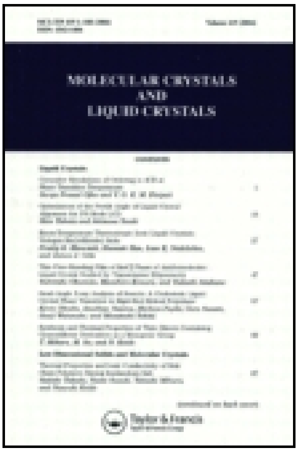

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Third Order Non-linear Optical Properties of Side Chain Liquid Crystalline Polymers Studied by Third Harmonic Generation from Thin Films

D. A. McI. Smith [a] [b] & H. J. Coles [a]

[a] Liquid Crystal Group, Physics Department, Schuster Laboratory, Manchester University, Manchester, M13 9PL, UK

[b] Currently at the Center for Self-Organising Molecular Systems, Leeds University, Leeds, LS2 9JT

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Third Order Non-linear Optical Properties of Side Chain Liquid Crystalline Polymers Studied by Third Harmonic Generation from Thin Films

D. A. MCL. SMITH* and H. J. COLES**

Liquid Crystal Group, Physics Department, Schuster Laboratory, Manchester University, Manchester M13 9PL, UK

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Highly-conjugated main chain polymers have been studied extensively in recent years as third order non-linear optical materials. However, in a non-centrosymmetric system such as a polyene which has been substituted with an electron donor and acceptor group, the relaxation of certain selection rules results in an increase in the static third order hyperpolarisibility. Consequently, there has been recent interest in the third order non-linear optical properties of materials more typically studied for their quardratic non-linear response. One of the driving forces for this work has been the possibility of producing single device substrates possessing significant second and third order non-linearities which could lead to highly integrated optical devices.

We present the third order non-linear susceptibilities of some asymmetrically-substituted, side-chain liquid crystalline polymers, measured in amorphous thin films by third harmonic generation at 1064 nm and 1579 nm. The highest $\chi^{(3)}$ value of $1.02 \times 10^{-18}\,\mathrm{m^2/V^2}$ from a polymer with an azo side group is expected to have some resonance contribution and is comparable with the non-resonant susceptibility of main chain polymers such as poly(phenylacetylene) and poly(*p*-phenylenebenzobisthiazole).

Keywords: Non-linear optics, third order non-linear optical susceptibility, side chain polymer, third harmonic generation, thin films

INTRODUCTION

Third order non-linear optical processes such as harmonic generation, optical bistability and phase conjugation find application in laser physics, optoelectronics and optical signal processing and this wide range of applications has lead to an increasing interest in and requirement for third order non-linear optical materials. Organic non-linear optical materials[1–9] can possess large off-resonant non-linearities when compared with inorganic crystalline materials, low absorption resulting in higher laser damage thresholds, a broad band response and in most cases, good environmental stability. The electronic polarisation which is the origin of the optical non-linearity in organic

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[*] Currently at the Center for Self-Organising Molecular Systems, Leeds University, Leeds LS2 9JT.

[**] Author to whom correspondence should be addressed.

materials occurs on a time scale of typically 10^{-15}–10^{-14} seconds which is faster than the ionic or atomic displacements or electrostrictive effects in inorganic crystals. Another feature which has lead to the interest in organic materials is the extent to which the structures may be modified at low cost, which allows detailed structure–property investigations to be performed. Organic polymers are easily processed into films and fibres which are highly suitable substrates for integrated optical devices, unlike inorganic crystalline materials which suffer from the requirement for large single crystal growth. However, further advances are still needed in the tuning of the non-linear optical properties of organic materials in order to satisfy the stringent requirements of photonics devices which mainly rely on inorgnic ferroelectric materials at present.

