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## Liquid Crystals

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## The second and third order non-linear optical properties of liquid crystalline polymers

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The second and third order non-linear optical susceptibilities of several donor-acceptor substituted side chain polymers, some of which exhibit mesophases, will be reported. The susceptibilities were measured by harmonic generation from thin films, typically 0.5  $\mu\text{m}$  thick, at a fundamental wavelength of 1064 nm and 1579 nm. For second harmonic generation, the spin coated films were contact poled on a glass substrate with an interdigitated electrode pattern. Typical values obtained were  $\chi_{31}^{(2)} = 1 \times 10^{-9}$  esu and  $\chi_{33}^{(2)} = 3 \times 10^{-9}$  esu, the largest value was  $\chi_{33}^{(2)} = 6.3 \times 10^{-9}$  esu. The difficulty in deriving reliable second order structure-property relations because of the large effect which the contact poling process has on the non-linear optical susceptibility of the films will be highlighted. The highest  $\chi^{(3)}$  value of  $5.8 \times 10^{-12}$  esu obtained from an amorphous film of a polymer with an asymmetrically substituted azo side group is comparable with the susceptibility of more typical third order non-linear materials such as the main chain polymers polyphenylacetylene and poly-*p*-phenylenebenzobisthiazole.

### 1. Introduction

Non-linear optical (NLO) processes [1, 2] such as harmonic generation, parametric amplification, optical bistability and phase conjugation find applications in the fields of optoelectronics and optical signal processing. Organic NLO materials, particularly those with delocalized  $\pi$ -electron systems distorted by donor and acceptor groups [3-6], have increasingly become the subject of study as second order NLO materials because of their large non-linearities when compared with inorganic crystalline materials. Early research into organic materials for second order processes considered the doping of polymer hosts with NLO dyes [7-9], however the solubility of the dye was limited and polymers with covalently attached dye side groups [10-14] were developed.

Typical third order organic non-linear optical materials reported so far have been main chain  $\pi$ -conjugated polymers such as polyphenylacetylene [15, 16], poly-*p*-phenylenebenzobisthiazole (PBT) [17], poly-(arylenevinylene) [18], poly-(2,5-thienylene vinylene) [19] and macrocycles such as phthalocyanines [20-22], although some interest has recently been shown in side chain polymers [23-25]. If side chain polymers can be developed to exhibit large second and third order non-linearities then a range of different non-linear optical processes may be integrated into a single material substrate.

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Organic materials and especially polymers allow great flexibility in molecular design and are easily processed into films and fibres for device applications. They also typically exhibit faster non-linear optical responses than inorganic materials, low absorption, broadband response and in most cases, good environmental stability. Organic polymer systems are therefore highly suitable for the non-linear optical devices of the future [26–29].

In this paper we will present values for the two non-zero elements of the second order NLO susceptibility tensor and the third order non-linear optical susceptibility measured from amorphous films for several side chain polymers and a novel main chain polymer. The susceptibility values were measured by harmonic generation from thin films, which in the case of the second harmonic were contact poled using an interdigitated electrode pattern. The dominant contribution to the macroscopic third order non-linearity in polymers containing conjugated linear side groups, is due to the component of the microscopic hyperpolarizability with all the electric fields along the side group long axis,  $\gamma_{zzzz}$ , and so the bulk third order susceptibility measured from amorphous films is often referred to as  $\chi_{3333}^{(3)}$ . A more accurate determination of the  $\chi_{3333}^{(3)}$  element of the third order susceptibility tensor requires bulk alignment of the non-linear optical side groups in the designated 3 direction and so the measured non-linear optical susceptibilities presented in this report will be referred to as  $\chi_{\text{film}}^{(3)}$ .

The significant effect which the contact poling process has on the susceptibility values will be discussed and the difficulty in deriving reliable second order structure–property relations because of this effect will be highlighted. The conductivity of the materials was investigated to determine whether this was the cause of the poor poling response of some of the materials.

