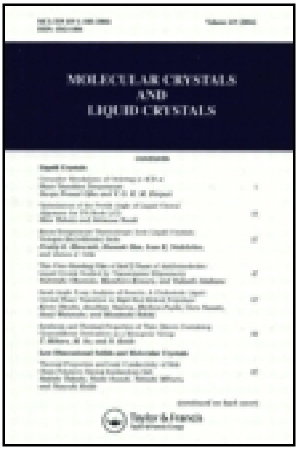

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The Synthesis and Characterisation of Nematic NLO Polymer Networks

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The Synthesis and Characterisation of Nematic NLO Polymer Networks

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Ultra-fast optical intensity modulators are required for high speed telecommunications and organic electro-optical materials offer the advantages of low cost and fast switching capability. We propose a new method to fabricate electro-optical waveguide modulators using low temperature processing and poling with low electric field strength. Our method uses nematic photoreactive mesogens with large second-order polarisability and low viscosity. They can be poled with an electric field of low strength and simultaneously photopolymerised to maintain polar order. A nematic mixture with a melting point of 30°C was successfully crosslinked when aligned by an electric field. New tolane based chromophores show second order polarisabilities up to 180×10^{-30} esu, ten times the value of *para*-nitroaniline.

Keywords: NLO; waveguides; nematics

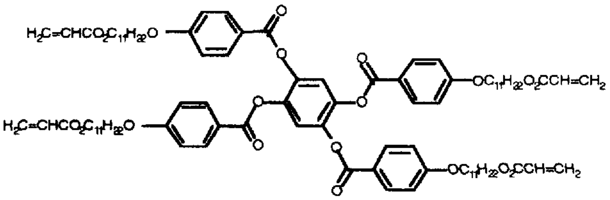
INTRODUCTION

There is a growing need for fast optical switches for the entrance and exit nodes of high-speed telecommunication systems. The Pockel electro-optical effect provides the required optical modulation proportional to an applied electric field in materials with large second-order non-linear optical (NLO) effects characterised by the second-order polarisability β. Organic materials are promising for these applications because of their low cost and ultra-fast switching capability.[1,2] The NLO chromophore must be non-centrosymmetric with electron-donor and acceptor ends and this polar order must be retained macroscopically. Electro-optical modulators employ optical waveguides in an interferometric configuration using material with a refractive index dependent on the

applied electric field. Sidechain polymers with NLO active side-chains deposited by spinning are often used.[1,2] Uniform polar order is achieved by poling with an electric field of high strength obtained by a corona discharge. The order can be fixed by simultaneous crosslinking of the polymer.[3-5] Corona poling is impractical for large scale processing and high temperatures are required to obtain the low viscosity required for efficient crosslinking. Our alternative approach is to use nematic liquid crystals of low molecular weight and photoreactive end-groups. These have a low viscosity and so can be poled by means of a low electric field applied between two surface electrodes in a standard LC cell. Photopolymerisation and crosslinking of the reactive end-groups to form a stable nematic network freezes in the polar order at room temperature.

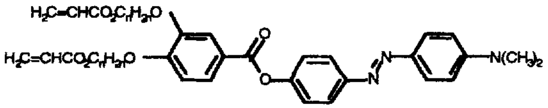
RESULTS AND DISCUSSION

Three series of photoreactive liquid crystals **1-9** have been synthesised, see Tables 1-3. The compounds are red monotropic liquid crystals incorporating non-linear optical chromophores with electron donating [$N(CH_3)_2$] and electron withdrawing groups [CN and NO_2] and photoreactive acrylate end-groups. The relatively low melting points allowed the preparation of a eutectic mixture using equal ratios of compounds **3** and **4**. Compound **10**, shown below, was synthesised for use as a cladding layer for the waveguides and also a component designed to lower the melting points of the NLO active mixtures.