Highly π-conjugated main chain polymers such as poly(phenylacetylene),[2,3] poly(*p*-phenylenebenzobisthiazole),[4] poly(arylenevinylene),[5] poly(2,5-thienylene vinylene)[6] and macrocycles such as phthalocyanines[7–9] have been studied as third order non-linear optical materials. These materials have been shown to possess large third order non-linear susceptibilities and relatively small linear and non-linear absorption coefficients which implies that optical power densities may be kept to a minimum, reducing heating of the substrate and permiting long device path lengths. In conjugated systems, it is an instantaneous shift in the π-electrons over the whole molecule which leads to large and fast polarisibilities taking place on the femtosecond time scale. In these essentially linear systems, the dependence of the non-linear response on the chain length has been of interest since there exists a trade-off between increasing non-linear efficiency due to greater conjugation and reduced packing densitiy of the larger molecules. Saturation of the non-linear efficiency has been consistently shown to occur after about 50 carbons.[10] Up to this saturation point the non-linear optical response has been shown to obey a power law dependence on the chain length. The power value itself has been shown theoretically[10] and experimentally[11] to take values in the range 2.5 to 7. In this type of material there also exists a strong electron-phonon coupling which can cause relaxation of the molecular geometry after excitation and may produce non-linear excitations such as solitons and polarons which can enhance the non-linear optical response.[12] In inorganic ferroelectric materials the non-linear response is governed by small ionic displacements, the speed of which is limited by vibrational relaxtion times and which are therefore inherently smaller and slower than the purely electronic response of organic materials.

In the three-state model of Kajzar and Messier,[13] Garito[14] and Dirk and Kuzyk,[15] which describes the origin of the electronic non-linear optical response in organic materials, the expression for the third order molecular hyperpolarisibility contains a term which is only present in a non-centrosymmetric system. This increase in the third order non-linearity due to asymmetric substitution of a poly(ene) has been demonstrated by Garito *et al.*[16] and in the light of this some recent interest, been shown in dye attached polymers[17] and push-pull aromatic-quinoidal structures[18] as third order non-linear optical materials.

In this report we present the third order non-linear optical susceptibilities of a range of side chain liquid crystalline polymers, with asymmetric substitution of the conjugated side groups by electron donors and acceptors. The second order non-linear optical susceptibilities of these materials have been previously reported.[19] The third order non-linear optical susceptibilities were measured in thin, amorphous, spin-coated films, typically 0.2 μm thick, by third harmonic generation at fundamental wavelengths of 1064 nm and 1579 nm, relative to a fused silica reference. A simple thin film approximation for the third order non-linear susceptibility is used which relies on the coherence length of the materials being much greater than the film thickness. When considering these types of material which contain only short conjugated side groups, a discussion of saturation of optical non-linearity as in the case of conjugated main chain polymers is clearly not required and since the side groups are all approximately the same size a power law dependence of susceptibility on conjugation cannot reliably be investigated. We will, however, attempt to interpret our results in terms of some simple structure-property relations and discuss the contribution of resonance enhancement at the two excitation wavelengths in the different materials.

EXPERIMENTAL

A range of side chain polymers some of which exhibit mesophases was studied as third order non-linear optical materials by third harmonic generation from thin amorphous films. The range of materials include polymers based on siloxane and acrylate backbones with asymmetrically-substituted biphenyl, stilbene, azo and benzylidene side groups. The materials were synthesised and characterised by our collaborators who are detailed in the acknowledgements. The thin films were produced by spin coating from solution in THF and the thicknesses, which typically lay in the range 0.2–0.3 μm, were measured using a mechanical profilometer. The films were cured at elevated temperatures for 12 hours to remove any remaining solvent before the thicknesses and susceptibilities were measured.

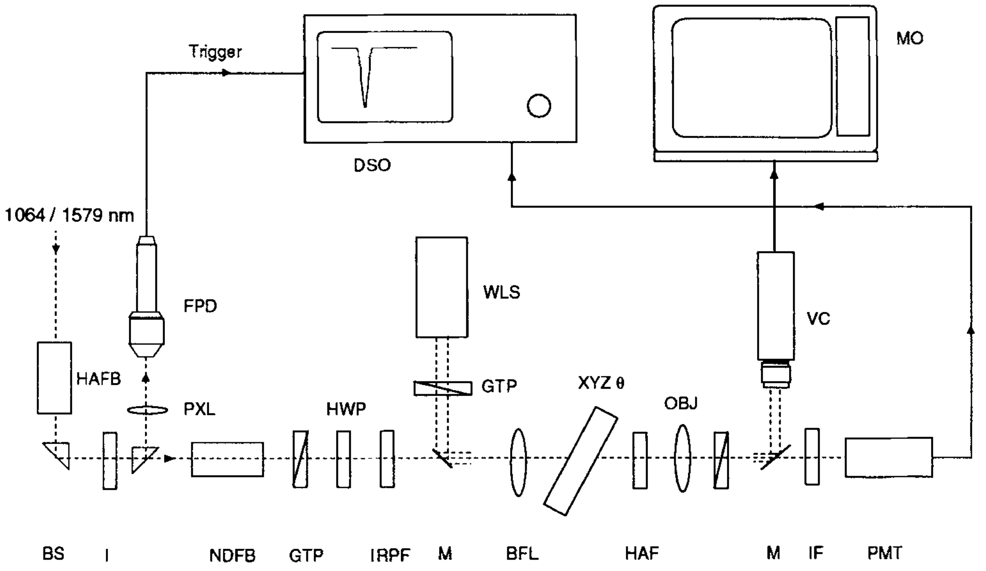
The 1064 nm fundamental from a Q-switched Nd:YAG laser (Quanta Ray DCR II) frequency doubled and used to pump hydrogen at 250 psi to obtain the Raman shifted wavelength at 1570 nm (Quanta Ray RS-1). In the experimental arrangement shown in Figure 1, the fundamental beam is filtered to remove lamp flash and the intensity is controlled by heat absorbing glass and neutral density filters. The fundamental and third harmonic are collected and slightly focused through a monochromating interference filter with a 2 nm bandwidth 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 54502 A), triggered by a fast photodiode (Spectra Physics 403).