## 2. Experimental

The structures and phase transitions of the materials are presented along with the susceptibility values in the table. All synthesis was performed by the collaborators who are detailed at the end of this paper. Phase identification was performed by optical microscopy and differential scanning calorimetry, unidentified phases are labelled M. The films were spin coated from solution in tetrahydrofuran on to glass substrates with interdigitated electrode patterns which typically produced films of 0.2–0.5  $\mu\text{m}$  thickness. The films were cured at elevated temperatures for 12 h to remove all traces of the solvent and the thickness measurements were made using a stylus profilometer.

The contact electric field poling method was used to achieve non-centrosymmetric ordering of the NLO side groups. The poling axis is in the plane of the glass resulting in the alignment geometry shown in figure 1. The materials were orientationally aligned in an alternating field at a temperature just below the transition to isotropic liquid. This alignment was stored as well as possible by rapidly cooling into the glass phase before applying the poling field of  $10 \text{ V } \mu\text{m}^{-1}$ , at a temperature a few degrees above the glass transition for a period of 24 h. The second order susceptibility was typically improved by a factor of three by the orientational alignment process when compared with application of the poling field to the material with no alignment history.  $\chi^{(2)}$  measurements were made immediately after the poling field had been removed.

The second and third order non-linear susceptibilities were measured by harmonic generation from the thin films at normal incidence at a fundamental wavelength of 1064 nm and the third order susceptibility was also measured at 1579 nm. The 1064 nm fundamental was obtained from a Q switched  $\text{Nd}^{3+}$ : YAG laser (Quanta Ray DCR II).

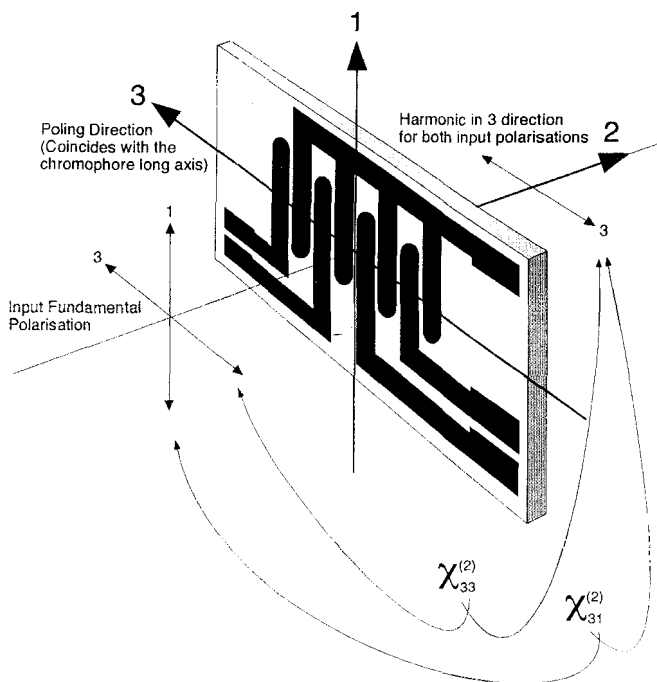


Figure 1. The interdigitated electrode cell and polarization orientation for second order nonlinear optical susceptibility measurements.

The 1579 nm fundamental was obtained by Raman shifting (Quanta Ray RS-1, hydrogen at 250 psi) the second harmonic of the 1064 nm fundamental produced by a commercial KDP harmonic generator. In the experimental arrangement shown in figure 2, the fundamental beam is filtered to remove lamp flash and the intensity controlled by neutral density filters. The fundamental and harmonics are collected and slightly focused through a monochromating filter and detected using a photomultiplier tube (Thorn EMI 9520). The fundamental and harmonic pulses are displayed and averaged on a fast digital oscilloscope (Hewlett Packard 54502A), triggered by a fast photodiode (Spectra Physics 403).

