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Relaxation Behavior of Twin Nonlinear Optical Chromophores: Effect of the Spacer Length

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A new series of twin nonlinear optical (NLO) molecules, having two 4-nitrophenol chromophores that are linked via a flexible polymethylene spacer of varying length [$(CH_2)_n$, $n = 1-12$], were synthesized. Powder second harmonic generation measurements of these twin samples indicated a pronounced odd−even oscillation, with the odd twins exhibiting a high SHG value while the even ones gave no measurable SH signal. This behavior reflects the crystal packing preferences in such twin NLO systems that have odd and even numbers of atoms linking them—the even ones appear to prefer a centrosymmetric packing arrangement. The orientational/disordering dynamics of these twin NLO molecules, doped in a polymer (poly(methyl methacrylate)) matrix, has also been studied using SHG in electric field poled samples. Interestingly, the maximum attainable SH signal, $\chi^{(2)}$, in the poled samples also showed an odd−even oscillation; the odd ones again having a higher value of $\chi^{(2)}$. This unprecedented odd−even oscillation in such molecularly doped systems is rationalized as being due to the intrinsically greater ease of a parallel alignment of the two chromophores in the twins with an odd spacer than in those with an even one. Further, the temporal stability of the SHG intensity at 70 °C, after the removal of the applied corona, was also studied. The relaxation of all the twin chromophores followed a biexponential decay; the characteristic relaxation time (τ_2) for the slow decay component suggests that while the twin with a single methylene unit relaxes relatively slowly, the relaxation is significantly faster in cases where $n = 2$ and 3. In the twins with even longer spacer segments, the relaxation again becomes slower and reaches a saturation value. The observed minimum appears to reflect the interplay of two competing factors that affect the chromophore alignment in such twin systems, namely, the electrostatic repulsion between neighboring oriented dipoles and the intrinsic flexibility of the spacer.

Introduction

In recent years, considerable work has been done wherein nonlinear optical (NLO) properties such as second harmonic generation (SHG) is employed as a tool[1,2] to study orientation and relaxation phenomena in polymer guest−host systems.[3−7] Typically, amorphous polymers doped with NLO chromophores are poled using an electric field at temperatures above their glass transition temperature. The temperature of the sample is then reduced to the desired temperature, and the field is turned off. In such poled samples the chromophores, being in a thermodynamically unfavorable state, will undergo reorientational relaxation to finally attain an isotropic distribution. This relaxation process would depend on the temperature and molecular structure of both the polymer and the chromophore. Apart from such molecularly doped polymeric systems, the NLO moieties can also be covalently bound to the polymer molecule, either as a pendant side chain[8,9] or as an integral part of the backbone.[10−19] The extent of

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order achievable in such covalently linked systems is typically lower than in doped systems, especially in cases where the chromophores form a part of the polymer backbone. Despite this disadvantage, the much higher number densities achievable in covalently linked systems make them attractive candidates for potential applications.

Several research groups have addressed the question of a possible enhancement of NLO property, arising from the "head-to-tail" connection of monomers along the polymer chain. Mitchell et al.[14] made a comparative study of different types of oligomers—one series had flexible methylene spacers between the NLO units, while the other had rigid piperidine spacers. With the fact that these systems did not display an enhancement of the NLO response ($\mu\beta_z$) despite their head-to-tail connectivity, they suggested that flexible spacers offer no advantage or disadvantage in poled polymer applications. Xu et al.,[15] on the other hand, studied the NLO properties of a series of main chain polymers where the NLO dipoles were randomly incorporated and showed that such polymers can be efficiently poled to yield large macroscopic nonlinearity, which is comparable to that in a side chain polymer with the same chromophore as a pendant group. The presence of flexible chain segments linking the chromophores made it possible for the chromophores to align in the field direction through bond rotations, when the films were poled. Although a few such reports have studied the role of the flexible spacer, no systematic study of the macroscopic NLO properties vis-à-vis the spacer length has been reported.