The polarisation of a material at the third harmonic frequency due to an applied optical electric field may be written in terms of the third order non-linear optical susceptibility,[1]

$$P_i(3\omega) = \chi^{(3)}_{ijkl}(-3\omega;\omega,\omega,\omega)E_j(\omega)E_k(\omega)E_l(\omega) \tag{1}$$

where standard tensor notation has been adopted. The third harmonic intensity may be obtained by solving Maxwell's equations incorporating the non-linearity in the polarisation given by Equation 1 and is approximately given by[1]

$$I_{3\omega} = \frac{(3\omega)^2}{n_{3\omega}n_\omega c^4\varepsilon_o^2}\frac{\sin^2(\Delta k(l/2))}{(\Delta k(l/2))^2}|\chi^{(3)}|^2 l^2 I_\omega^3 \tag{2}$$



GTP	Glan-Taylor Polariser	M	Mirror (Removable)	PMT	Photomultiplier Tube
FPD	Fast Photodiode	DSO	Digital Storage Oscilloscope	IF	Interference Filter
PXL	Plano Convex Lens	TC	Temperature Controller	WLS	White Light Source
NDFB	Neutral Density Filter Box	VC	Video Camera	IRPF	Infra Red Pass Filter
HWP	Half Wave Plate	MO	Monitor	XYZ θ	Rotating Sample Holder
BS	Beam Stearing Prism	I	Iris	HAF	Heat Absorbing Filter
HAFB	Heat Absorbing Filter Box	BFL	Best Form Lens	OBJ	Collection Objective

FIGURE 1 The nonlinear optical experimental arrangement.

where n is the refractive index at the frequency indicated by the subscript, l is the sample thickness, I_ω is the intensity of the fundamental and Δk is the mismatch between the wave vector at the fundamental and the third harmonic frequencies.

In the case of thin amorphous polymer films, where the sample thickness is much less than the coherence length[1] of the material, the third order susceptibility, relative to a reference sample is given by Equation 3,[19]

$$\chi^{(3)}_{\text{film}} = \frac{2}{\pi}\chi^{(3)}_{fs}\left(\frac{I^{(3\omega)}_{\text{film}} - I^{(3\omega)}_{\text{glass}}}{I^{(3\omega)}_{fs}}\right)^{1/2}\frac{l_{c,fs}}{l_{\text{film}}} \tag{3}$$

where $\chi^{(3\omega)}_{fs}$ is the third order non-linear optical susceptibility of the fused silica reference material, ($5.5 \times 10^{-21}\,\text{m}^2/\text{V}^2$ and $5.0 \times 10^{-21}\,\text{m}^2/\text{V}^2$ at 1064 nm and 1579 nm respectively), $l_{c,fs}$ is the coherence length of fused silica, (18.24 μm and 18.35 μm at 1064 nm and 1579 nm respectively) and l_{film} is the film thickness. $I^{(3\omega)}_{\text{film}}$ and $I^{(3\omega)}_{fs}$ are the peak third harmonic intensities from the sample and fused silica reference respectively and $I^{(3\omega)}_{\text{glass}}$ is the third harmonic intensity obtained from a clean glass substrate at the same input fundamental power. In most cases no third harmonic signal was detected from the glass substrate at the low power levels used in these measurements, however, at 1579 nm a small signal was detected in some cases. The third harmonic intensities were crudely corrected for absorption by the coloured polymer films by *in situ* absorption measurements. The form of the absorption spectra, shown in Figure 2, were obtained from 1 cm path length solutions in THF.