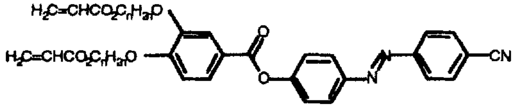
These materials are highly birefringent and are particularly suitable for polarisation-preserving waveguides. A mixture containing compounds **1**, **3** and **10** in the ratio 6:5:1 forms a nematic phase with a melting point of 30° C. A cell filled with the mixture shows multidomain homogeneous alignment. Homeotropic alignment was obtained on application of an electric field to the cell because of the positive dielectric anisotropy of the mixture. Whilst maintaining the applied field at 54°C, the sample was exposed to UV light from a Mercury lamp. Large regions of the sample retained homeotropic alignment on removal of the field showing that photopolymerisation occurred.

TABLE 1. Transition temperatures (°C) for the compounds **1**-**3**.



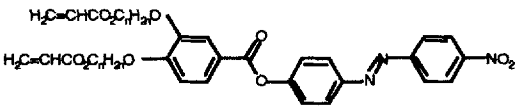
	n	Cr		N		I
1	6	•	92	(•	75)	•
2	8	•	99		-	•
3	11	•	89	(•	72)	•

TABLE 2. Transition temperatures (°C) for the compounds **4**-**6**.



	n	Cr		N		I
4	6	•	86	(•	84)	•
5	8	•	78	(•	76)	•
6	11	•	86	(•	78)	•

TABLE 3. Transition temperatures (°C) for the compounds **7**-**9**.



	n	Cr		N		I
7	6	•	90	(•	88)	•
8	8	•	87	(•	84)	•
9	11	•	95		-	•

( ) Represents a monotropic transition temperature

Two representatives **11** and **12** of a new class of colourless tolanes with more active NLO chromophores are shown in table 4. They are also more stable than the azo compounds **1-9**. Unfortunately the two and three ring diacrylate final products were not liquid crystalline probably because of their high melting points. Other homologues with LC phases are required in order to prepare room temperature nematic mixtures. The second order polarisability β of these two new chromophores was measured using a second harmonic light scattering or Hyper Rayleigh scattering (HRS) experiment.[6] Chromophores are measured in solution and thermal fluctuations provide the noncentrosymmetric environment necessary to give a scattering at 2ω where ω is the frequency of the incident beam. The intensity of the HRS radiation, I(2ω), from a binary chromophore/solvent solution is given by.[6,7]

$$I(2\omega) = K(\rho_s\beta_s^2 + \rho_c\beta_c^2)I^2(\omega) \qquad (1)$$

where I(ω) is the intensity of the incident beam and K is a constant depending on local field corrections. $\rho_{s(c)}$ refers to the number density of the solvent and chromophore respectively. Figure 1 shows of the variation of I(2ω) with $I^2(\omega)$ for different densities of **12** in chloroform. The expected quadratic dependence is found.

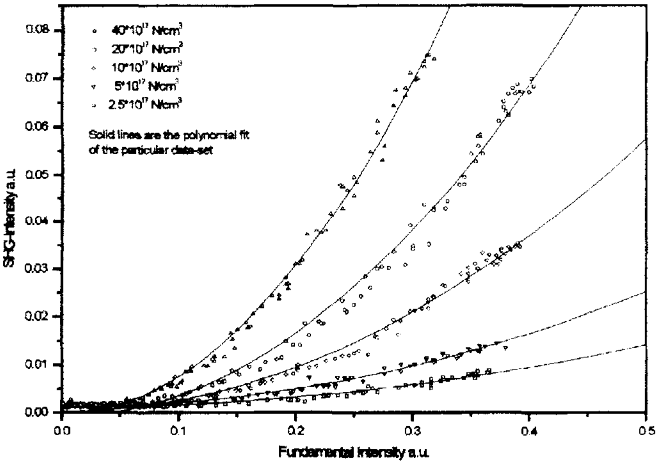


FIGURE 1. I(2ω) as a function of I(ω) for compound **12** in acetone.