Twin NLO molecules, in which the two chromophores are connected by a flexible spacer in the manner chromophore−spacer−chromophore, would serve as ideal models for understanding the structural factors that affect the properties of main chain NLO polymers. A similar analogy between dimeric liquid crystals, in which two mesogens are linked by a flexible spacer in the sequence mesogen−spacer−mesogen, and main chain liquid crystalline polymers (MCLCP) is well-established.[20−24] As in the case of MCLCP's, an odd−even oscillation of isotropization temperatures and isotropization entropies with spacer length is also observed in these dimeric liquid crystals.[20,21] The odd−even oscillation in these systems was ascribed to the preference of the polymethylene spacer to adopt a conformation that leads to a collinear arrangement of the two mesogens in the even cases, while it leads to a biaxial one in the odd cases.[25−28]

In an effort to understand the role of the linking spacer in main chain NLO polymers, we reported in an earlier communication[29] a series of twin NLO molecules having two nitro−alkoxy azobenzene chromophores linked via flexible polymethylene spacers. These twins were also liquid crystalline, and most of them exhibited a nematic phase. Their isotropization temperatures as well as isotropization entropies showed the expected odd−even oscillation with spacer length. Furthermore, their powder SHG measurements also showed an odd−even oscillation of the SHG efficiency; the odd twins exhibited a fairly high value of SHG efficiency, while the even ones had near-zero values. Unfortunately, due to their poor solubility these azo twins could not be used for relaxation studies in a polymer matrix.

We report here a new series of twin NLO molecules (PNP-*n*), wherein two *p*-nitro phenoxy units are connected by a polymethylene spacer of varying length (*n*). These were very readily soluble in most organic solvents. Powder SHG measurements of these samples also exhibited similar odd−even oscillation of SHG efficiency as in the case of the azo twins,[29] with all even ones giving no measurable SH signal. These twin systems were doped in PMMA and subjected to corona poling. The maximum-attainable SH signal in these systems was measured and their temporal stability studied. The effect of the spacer length on both the maximum SH signal and their temporal stability has been examined.

Experimental Section

^{1}H 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 $CHCl_3$. The glass transition temperature (T_g) of the doped polymer was measured using a Rheometric Scientific DSC Plus instrument, which was calibrated with pure metal standards. A slow purge of nitrogen gas (5 mL/min) was maintained during the scans. The thickness of the spin-coated film was measured using a Taylor−Hobson step profilometer. All solvents were purified before use by standard methods.[30] 4-Nitrophenol was purchased from s.d. fine chem Ltd. and purified by sublimation under vacuum (0.7−1 mmHg) at 125 °C. The α,ω-dibromoalkanes were either purchased from Aldrich Chemical Co. or prepared from the corresponding diols using red phosphorus and bromine.[31]

Synthesis. In a typical procedure for the synthesis of a PNP-*n* twin, 1.75 g (12.6 mmol) 4-nitrophenol and 0.65 g (3.2 mmol) of 1,3-dibromopropane were dissolved in 25 mL of dry acetone. To this clear yellow solution, 3.4 g (24.6 mmol) of K_2CO_3 and 1.1 g (3.4 mmol) of tetrabutylammonium bromide were added and the contents of the flask refluxed for 96 h under nitrogen atmosphere. The acetone was then removed using a rotary evaporator, and distilled water was added to the residue. The insoluble organic precipitate was washed several times with water, filtered, and dried. The solid

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residue was further washed with methanol to ensure complete removal of any residual starting material. The product, after recrystallization from acetone, was obtained in 61% yield.

The yield, melting point, the elemental analyses, and NMR data for all 12 compounds are listed in the Table 1.

