 6.9 ppm (d, 2H, Ar-H); 5.6 ppm (s, 1H, Ar-OH); 3.1 ppm (t, 2H, SO₂-

CH_2); 1.7 ppm (m, 2H, $\text{SO}_2\text{-CH}_2\text{-CH}_2$); 1.3 ppm (m, 10H, $\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-(CH}_2)_5$); 0.86 ppm (t, 3H, $-\text{CH}_3$).

Typical Procedure for Sulfazo Twin Series S-n: S-4

500 mg (1.34 mmol) of the azo dye, 96 mg (0.45 mmol) dibromo butane, 926 mg (6.7 mmol) K_2CO_3 and 100 mg (0.17 mmol) KI were placed in 10 ml dry DMF and refluxed under nitrogen atmosphere for 2 days at 90°C . For work up, the reaction mixture was poured into water and extracted into CH_2Cl_2 . The organic layer was washed with 1% NaOH until the washings were colorless. It was then washed with water and dried over anhydrous Na_2SO_4 . The CH_2Cl_2 was then removed and the solid obtained was washed with acetone to remove any trace of the starting material. It was then recrystallized from CHCl_3 . Melting point = 206°C . Yield = 100 mg (20%). All the members of the S-(n) series except S-1 and S-2 were prepared using the same procedure. For S-1 and S-2, all the reagents were taken in modified boiling tube, purged with N_2 and the tube cooled using acetone – liquid N_2 mixture. It was then pumped and vacuum-sealed. The sealed tube was then heated for 4 days at 90°C . The yields of S-1 and S-2 are respectively; 34% and 10%. The yields, melting points and elemental analysis data of all the twin series are given below.

S-1: Yield (34%); Melting Point (225.0°C); Elemental Analysis, Calculated: (C 64.7; H 6.8; N 7.4) Found: (C 63.6; H 7.0; N 6.8); $^1\text{H NMR}$ (CDCl_3): ppm 8.0, 7.3 (m, 12H; d, 4H Ar-H); 5.9 (s, 2H, Ar- OCH_2); 3.1 (t, 4H, $-\text{SO}_2\text{CH}_2$); 1.74–1.23 (m, 24H, $-\text{OCH}_2\text{CH}_2$, $-\text{SO}_2\text{CH}_2\text{CH}_2$, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_n$, $(\text{CH}_2)_5\text{CH}_3$); 0.86 (t, 6H, $(\text{CH}_2)_5\text{CH}_3$).

S-2: Yield (10%); Melting Point (247.0°C); Elemental Analysis, Calculated: (C 65.1; H 7.0; N 7.2) Found: (C 64.9; H 7.3; N 6.6); $^1\text{H NMR}$ (CDCl_3): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.5 (s, 4H, Ar- OCH_2); 3.1 (t, 4H, $-\text{SO}_2\text{CH}_2$); 1.70–1.24 (m, 24H, $-\text{OCH}_2\text{CH}_2$, $-\text{SO}_2\text{CH}_2\text{CH}_2$, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_n$, $(\text{CH}_2)_5\text{CH}_3$); 0.86 (t, 6H, $(\text{CH}_2)_5\text{CH}_3$).

S-3: Yield (25%); Melting Point (215.0°C); Elemental Analysis, Calculated: (C 65.5; H 7.1; N 7.1) Found: (C 64.4; H 7.3; N 6.4); $^1\text{H NMR}$ (CDCl_3): ppm 8.1, 7.1 (m, 12H; d, 4H Ar-H); 4.3 (t, 4H, Ar- OCH_2); 3.1 (t, 4H, $-\text{SO}_2\text{CH}_2$); 2.36–1.23 (m, 26H, $-\text{OCH}_2\text{CH}_2$, $-\text{SO}_2\text{CH}_2\text{CH}_2$, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_n$, $(\text{CH}_2)_5\text{CH}_3$); 0.86 (t, 6H, $(\text{CH}_2)_5\text{CH}_3$).

S-4: Yield (20%); Melting Point (206.0°C); Elemental Analysis, Calculated: (C 65.8; H 7.2; N 7.0) Found: (C 64.8; H 7.4; N 6.5); $^1\text{H NMR}$ (CDCl_3): ppm 8.1, 7.1

(m, 12H; d, 4H Ar-H); 4.2 (s, 4H, Ar- OCH_2); 3.1 (t, 4H, $-\text{SO}_2\text{CH}_2$); 2.08–1.23 (m, 28H, $-\text{OCH}_2\text{CH}_2$, $-\text{SO}_2\text{CH}_2\text{CH}_2$, $-\text{OCH}_2\text{CH}_2(\text{CH}_2)_n$, $(\text{CH}_2)_5\text{CH}_3$); 0.86 (t, 6H, $(\text{CH}_2)_5\text{CH}_3$).

S-5: Yield (20%); Melting Point (175.0°C); Elemental Analysis, Calculated: (C 66.2; H 7.4; N 6.9) Found: (C 65.5; H 7.6; N 6.5); $^1\text{H NMR}$ (CDCl_3): ppm 8.0,

7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.95–1.23 (m, 30H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.86 (t, 6H, (CH₂)₅CH₃).

S-6: Yield (40%); Melting Point (172.0°C); Elemental Analysis, Calculated: (C 66.5; H 7.5; N 6.8) Found: (C 66.5; H 7.8; N 6.5); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.70–1.57 (m, 32H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.86 (t, 6H, (CH₂)₅CH₃).