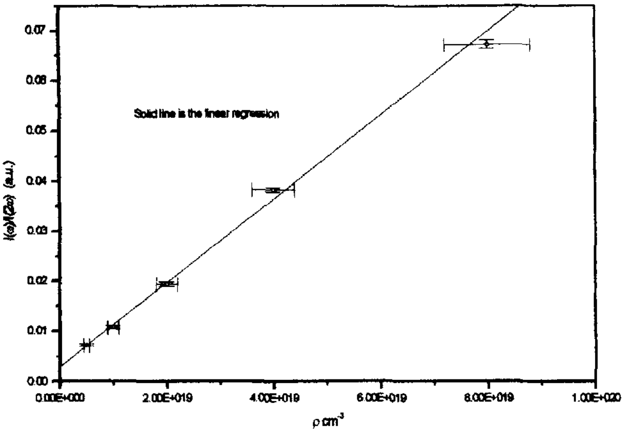


Figure 2. $I(2\omega)/I^2(\omega)$ as a function of number density of **13** in methanol.

The experiment was carried out using a pulsed Nd^{3+}:YAG laser at 1.06 μm and the intensity at 2ω obtained using an interference filter and photomultiplier tube. The HRS signal was averaged over typically 128 shots and the data recorded on a computer. $I(2\omega)/I^2(\omega)$ plotted as a function of chromophore density gives a linear graph as shown in Figure 2. According to equation one, β_c can be found by dividing the slope by the intercept ($=\beta_c^2/\rho_s\beta_s^2$) when β_s is known. The spectral response of the scattered signal about 2ω was measured to unambiguously determine the nature of the scattered light. The HRS signal is found at 532 nm but other non-linear effects, such as multiphoton-induced fluorescence, may induce a broad background signal.[8] Figure 3 shows the spectral response of scattered light for **11**, where two photon induced fluorescence (TPF) is observed. This is a second-order effect with the same dependence on $I(\omega)$ and ρ_c as the HRS signal. A corrected value of β_c can be obtained from the relationship

$$\beta_c = \frac{\beta_c(\text{meas.})}{\sqrt{1+\tau}},$$

where τ ($=I(TPF)/I(HRS)$ at 2ω) is interpolated from the spectrum.

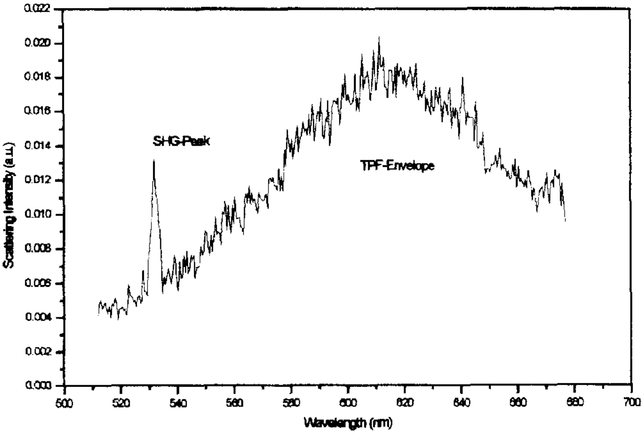


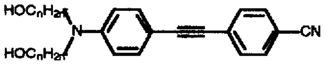
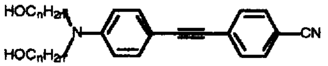
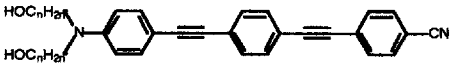
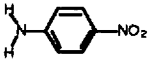
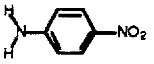
Figure 4. Spectral response of scattered signal about 2ω of **11**.