Powder SHG Measurements. The recrystallized samples were powdered, sieved (<100 μm), and taken in a glass capillary. The fundamental of a Q-switched Nd:YAG laser (1064 nm, 10 Hz) was used as incident light. The second harmonic light (532 nm) was collected using a previously described setup[29] and was directed toward a photocathode of a UV−visible photomultiplier tube. Scattered radiation other than the second harmonic frequency was eliminated by using a 4 nm bandwidth, 532 nm interference filter and a cell containing $CuSO_4$ solution. A similar measurement was carried out for a standard sieved sample of urea, and the SHG efficiencies are taken as the ratio ($I_{2\omega(\mathrm{sample})}/I_{2\omega(\mathrm{urea})}$).

Film Preparation. In a typical procedure, a solution containing the appropriate NLO twin (10 wt %) and poly(methyl methacrylate) (PMMA) in chloroform was used to spin-coat thin films onto a soda lime glass substrate (2.5 × 2.5 cm^2 and 0.2 cm thickness). Films were then dried at 70 °C for 36 h 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. The T_g's of two PMMA doped samples, with PNP-1 and PNP-11 (two extreme members of the series), were measured and found to be nearly the same, that is, 84 and 86 °C, respectively. Hence, the poling was carried out at 100 °C, approximately 15 °C above the expected T_g.

SHG Measurements of Films. For SHG measurements of the doped polymer films, the fundamental of a Q-switched Nd:YAG (1064 nm, 10 Hz) was employed. SHG 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 MΩ resistor connected in series. In situ poling was performed with the film placed at an angle of 45° with respect to the fundamental beam.

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

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

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.[32] For a typical poling experiment the film was heated to 100 °C (15 °C above T_g) and allowed to equilibrate at that temperature for 15 min, and then a voltage of 5 KV was applied for 10 min. The temperature was then reduced to the desired

Table 1.

sample	yield (%)	melting point (°C)	elemental analysis			^{1}H NMR (ppm)
			formula	calculated	found	
PNP-1	15	148	$C_{13}H_{10}N_2O_6$	C, 53.79; H, 3.45; N, 9.66	C, 53.88; H, 3.43; N, 9.38	8.25, 7.23 (2d, 8H, Ar-*H*), 5.91 (s, 2H, $-OCH_2$)
PNP-2	32	151	$C_{14}H_{12}N_2O_6$	C, 55.26; H, 3.95; N, 9.21	C, 55.78; H, 3.96; N, 9.06	8.25, 7.04 (2d, 8H, Ar-*H*), 4.45 (s, 4H, $-OCH_2$)
PNP-3	61	130	$C_{15}H_{14}N_2O_6$	C, 56.60; H, 4.4; N, 8.81	C, 57.33; H, 4.47; N, 8.70	8.24, 7.0 (2d, 8H, Ar-*H*), 4.26 (t, 4H, $-OCH_2$), 2.38 (m, 2H, $-OCH_2CH_2$)
PNP-4	61	147	$C_{16}H_{16}N_2O_6$	C, 57.83; H, 4.82; N, 8.43	C, 58.34; H, 4.88; N, 8.30	8.22, 6.97 (2d, 8H, Ar-*H*), 4.17 (t, 4H, $-OCH_2$), 2.06 (m, 4H, $-OCH_2CH_2$)
PNP-5	76	103	$C_{17}H_{18}N_2O_6$	C, 58.96; H, 5.20; N, 8.09	C, 58.97; H, 5.22; N, 7.87	8.21, 6.96 (2d, 8H, Ar-*H*), 4.1 (t, 4H, $-OCH_2$), 1.93 (m, 4H, $-OCH_2CH_2$), 1.73 (m, 2H, $-OCH_2CH_2CH_2$)
PNP-6	33	109	$C_{18}H_{20}N_2O_6$	C, 60.00; H, 5.56; N, 7.78	C, 60.30; H, 5.69; N, 7.58	8.2, 6.97 (2d, 8H, Ar-*H*), 4.1 (t, 4H, $-OCH_2$), 1.88 (m, 4H, $-OCH_2CH_2$), 1.6 (m, 4H, $-OCH_2CH_2(CH_2)_2$)
PNP-7	81	117	$C_{19}H_{22}N_2O_6$	C, 60.96; H, 5.88; N, 7.49	C, 61.06; H, 6.00; N, 7.21	8.2, 6.95 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.85 (m, 4H, $-OCH_2CH_2$), 1.53 (m, 6H, $-OCH_2CH_2(CH_2)_3$)
PNP-8	63	123	$C_{20}H_{24}N_2O_6$	C, 61.86; H, 6.19; N, 7.22	C, 62.01; H, 6.34; N, 6.90	8.2, 6.96 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.83 (m, 4H, $-OCH_2CH_2$), 1.4 (m, 8H, $-OCH_2CH_2(CH_2)_4$)
PNP-9	37	94	$C_{21}H_{26}N_2O_6$	C, 62.69; H, 6.47; N, 6.97	C, 62.96; H, 6.67; N, 6.72	8.2, 6.96 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.83 (m, 4H, $-OCH_2CH_2$), 1.38 (m, 10H, $-OCH_2CH_2(CH_2)_5$)
PNP-10	48	89	$C_{22}H_{28}N_2O_6$	C, 63.46; H, 6.73; N, 6.73	C, 63.93; H, 6.76; N, 6.55	8.2, 6.96 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.83 (m, 4H, $-OCH_2CH_2$), 1.35 (m, 12H, $-OCH_2CH_2(CH_2)_6$)
PNP-11	70	86	$C_{23}H_{30}N_2O_6$	C, 64.19; H, 6.98; N, 6.51	C, 64.97; H, 7.05; N, 6.37	8.2, 6.96 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.83 (m, 4H, $-OCH_2CH_2$), 1.32 (m, 14H, $-OCH_2CH_2(CH_2)_7$)
PNP-12	46	82	$C_{24}H_{32}N_2O_6$	C, 64.86; H, 7.2; N, 6.31	C, 65.31; H, 7.46; N, 5.81	8.2, 6.96 (2d, 8H, Ar-*H*), 4.06 (t, 4H, $-OCH_2$), 1.83 (m, 4H, $-OCH_2CH_2$), 1.3 (m, 16H, $-OCH_2CH_2(CH_2)_8$)