It should be noted that Equation 3 is only applicable when the film thickness is much less than the coherence length of the polymer, typically 5–15 μm. Whether this condition is met may be verified by rotating the sample film and observing the dependence of the third harmonic signal. If the films are thicker than the coherence length of the material then a Maker fringe pattern would be observed, however, all the films exhibited a monotonic variation of third harmonic intensity with incident angle indicating that the assumption made in deriving Equation 3 is valid.

RESULTS AND DISCUSSION

The third order non-linear optical susceptibilities and structures of the polymer side groups are summarised in Table 2. Since the third order susceptibility is not restricted by the same symmetry requirements as the second order susceptibility, the backbone in a side chain polymer will contribute to the measured third order susceptibility of the material. The three backbone structures are shown in Table 1. In order to derive reliable structure-property relations regarding the side groups, the third order susceptibilities of the backbones were determined by third harmonic generation from poly(methylmethacrylate) and poly(siloxane) thin films and are also given in Table 1. The poly(phosphazine) backbone of material **IV** was not available in an unsubstituted form and consequently the contribution of the backbone to the third order non-linear optical susceptibility of this polymer is unknown. If the contributions of the backbone and side groups are crudely assumed to be additive then in most cases the contribution due to the backbone in side chain polymers is seen to be small, especially in the case of the acrylate backbone which is not conjugated. However, in the simple cyanobiphenyl side chain polymer **V**, the siloxane backbone seems to contribute significantly to the value obtained. The origin of a third order susceptibility in the siloxane backbone is due to delocalisation of the σ electrons. Some interest has been shown recently[20] in the third order non-linear optical properties of related materials such as poly(silane) and poly(germane) which have susceptibilities an order of magnitude greater than poly(siloxane).

The largest third order susceptibilities are exhibited by materials containig azo-, stilbene- and benzylidene-based side groups. The increase in susceptibility when compared with the simple biphenyl group is due to increased conjugation and a more favourable conformation for polarisation i.e. more planar. The materials containing the benzoate and biphenyl side groups typically exhibit and order of magnitude lower third order susceptibility. However, these groups may also be expected to have a smaller resonance contribution than the azo, benzylidene and stilbene groups on the basis of their absorption spectra. The relative efficiencies of the azo and benzoate groups may be compared in copolymers **VIII** and **X**, which possess both groups in different proportions. In materiral **VIII**, 50% of the side groups contain the azo linkage