Compound **12** has a significant absorption at 2ω. This effectively reduces the detected HRS signal. The corrected value of I(HRS) is given by[9]

$$I(\rho_c,2\omega) = \frac{I_{meas}(\rho_c,2\omega)}{\exp(-\alpha\rho_c L)}, \tag{3}$$

where $\alpha\rho_c L$ is the absorption of the chromophore in the cell of effective path length L. The corrected values of β_c are given in Table 4. The standard NLO chromophore *para*-nitroaniline (pNA) is also measured to provide a check to our experimental set-up.

TABLE 4. The molecular structure and β_c values (10^{-30} esu)

	Chromophore	β_c	
11		C	95±13
12		A	120±17
12		B	180±25
13		A	34±5
13		B	17±3

Solvent A = methanol; B = acetone; C chloroform

The measured values of β_c represent an average over all molecular orientations. It is expected that the tensor has one dominant component β_{zzz}, where z is the direction of the molecular axis. **13** (pNA) in methanol has a literature value of 34.5 × 10^{-30} esu[7] and our measured value agrees with this. The β_c value is shown to depend on the solvent. Similar solvent variations are found elsewhere and depend on the polarity of the solvent.[9] Dispersion can also give solvent variations[10]: the magnitude of β_c depends on the proximity of the incident frequency to the resonant frequency of the charge transfer band of the chromophore, which varies with the nature of the solvent. Chromophores **11** and **12** were soluble in different solvents so that their β_c values cannot be compared directly. However their values are 10.5 and 3.5 times that of **13** (pNA) respectively. The higher value of β_c for **12** is expected because of its extra conjugated length. All the polarisability values reported here are low compared to the best compounds reported elsewhere. However our chromophores can be modified to form photoreactive liquid crystals that are easily processed to achieve a high chromophore density when poled and photopolymerised.

CONCLUSIONS

We propose a new method to fabricate waveguide electro-optical modulators based on the Pockels effect. Photoreactive mesogens containing NLO active chromophores with nematic phases close to room temperature can be poled using electric fields of low strength and photopolymerised to maintain polar order. Photoreactive NLO active nematic liquid crystals and crosslinking agents have been synthesised. A three component eutectic mixture was found with a melting point of 30° C. An electric field was applied to this mixture and the induced homeotropic alignment was maintained after exposure to UV radiation. This shows the validity of our method but the degree of polar ordering has yet to be ascertained. The second order polarisability of novel NLO chromophores are reported. Values up to 180×10^{-30} esu, which is over ten times greater than that of pNA, are found. These chromophores are more photochemically stable than the azo compounds and can be modified to form photoreactive nematic mesogens for use in electro-optical modulators.

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References

[1] P.N. Prasad and D.H. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley and Sons, New York (1991).
[2] R.A. Norwood, T. Findakly, H.A. Goldberg, G. Khanarian, J. B. Stamatoff and H.N. Yoon, in *Polymers for Lightwave and Integrated Optics*, ed., L.A. Hornak, Marcel Dekker, New York, 287 (1992).
[3] H. Müller, I. Müller, N. Nuyken and P. Strohriegel, *Makromol. Chem., Rapid Commun.*, **13**, 289 (1992).
[4] M. Chen, L. Yu and L. Dalton, Y. Shi and W.H. Steier, *Macromolecules*, **24**, 5421 (1991).
[5] R.-P. Herr, M. Schadt and K. Schmitt, CH 1946/92, 1992; WO 94 00,979 (1994).
[6] K. Clays and A. Persoons, *Phys. Rev. Lett.*, **66**, 2980 (1991).
[7] K. Clays and A. Persoons, *Rev. Sci. Instrum.*, **63**, 3285 (1992).
[8] N.W. Song, T-I Kang, S.C. Jeoung, S-J. Jeon, B.R. Cho and D. Kim, *Chem. Phys. Lett.*, **261**, 307 (1996).
[9] P.C. Ray and P.K. Das, *J. Phys. Chem.*, **99**, 14414 (1995).
[10] M.A. Pauley, C.H. Wang and A.K.-Y. Jen, *J. Chem. Phys.*, **102**, 6400 (1996).