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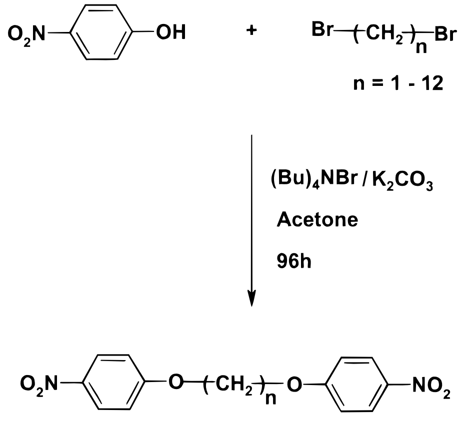
Scheme 1



P(n) (n = 1- 12)

temperature (25 °C/70 °C) with the field still on. The field was switched off after the temperature stabilized for 5 min. 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.

Results and Discussion

The twin chromophores were synthesized from 4-nitrophenol and the appropriate α,ω-dibromoalkanes in the presence of a phase-transfer catalyst (Scheme 1). All the twin molecules were purified by recrystallization from acetone. The yields, melting points, and elemental analyses are given in Table 1. The twins are denoted as PNP-*n*, where $n = 1-12$. The structures of the twin molecules were confirmed by their ^{1}H NMR spectra, and their chemical shifts are given in Table 1. The UV–visible spectra, recorded in $CHCl_3$ (at $\sim 10^{-5}$ M), indicated that all the twins exhibited λ_{max} values around 307–312 nm ($\epsilon = (1.9-2.0) \times 10^4$ L mol^{-1} cm^{-1}), except PNP-1, which had a λ_{max} value of 295 nm ($\epsilon = 1.85 \times 10^4$ L mol^{-1} cm^{-1}). This confirms that the two chromophores in all the twins are electronically isolated except in the case of PNP-1.