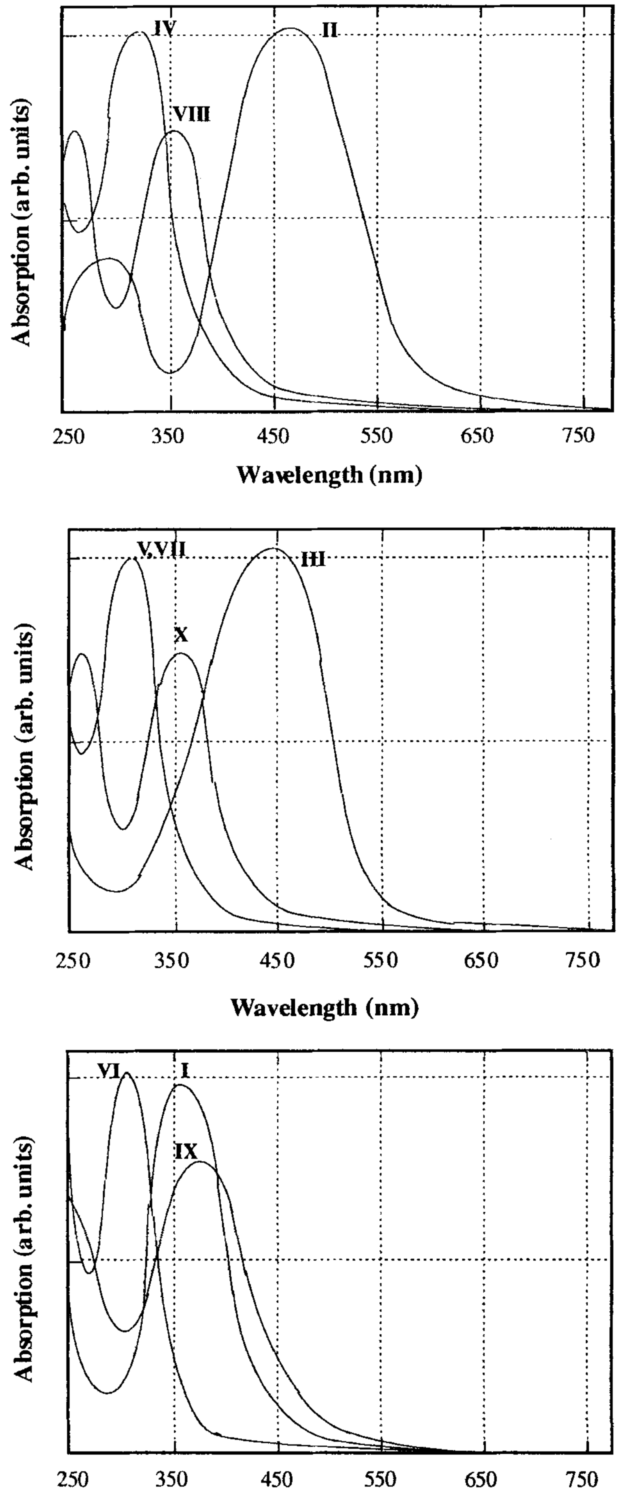
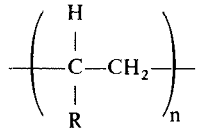
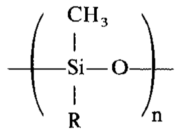
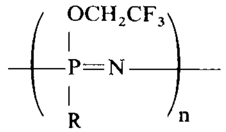


FIGURE 2 The absorption spectra of the materials obtained in solution in tetrahydrofuran.

TABLE I

The structure of the three types of polymeric backbone in the side chain liquid crystalline polymers and the third order nonlinear optical susceptibility determined by third harmonic generation from thin films at 1064 nm and 1579 nm

Backbone Structure		$\chi^{(3)}_{\mathrm{eff}}$ (× 10^{-21} m^2/V^2)	
		1064 nm	1579 nm
(A) Polyacrylate	 $\left(-\underset{R}{\overset{H}{C}}-CH_2-\right)_n$	14.7 ± 2.2	5.2 ± 0.8
(B) Polysiloxane	 $\left(-\underset{R}{\overset{CH_3}{Si}}-O-\right)_n$	22.8 ± 3.4	8.8 ± 1.3
(C) Polyphosphazine	 $\left(-\underset{R}{\overset{OCH_2CF_3}{P}}=N-\right)_n$	–	–

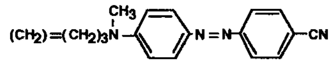
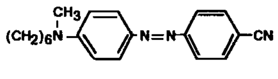
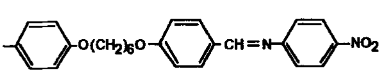
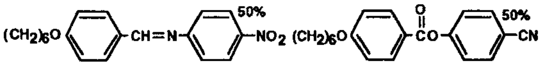
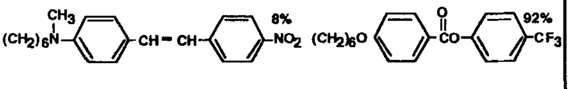
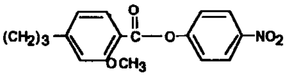
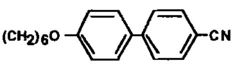
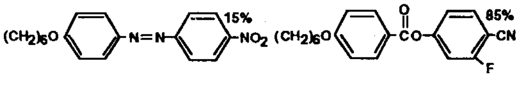
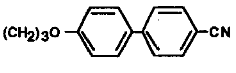
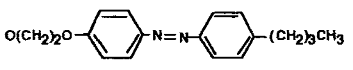
when compared with material **X**, in which this group occur at 14.7% concentration and this leads to an order of magnitude larger third order susceptibility in material **VIII**.