A poled polymer is represented by the  $C_{v\infty}$  symmetry [3, 30] for which the second order susceptibility tensor has been shown to be [3]

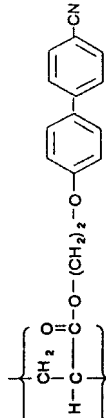
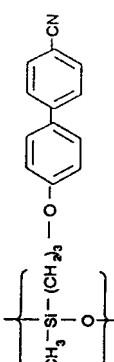
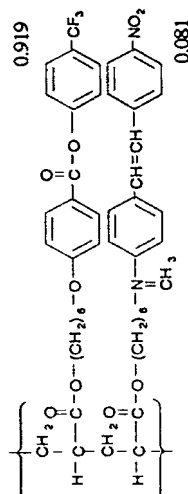
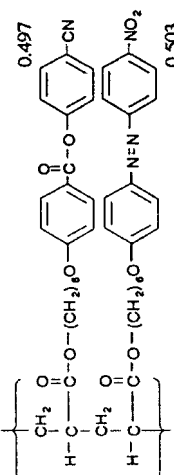
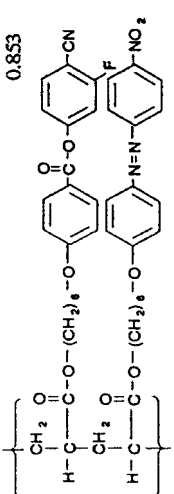
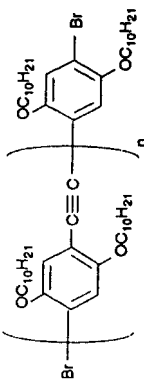
$$\begin{pmatrix} 0 & 0 & 0 & 0 & \chi_{31}^{(2)} & 0 \\ 0 & 0 & 0 & \chi_{31}^{(2)} & 0 & 0 \\ \chi_{31}^{(2)} & \chi_{31}^{(2)} & \chi_{33}^{(2)} & 0 & 0 & 0 \end{pmatrix} \quad (1)$$

for the geometry shown in figure 1. In the contracted notation  $31 = 311$  and  $33 = 333$  where 3 is along the poling direction.

The  $\chi^{(2)}$  values were calculated from the harmonic intensity measurements from the sample and the quartz reference using equation (2) [11],

$$\chi_s^{(2)} = \frac{2}{\pi} \chi_q^{(2)} \left( \frac{I_s^{(2\omega)}}{I_q^{(2\omega)}} \right)^{1/2} \frac{l_{c,q}}{l_s} \quad (2)$$

Material and phase behaviour	Structure	1064 nm		1579 nm
		$\chi_{33}^{(2)} \times 10^9$ esu	$\chi_{31}^{(2)} \times 10^{-9}$ esu	
A G 50°C M 160°C CI x = 11		$6.30 \pm 1.58$	$1.90 \pm 0.48$	$13.1 \pm 2.0$
B G 120°C CN 150°C CI		$6.00 \pm 1.50$	$1.24 \pm 0.31$	—
C G 32°C M 80°C CS <sub>A</sub> 124.5°C CN 132°C CI		$3.36 \pm 0.84$	$0.62 \pm 0.16$	$1.2 \pm 0.2$
D G 40.5°C CN 104°C CI		$3.00 \pm 0.75$	$0.87 \pm 0.22$ 0.88	—
E G 110°C CI		$2.55 \pm 0.64$	$0.86 \pm 0.22$	$5.6 \pm 0.8$
F G 30°C CS 125°C CI		$1.89 \pm 0.47$	$0.47 \pm 0.12$	$10.0 \pm 1.5$

<b>G</b> <b>G84°CN113.5°C I</b>		1.30 ± 0.33	0.23 ± 0.06	—	—
<b>H</b> <b>G30°CS<sub>A</sub>145°C I</b>		0.55 ± 0.14	0.13 ± 0.03	4.6 ± 0.7	0.6 ± 0.1
<b>I</b> <b>C59°CS<sub>A</sub>110°C I</b>		0.25 ± 0.06	0.06 ± 0.01	4.0 ± 0.6	1.3 ± 0.2
<b>J</b> <b>G14°CS<sub>A</sub>90°CN107.5°C I</b>		—	—	16.1 ± 2.4	3.2 ± 0.5
<b>K</b> <b>G10°CM90°C I</b>		—	—	3.5 ± 0.5	2.1 ± 0.3
<b>L</b> <b>G7°S<sub>A</sub>65°C N 100°C I</b>		—	—	35 ± 5.0	21 ± 3.0

where  $3 \leq n \leq 150$ 

The material phases, structures and second and third order non-linear optical susceptibilities measured at 1064 nm and 1579 nm.