Powder SHG Measurements. The powdered and sieved (<100 μm) samples of the twin molecules were examined for their SHG efficiency. The SHG efficiencies were 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*" is shown in Figure 1. As was previously reported for the azo twin series,[29] the PNP-*n* series also showed an odd–even oscillation of the SHG efficiency with the odd ones having high values and the even ones showing no measurable SH signal in the powder form. The higher SHG efficiency for the odd twin is probably due to the less effective cancellation of dipoles in their crystalline state as compared with the even ones. In the even twins, the all-trans extended conformation of the methylene spacer will lead to conformers that possess a center of symmetry, while in the odd twins it could lead to ones which possess a mirror plane. On the basis of simple close packing principles,[33] the even twins may be expected to crystallize in a centrosymmetric arrangement, leading to a more effective cancellation of the chromophoric dipoles. Confirmation of this hypothesis and the understanding of the variation of the SHG efficiencies within the odd members of the series are, of course, possible only from their single crystal X-ray crystal structure. Most of the members of the PNP-*n* series formed good single crystals, and their crystal structure elucidation is currently in progress and will be published separately.

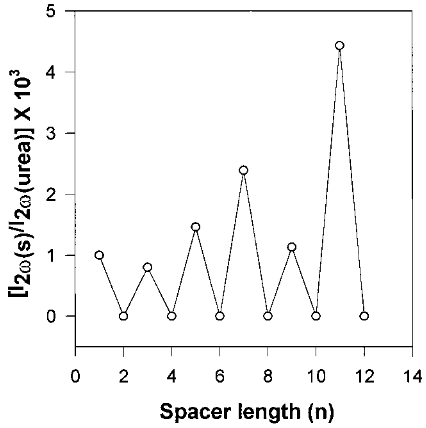


Figure 1. Plot of powder SHG efficiencies of the PNP-*n* twins taken as the ratio $[I_{2\omega(\text{sample})}/I_{2\omega(\text{urea})}] \times 10^3$ versus the spacer length (*n*).

Maximum SHG in Poled Films. Typically, PMMA films doped with 10 wt % of the twin chromophores, PNP-*n*, were poled using the setup described in the Experimental Section. The poling setup was standardized using a pure sample of disperse red (DR-1), and the order parameter was estimated in the usual manner from the absorbances in their UV–visible spectra before and after poling. The value obtained for DR-1 in PMMA using our setup was found to lie between 0.27 and 0.3, which was comparable to the earlier reported values.[34,35] The expected small shift in the λ_{max} value to slightly longer wavelengths upon poling was also noticed. Further, the poled samples were annealed at a temperature slightly above their T_g, to ascertain complete recovery to the original absorbance value. In all cases the extent of recovery was around 95%. This ensured that the decrease in absorbance upon poling was indeed due to the alignment of the chromophores and not due to an inadvertent loss of dye during the heating–poling–cooling cycle. Typically, the film thickness varied from 2.2 to 5 μm. The $\chi^{(2)}$ values were calculated using the equation[7,36]

$$\chi^{(2)}_{(\text{film})} = (2/\pi)\chi^{(2)}_{(\text{quartz})} \{[I_f(n_f)^3(l_{c,Q})^2]/[I_Q(n_Q)^3(l_f)^2]\}^{1/2} \quad (2)$$

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 the film and quartz, l_f and $l_{c,Q}$ are the film thickness and coherence length of quartz, respectively. $\chi^{(2)}_{(\text{quartz})}$ is taken as 1 pm/V, $l_{c,Q}$ as 20.6 μm, n_Q as 1.46, and n_f as 1.49. In addition, the $\chi^{(2)}_{(\text{film})}$ obtained using eq 2 was