S-7: Yield (58%); Melting Point (165.0°C); Elemental Analysis, Calculated: (C 66.8; H 7.6; N 6.6) Found: (C 65.8; H 7.9; N 6.1); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.67–1.24 (m, 34H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.87 (t, 6H, (CH₂)₅CH₃).

S-8: Yield (42%); Melting Point (165.0°C); Elemental Analysis, Calculated: (C 67.1; H 7.7; N 6.5) Found: (C 66.1; H 7.9; N 6.1); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.65–1.23 (m, 36H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.87 (t, 6H, (CH₂)₅CH₃).

S-9: Yield (23%); Melting Point (145.0°C); Elemental Analysis, Calculated: (C 67.4; H 7.8; N 6.4) Found: (C 66.6; H 8.0; N 6.1); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.67–1.24 (m, 38H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.87 (t, 6H, (CH₂)₅CH₃).

S-10: Yield (26%); Melting Point (155.0°C); Elemental Analysis, Calculated: (C 67.7; H 7.9; N 6.3) Found: (C 67.7; H 8.1; N 6.1); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.87–1.23 (m, 40H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.87 (t, 6H, (CH₂)₅CH₃).

S-11: Yield (45%); Melting Point (135.0°C); Elemental Analysis, Calculated: (C 68.0; H 8.0; N 6.2) Found: (C 68.0; H 8.2; N 6.0); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.2 (t, 4H, -SO₂CH₂); 1.55–1.23 (m, 42H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.86 (t, 6H, (CH₂)₅CH₃).

S-12: Yield (40%); Melting Point (145.0°C); Elemental Analysis, Calculated: (C 68.3; H 8.1; N 6.1) Found: (C 66.9; H 8.2; N 5.5); ¹H NMR (CDCl₃): ppm 8.0, 7.1 (m, 12H; d, 4H Ar-H); 4.1 (t, 4H, Ar-OCH₂); 3.1 (t, 4H, -SO₂CH₂); 1.67–1.23 (m, 44H, -OCH₂CH₂, -SO₂CH₂CH₂, -OCH₂CH₂(CH₂)_n, (CH₂)₅CH₃); 0.87 (t, 6H, (CH₂)₅CH₃).

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REFERENCES

1. Blumstien, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.
2. Griffin, A.C.; Havens, S.J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 951.
3. Roviello, A.; Sirigu, A. *Makromol. Chem.*, **1982**, *183*, 895.
4. Koide, N.; Iimura, K. *Mol. Cryst. Liq. Cryst.*, **1987**, *153*, 73.
5. Griffin, A.C.; Vaidya, S.R.; Hung, R.S.L.; Gorman, S. *Mol. Cryst. Liq. Cryst.*, **1985**, *1(5)*, 131.
6. Abe, A.; Furuya, H.; Yoon, D.Y. *Mol. Cryst. Liq. Cryst.*, **1988**, *159*, 151.
7. Abe, A.; Nam, S.Y. *Macromolecules* **1995**, *28*, 90.
8. Abe, A.; Furuya, H.; Shimizu, R.N.; Nam, S.Y. *Macromolecules* **1995**, *28*, 96.
9. Blatch, A.E.; Luckhurst, G.R. *Liquid Crystals* **2000**, *27(6)*, 775.
10. Malpezzi, L.; Bruckner, S.; Galbiati, E.; Luckhurst, G.R. *Mol. Cryst. Liq. Cryst.*, **1991**, *195*, 179.
11. Asha, S.K.; Ray, P.C.; Ramakrishnan, S. *Polym. Bull.* **1997**, *39*, 481-487.
12. Asha, S.K.; Kavita, K.; Das, P.K.; Ramakrishnan, S. *Chem. Mater.*, **1999**, *11*, 3352-3358.
13. Prasanna, M.D.; Asha, S.K. Mallinson. P.R.; Ramakrishnan, S.; Guru Row, T.N. To be published.
14. Asha, S.K. Ph.D. Thesis: Liquid Crystallinity and Nonlinear Optical Properties of Molecular Twins, Indian Institute of Science, (2000).
15. Dalton, L.R.; Harper, A.W.; Robinson, B.H. *Proc. Natl. Acad. Sci. U. S. A.* **1997**, *94*, 4842.
16. Ray, P.C.; Das, P.K. *Eur. Polym. J.* **1996**, *32*, 51.
17. Hampsch, H.L.; Yang, J.; Wong, G.K.; Torkelson, J.M. *Macromolecules* **1990**, *23*, 3640.
18. Hampsch, H.L.; Yang, J.; Torkelson, J.M. *Macromolecules* **1990**, *23*, 3648.
19. Branger, C.; Lequan, M.; Lequan, R.M.; Large, M.; Kajzar, F. *Chem. Phys. Lett.*, **1997**, *272*, 265.
20. Guan, H.W.; Wang, C.H.; Gu, S.H. *J. Chem. Phys.*, **1994**, *100 (11)*, 8454.
21. Gerbi, D.; Boyd, G.T.; Ender, D.A.; Henry, R.M.; Kam, K.K.; Leung, P.C.W.; Stofko, J.J. Presentation at the Topical Workshop on Organic and Polymeric Nonlinear Optical Materials, American Chemical Society, Division of Polymer Chemistry, 1988.
22. Brian, S.F.; Antony, J. H.; Peter, W.G. S.; Austin, R.T. *Vogels Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical, Longman Group Ltd.: Essex, U. K.; 1989.
23. Perrin, D.D.; Armarego, W.L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: Oxford, U. K.; 1980.
24. Kohler, W.; Robello, D.R.; Willand, C.S.; Williams, D.J. *Macromolecules* **1991**, *24*, 4589.