impurities in the polymers. The conductivity of the materials was investigated and was found to be low in all cases, about  $10^{-7} (\Omega \text{ m})^{-1}$ . This suggests that the charge is injected from the electrodes or possibly from the glass substrate which will contain alkali metal ions which are known to migrate to the surface. The difference in poling response of each material due to different levels of impurities and structural differences in the backbone and spacer unit make the determination of reliable second order structure–property relations difficult. This is demonstrated well by materials C, G and H, which all contain the same cyanobiphenyl NLO group, but exhibit  $\chi_{33}^{(2)}$  which differ considerably. The different spacer length and backbone type have an effect on the poling response and the different packing densities of the NLO side groups will also affect the measured susceptibility values. The increase in conjugation and planarity present in the azo and stilbene based side groups leads to an increase in susceptibility in general over the simple biphenyl side group and materials with the nitro acceptor group exhibit larger values in general than the cyano based materials.

The typical response of the materials to the poling field is shown in figure 3. In the simple thermodynamic model [32] of the poling process, the  $\chi_{33}^{(2)}$  element of the tensor is shown to be proportional to the third order Langevin function  $L_3(p)$ ,

$$L_3(p) = \left(1 + \frac{6}{p^2}\right)L_1(p) - \frac{2}{p^2} + \dots, \tag{4}$$

where

$$L_1(p) = \coth\left(\frac{p-1}{p}\right) \quad \text{and} \quad p = \mu E/kT. \tag{5}$$

$\mu$  is the microscopic non-linear optical dipole moment,  $E$  is the poling field strength,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The expression for  $L_3(p)$  may be expanded to give,

$$L_3(p) = \frac{p}{5} - \frac{p^3}{105} + \dots \tag{6}$$

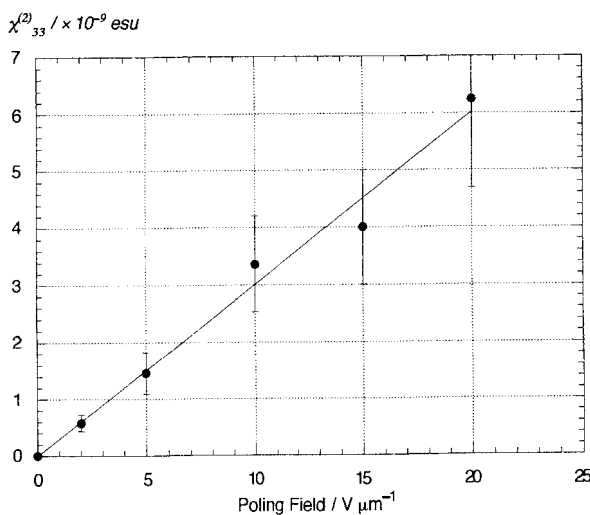


Figure 3. The second order nonlinear optical susceptibility as a function of the poling field strength. Note the linear behaviour, which corresponds to the linear regime of the thermodynamic model for poling.



The linear increase in  $\chi_{33}^{(2)}$  with poling strength shown in figure 3, is consistent with the linear region of the third order Langevin of equation (6). The linear behaviour implies that the  $\chi_{33}^{(2)}$  can be significantly increased, since the poling response is well below saturation according to the model; however, an increase in the poling field strength leads to increased damage of the material and electrodes and this must be overcome by an improvement in the poling technique. In the linear or low field region of the poling response, the thermodynamic model predicts that  $\chi_{31}^2 = \chi_{33}^{(2)}/3$  for a poled isotropic material and  $\chi_{31}^{(2)} = 0$ , if the liquid crystallinity of the material is accounted for using the Ising model. The results indicate that the liquid crystallinity has some effect on poled ordering, which was first reported by Amano *et al.* [11], since  $\chi_{31}^{(2)} < \chi_{33}^{(2)}/3$  for many of the liquid crystalline materials. The results for material E, which does not exhibit mesophase behaviour, coincide well with the factor of 3 relationship between the two susceptibilities for a poled isotropic material. Although, according to the thermodynamic model, liquid crystalline ordering may lead to an increase in the  $\chi_{33}^{(2)}$  value by a factor of 5 over the poled isotropic case, this element of the tensor cannot be angle phase matched and the decrease in the phase matchable element,  $\chi_{31}^{(2)}$ , in liquid crystalline materials may not be desirable.