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Table 2

sample	$I_{2\omega(\text{sample})}/I_{2\omega(\text{urea})}$ ($\times 10^3$)[a]	l_{film}[b] (μm)	N[c] (10^{20}/cm^3)	$\chi^{(2)}$[d] (pm/V)	τ_2[e] (min)	τ_1[e] (min)
PNP-1	1.0	2.2	2.2	1.7	179	1.4
PNP-2	0	4.9	2.1	1.2	132	2.2
PNP-3	0.8	4.8	2.1	1.4	112	2.3
PNP-4	0	4.1	2.0	1.2	159	1.2
PNP-5	1.5	4.2	1.9	1.7	211	1.6
PNP-6	0	4.6	1.8	1.5	164	1.6
PNP-7	2.4	4.2	1.7	1.9	158	2.1
PNP-8	0	4.8	1.7	1.8	148	2.7
PNP-9	1.1	3.6	1.6	2.3	211	1.8
PNP-10	0	5.0	1.6	1.9	144	1.8
PNP-11	4.4	3.2	1.5	2.7	149	1.4
PNP-12	0	2.9	1.5	1.7	173	2.1

[a] Powder SHG measurements. [b] These were measured using Profilometer, and the average error bar is ca. 2%. [c] Number density of doped films calculated using eq 1. [d] Second-order susceptibility of doped film poled at 100 °C and measured at 25 °C. Values normalized with respect to film thickness and number density. [e] Characteristic relaxation times from eq 2 for films poled at 100 °C and relaxation studied at 70 °C.

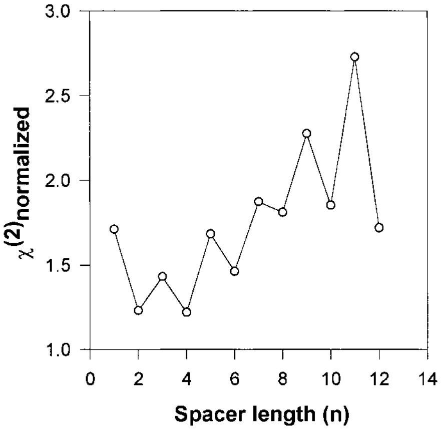

Figure 2. Plot of maximum attainable SHG in doped films at 25 °C: $\chi^{(2)}$(normalized) versus spacer length (*n*).

normalized with respect to both the thickness of the film and the number density.[37] The normalized values thus obtained are reported in Table 2. Interestingly, the plot of $\chi^{(2)}_{(\text{film})}$ vs spacer length *n* (Figure 2) showed an odd–even variation; the even ones exhibit a finite although smaller value compared to their odd counterparts. This is unlike the findings in the powder measurements, where the even ones produced no SH signal. The $\chi^{(2)}_{(\text{film})}$ values typically ranged from 1.2 to 2.7 pm/V, with PNP-11 having the highest value—an observation that reflects a rather unexpected similarity to the powder data. It is, of course, not surprising that the even twins exhibit a significant SH signal in doped systems unlike that in the crystalline form, 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 crystal packing considerations. Although the even twins have nonzero SHG values, they are less than that of their odd counterparts. In the presence of an electric field, the dipoles associated with the chromophores of each twin molecule are subjected to a torque, which forces them to take up a "U-shaped" geometry with the chromophoric dipoles aligned in the field direction. In the most stable conformation, the polymethylene spacers will tend to adopt an extended all-trans geometry—distortion from this geometry to one where the two chromophoric dipoles are oriented in the same direction (the field direction) appears to be more difficult in the even cases as compared to the odd ones, leading to this observed odd–even oscillation in these systems. *This rather unprecedented behavior in doped systems suggests that it may not be the overall flexibility of the spacer alone that governs the maximum attainable SHG values but that the exact number of atoms that link neighboring chromophores in main chain NLO polymers could play an important role.* This effect, of course, would be expected to disappear when the spacer lengths are very long.