The exact contributions of resonance enhancement to the values discussed above are not known and the results appear to contradict what might be expected from a simple analysis of the absorption spectra in Figure 2. For example, in the case of those materials which have an absorption peak centred at 350 nm and a very low optical density in the absorption tail at 526 nm (**I**, **VII**, **X**), one would expect a significantly larger susceptibility for excitation at 1064 nm due to resonance enhancement but this does not appear to be the case. The reason for this is unclear and may be due to a difference in the film quality, but is more likely due to a trade-off between resonance enhancement and absorption in the materials. It is possible that the absorption spectra taken in dilute solution shown in Figure 2 are misleading since the optical density in the absorption tail is more significant in the solid films than these spectra would suggest and could be leading to a larger resonance enhancement at 526 nm than first appears likely.

The susceptibility values presented here suggest that the relatively small conjugated side groups in these polymers can exhibit significant third order non-linear optical susceptibilities, however these values have a resonance contribution. The largest values of side chain polymers **II** and **III** have susceptibilities of order 10^{-18} m^2/V^2 which is comparable to non-resonant values for main chain polymers such as poly(phenylacetylene) and poly-(*p*-phenylenebenzobisthiazole). Main chain polymers, such as poly

TABLE II

The side group structures, phase behaviour and third order nonlinear optical susceptibilities of the materials at 1064 nm and 1579 nm. The polymeric backbone of each materials is indicated by structures A, B and C given the Table 1

Phase Behaviour	**Backbone Type / Side Group Structure R**	$\chi^{(3)}_{film}$ (x 10^{-21} m^2/V^2)	
		1064nm	1579 nm
III G 110 I	**B** 	1017 ± 152	98 ± 14
II G 30 S_A 125 I	**B** 	937 ± 141	175 ± 26
I G 50 S_A 160 I	**A** 	386 ± 57	228 ± 34
VIII G 14 S_A 90 N 107.5 I	**A** 	281 ± 42	56.1 ± 8.4
IX K 59 S_A 110 I	**A** 	70.2 ± 10.5	22.8 ± 3.4
VI G <-30 I	**B** 	67.7 ± 10.2	31.6 ± 4.7
VII G 32 M 80 S_A S_A 124.5 N 132 I	**A** 	64.9 ± 9.7	21.1 ± 3.2
X G 10 M 90 I	**A** 	61.4 ± 9.2	36.8 ± 5.5
V (Not liquid crystalline)	**B** 	36.8 ± 5.5	10.5 ± 16
IV (Not liquid crystalline)	**C** 	30.7 ± 4.6	17.4 ± 2.6

(diacetylene) and related materials, exhibit a non-resonant third order non-linear optical susceptibility two orders of magnitude larger[1] and it is unlikely that this could be achieved in side chain systems, since the length of the conjugated region is limited by the size of the side group. Realistically, if amorphous side chain polymers are to be useful as third order non-linear optical materials then they must display non-resonant values at least an order of magnitude greater than the values presented here. An advantage of amorphous polymers is that they often exhibit processibility, mechanical properties and transparency superior to polymer crystals like poly(diacetylene) and in the case of the materials discussed here can exhibit a quadratic non-linearity as well a third order response which presents the opportunity to integrate several non-linear optical processes in the device substrate.

CONCLUSIONS

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, $1.02 \times 10^{-18}\ \mathrm{m}^2/\mathrm{V}^2$ which is resonance enhanced is comparable with the non-resonant values for long conjugated third order main chain polymers such as poly(phenylacetylene). An increase in third order response of azo, benzylidene and stilbene side groups when compared with biphenyl and benzoate side groups has been shown. This is due to an increase in conjugation and an increase in the degree of planarity which enhances the charge mobility in the side groups. Improvements in the third order response of side chain polymers is expected if the conjugation length is increased by adding further azo or stilbene linkages. Work is continuing on the third order non-linear optical properties of these materials at other excitation wavelengths to determine the contribution of resonant processes to susceptibility in more detail. These side-chain polymers are also being studied in ordered systems and preliminary measurements have shown an increase in the third order susceptibility by a factor of between two and three in mechanically aligned samples.

Although there exists a need to improve the non-resonant non-linear optical susceptibility of side chain polymers by several orders of magnitude before they could be considered as device substrates, the processibility and mechanical properties of this type of polymer may be considered as advantages when compared with polymer crystrals such as poly(diacetylene). The high degree of freedom in the molecular design of side chain polymers at relatively low cost and the possibility of both a large second order and third order susceptibility in the same material suggests, we believe, that side chain polymers merit continued investigation as non-linear optical materials for photonics applications.

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