### 3. Third order results

The largest  $\chi_{\text{film}}^{(3)}$  value of  $5.8 \times 10^{-12}$  esu, obtained from material E, is comparable with the susceptibilities of more typical third order main chain polymers such as polyphenylacetylene [15, 16]. The larger susceptibilities at 1064 nm are due to resonant enhancement since the third harmonic at 355 nm lies well within the absorption region of the materials. Those materials which exhibit significant absorption at 526 nm, mainly the azo dye based materials, also show a resonantly enhanced third order susceptibility at the higher wavelength when compared with the simple biphenyl side groups, which have very low absorption in the visible range. The increase in third order response of the azo and stilbene side groups is also due to the increase in conjugation when compared with the biphenyl groups, since the power law dependence of the third order susceptibility on number of conjugated electrons has been shown to have an exponent between 3.5 [23] and 5 [33]. The third order response of the azo and stilbene based materials reported here, which are slightly higher than in similar materials reported in the literature [23], can be expected to increase by an order of magnitude [24] with the addition of another azo unit. The increase in planarity of the more conjugated units when compared with the biphenyl group may also increase electron mobility and third order response. The poor conjugation in the benzoate side groups results in a significant decrease in the third order response at both wavelengths.

The third order results for the side chain polymers may be compared with the novel main chain polymer, material L. This material is highly conjugated and although it does not show the largest non-linear susceptibility, it exhibits a wide band response which is not typical of the side chain polymers.

### 4. Conclusions

The second and third order NLO susceptibilities of some side chain polymers have been presented. The largest  $\chi_{33}^{(2)}$  value obtained is nearly three times the  $\chi_{36}^{(2)}$  value of KDP. The effect of liquid crystalline ordering on the second order NLO susceptibility of poled side chain liquid crystal polymers has been demonstrated, however, the effect is not as great as the simple thermodynamic model would suggest. The disadvantage of

the effect of self ordering for angle phase matched second harmonic generation in such materials, that is the reduction in the size of the phase matchable element,  $\chi_{31}^{(2)}$ , was discussed.

The difficulty in deriving reliable second order structure–property relations, due to the large effect which the poling process has on the second order bulk susceptibility has been highlighted and consequently only the broad trends in the susceptibility values have been correlated with the conjugation and acceptor groups. The second order NLO potential of side chain polymers is restricted by the poor degree of poled ordering which can be obtained and the results indicate that a significant increase in the susceptibility values can be expected if larger poling fields could be applied without damaging the materials. Work is continuing to improve the poling process, which has already been enhanced by initially orientationally aligning the materials in an alternating electric field before the poling field is applied.

Third order non-linear optical susceptibilities have been presented for a range of side chain polymers with relatively short conjugation lengths, the largest of which,  $5.8 \times 10^{-12}$  esu, is comparable with more typical long conjugated third order main chain polymers such as polyphenylacetylene. This value is still between one and two orders of magnitude smaller than the best organic material such as polydiacetylene and phthalocyanine; however, since the asymmetrically substituted side chain polymers have also been shown to possess large second order responses, they may be considered as ideal materials for non-linear optical devices in which both second and third order processes can be performed in a single material substrate. An increase in third order response in side chain polymers due to increased conjugation in azo and stilbene groups when compared with biphenyl and benzoate groups has been shown.

Improvements in the third order response of this type of material, by at least an order of magnitude, may be achieved by increasing the conjugation length of the side group by adding another azo linkage and benzene ring. Alignment of the side groups either in electric fields or using the liquid crystalline ordering exhibited by most of these materials may also increase the bulk susceptibility.

The good optical quality, processibility and degree of freedom in molecular design combined with a significant third order response as well as the more commonly reported large second order susceptibilities suggests that side chain polymers are ideal materials for the non-linear optical devices of the future.

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