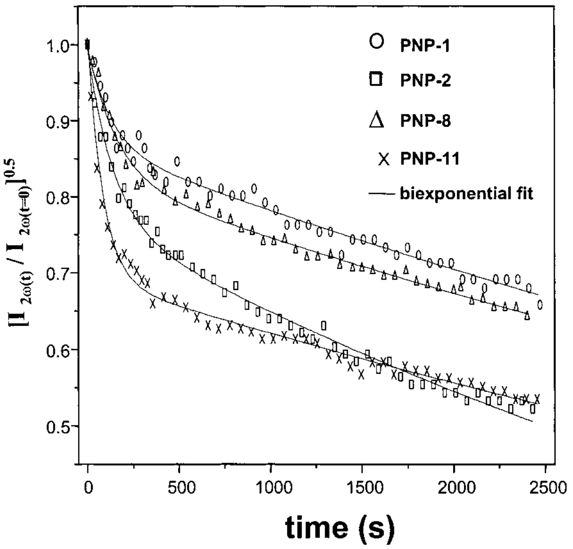

Figure 3. Typical relaxation profile of the SHG signal, $[I_{2\omega(t)}/I_{2\omega(t=0)}]^{0.5}$ versus time (s): (○) PNP-1; (□) PNP-2; (△) PNP-8; (×) PNP-11. The full line is the biexponential fit to the relaxation.

SHG Relaxation Studies. To understand the role of the spacer in governing the temporal stability of 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 min of poling at 100 °C, 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. The threshold field for the appearance of a measurable signal in most systems was about 2.4 KV; thereafter the signal increased steadily and reached a maximum at 5 KV in about 1–2 min. During the 10 min poling time at 100 °C, the signal reduced to about 90–95% of the maximum initially attained intensity. Thereafter, while the temperature was being reduced to 70 °C (which took about 20 min), the signal decreased further to about 65% of the initial value. Such behavior was also observed by others and has been ascribed to the corona field effect.[38] A few typical relaxation profiles of the SHG signal are shown in Figure 3. Attempts to

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(37) Here we have assumed that the concentration of the doped dye is in the regime where the SH signal varies linearly with the number density. Since the maximum concentration we are working with is 10 wt %, this assumption is reasonable—the onset of nonlinearity in most systems investigated thus far occurs at a much higher concentration.

(38) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds., *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

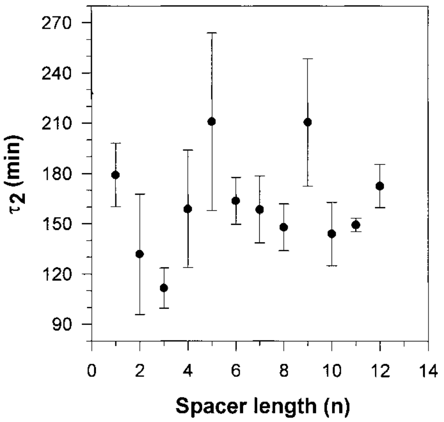

Figure 4. Plot of characteristic relaxation time τ_2 versus spacer length (n).

fit these data to the commonly used stretched exponential (KWW) function did not yield satisfactory results. However, the data could be readily fit to a simple biexponential function[36,39−40] of the form

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

Here $I_{2\omega(t)}$ is the SHG intensity at any given time and $I_{2\omega(t=0)}$ is that at the start of the relaxation, at which point the high voltage was turned off. τ_1 and τ_2 are the characteristic relaxation times for the fast and slow components of the decay, respectively. τ_1 values typically lie between 1 and 3 min for all the members of the series, and this process is probably due to the depletion of surface charge effects. τ_2, on the other hand, represents the chromophore reorientation dynamics and hence is often related to both the structure of the chromophore and the polymer matrix as confirmed by many earlier studies. The plot of τ_2 versus the spacer length, n, is shown in Figure 4, and the actual values of both τ_1 and τ_2 are given in Table 2. It is apparent from the plot that the τ_2 value goes through a minimum for $n = 3$ and then increases until it levels off (within experimental error) after $n = 5$. Each relaxation experiment was carried out twice with two different films using the same dye concentration. The error bars in some of these measurements were somewhat high, in a few cases as high as 27%. The average value obtained from the two measurements was used for the analysis. The presence of several variables, during the film preparation, film drying, poling, and the SHG measurements, leads to these composite high error bars in the final SHG values obtained. Despite this intrinsically high uncertainty, it is apparent that the τ_2 value appears to go through a minimum for short spacer lengths. This variation of the τ_2 values with n can be rationalized as follows: upon application of an electric field two competing forces operate—one that results in the orientation of the chromophores in the direction of the field, while the other that affects a disordering. The disordering in simple isolated chromophores (under dilute conditions) is primarily entropy-driven, while at high concentration (high number densities) repulsive electrostatic interactions between aligned dipoles can drive the disordering process. Previous workers[32,41] have shown that in electric-field poling experiments, the NLO response initially increases linearly with the number density, N, before it reaches a maximum value; beyond this it decreases with increasing N. This decrease has been ascribed to the electrostatic repulsion between closely spaced oriented dipoles. The expected onset of nonlinearity of the SH signal with the number density was calculated to occur around $(8-30) \times 10^{20}/\text{cm}^3$ for systems having a dipole moment ranging from 5 to 10 D. The chromophore number density in the current study is fairly low, typically in the range of $(1.5-2.2) \times 10^{20}/\text{cm}^3$, and hence intermolecular chromophore−chromophore interactions would be negligible. However, due to the fact that two chromophores are linked together in the twin systems by spacers of varying length, it is very likely that electrostatic repulsion between oriented dipoles can indeed contribute to drive the disordering process. This would especially be true when the spacer segments are small, while this effect would be far less when the spacer is long. Thus, the minimum in the plot of τ_2 versus n is perhaps due to this electrostatic repulsion-driven intramolecular reorientation process, which dominates at the short spacer lengths. At spacer lengths >5, this factor, it appears, does not contribute significantly to the overall relaxation process and the value of τ_2 becomes less sensitive to n. Beyond this "optimum" spacer length, the number of conformations where the two chromophores are parallel but close to each other becomes small, and the two chromophores of a single twin molecule can remain oriented in the field direction without having to experience the presence of the other. In the case of PNP-1, it appears that due to the significantly reduced conformational degrees of freedom, the electrostatic repulsion is not readily overcome by adoption of alternate conformations (which are invariably of higher energy), the lowest energy conformation being one where the chromophores are biaxially oriented with their dipoles adding cumulatively. It must be added here that while this hypothesis presupposes that a significant contribution to the overall disordering process comes from the intramolecular component, the effect of complete rotational reorientation (molecular tumbling), as seen in simple systems, could also be important. The latter, however, is unlikely to exhibit the kind of dependence with n that we observe in the case of the twin systems and furthermore would require a much larger free volume—probably one that would not be readily available at temperatures significantly lower than T_g.

In conclusion, we have demonstrated that twin chromophoric molecules represent a unique class of NLO systems that exhibit several novel features both in the crystalline solid form and when dispersed in a polymer matrix. The interesting odd−even oscillation of the SHG intensity in the powder measurements points to the dominant role of the spacer in governing the packing in the crystalline solid, the even ones appearing to pack

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(39) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3648.

(40) Branger, C.; Lequan, M.; Lequan, R. M.; Large, M.; Kajzar, F. *Chem. Phys. Lett.* **1997**, *272*, 265.

(41) Harper, A. W.; Sun, S.; Dalton, L. R.; Garner, S. M.; Chen, A.; Kalluri, S.; Steier, W. H.; Robinson, B. H. *J. Opt. Soc. Am. B* **1998**, *15*, 329.

in a centrosymmetric manner. The unprecedented observation of a similar oscillation in the maximum attainable SHG value in molecular doped poled polymer systems further strengthens the case for a more detailed study of the role of the spacer in main chain NLO polymers, a model of which these twin chromophores represent. Furthermore, the characteristic relaxation time τ_2, for the reorientational dynamics of these twin systems, demonstrates the interplay between two factors that dominate the relaxation, namely, the electrostatic repulsion between two oriented dipoles and the conformational flexibility of the linking spacer.

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