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Synthesis and Non-Linear Optical Properties of Diacetylenes with Conjugated Side Groups

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Seven novel diacetylenes have been synthesised, with six of these containing a pyridine ring directly conjugated to the main diacetylene unit. Values of χ^2 and χ^3 for these diacetylenes as guests in a guest-host polymer matrix (polysiloxane) have been obtained. High values of χ^2 are shown to depend on the presence of the pyridine ring whereas the highest values of χ^3 are obtained for the lesser conjugated diacetylenes.

Keywords: Non-linear optical properties, diacetylenes, liquid crystals.

INTRODUCTION

Non-linear optical processes are an integral part of the science of photonics, described as the technology of the 21st century.[1] A variety of optically active devices, which make use of the non-linear optical processes occurring in materials at high optical intensities, have been produced for application in data storage, processing and display.[2–6]

The behaviour of these materials under intense electromagnetic fields is described by the equation:

$$P = \varepsilon_0(\chi^1 E + \chi^2 EE + \chi^3 EEE + \ldots)$$

where ε_0 is the dielectric permittivity of free space, P is the induced polarisation, E is the applied field and the susceptibilities χ^n are tensorial quantities which indicate the polarising effect of the electromagnetic field on the outer electrons of molecules. When $n = 1$, the susceptibility refers to linear effects whereas for $n \geq 2$, the susceptibilities give rise to non-linear effects. Relatively large values of tensor components in χ^2 and χ^3 in some materials indicate that these materials may be suitable for application in non-linear optical devices.

Monomeric highly conjugated organic molecules or polymers with a large degree of π electron delocalisation are expected to have large values of components in χ^2 and χ^3 and have therefore been intensively studied.[6–11]

Diacetylenes and polydiacetylenes have aroused considerable interest in their capacity to exhibit large χ^2 and χ^3 susceptibilities. These materials, which are chemically stable and possess good optical qualities can be used in devices utilising, e.g., fast switching times or optical mixing.[9,12,13] Initial interest in diacetylenes was concerned with their topochemical polymerisation in the crystal phase, resulting in highly ordered, crystalline, polyconjugated macromolecules.[14–17] However, only a small number of diacetylenes satisfy the specific geometrical requirement within the crystalline lattice to undergo topochemical polymerisation. This limitation and the difficulties of obtaining large monomeric crystals of high quality, makes it desirable to consider the use of diacetylenes in a different physical form in order to exploit their inherent properties. This has led to many investigations of the application of diacetylenes in the form of thin films, liquid crystals, copolymers and organometallic compounds, as well as single crystals.[18–21]

Our researches have focused on the production of unsymmetrically disubstituted diacetylenes showing enhanced susceptibilities. These diacetylenes have extended conjugation adjacent to the diacetylene unit, and incorporate electron donating and electron withdrawing groups at opposite ends of the diacetylene moiety to provide an electronic "push-pull" effect.[22–24] A number of these materials have been found to exhibit liquid crystalline phase behaviour and enhanced non-linear optical behaviour.[25–27]

Recent publications have indicated that materials containing a pyridine ring show considerable enhancement in χ^2 properties over analogous compounds containing benzene rings.[28,29]

In this paper we report on the synthesis, properties and results of non-linear optical testing of a number of novel polar conjugated diacetylenes with a pyridine ring directly bonded to one end of the diacetylene unit and a selection of electron acceptor and donor groups attached to the other.

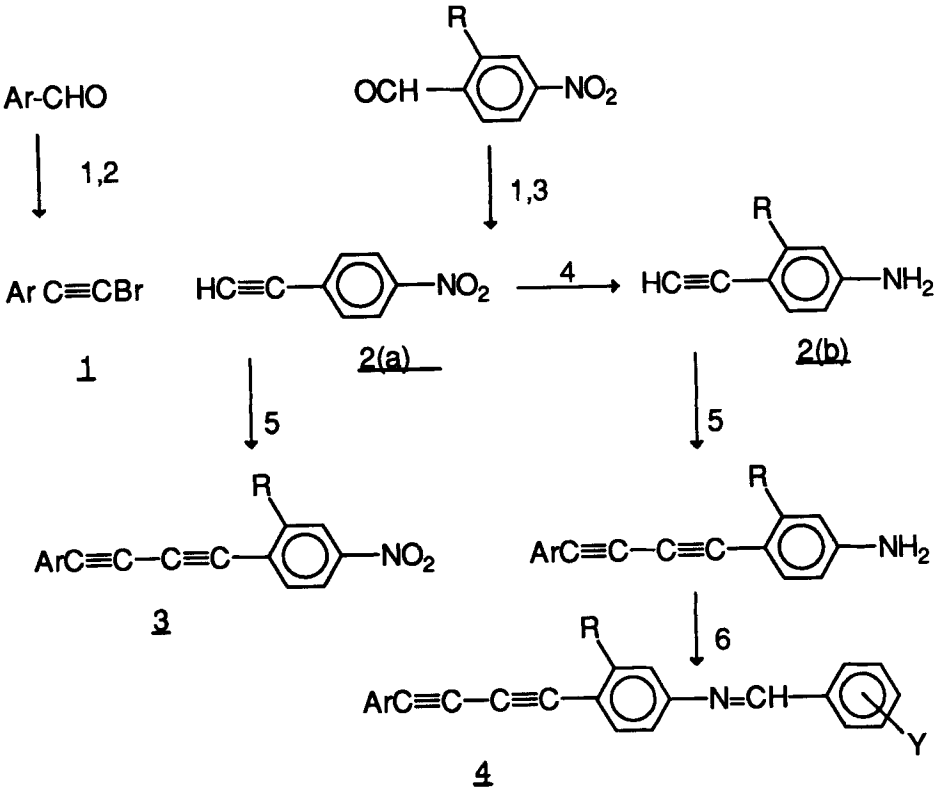
EXPERIMENTAL

1-Bromoacetylenes **1**, terminal acetylenes **2**, diaryldiacetylenes **3**, and the imines **4**, were synthesised, as outlined in Scheme 1, according to procedures previously reported.[30–33]

The bromoacetylenes **1** and terminal acetylenes **2** were synthesised via the dibromoalkenes from the corresponding aldehydes by chain extension.[30–31] The bromoacetylenes were formed by refluxing the dibromoalkene with equimolar amounts of potassium *t*-butoxide in toluene with typical overall yields of 60–70%.[30]

The transformation of the dibromoalkenes into the corresponding terminal acetylenes **2**, was brought about by reaction with two equivalents of *n*-butyllithium in tetrahydrofuran at $-78°C$ for two hours, followed by stirring for another hour with water at room temperature.[31]

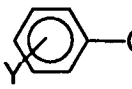
Reduction of **2(a)** to **2(b)** was achieved with zinc in aqueous ammonia, followed by purification by steam distillation, yielding the desired aminophenyl acetylenes **2(b)**.



1. $PPh_3 / CBr_4 / Zn$ in CH_2Cl_2 2. $KOBu^t$ [30]

3. n-BuLi /-78° / THF [31] 4. $Zn / NH_3 / H_2O$ [32]

5. Compound 1 / Cu (1) Cl / $NH_2OH.HCl$ / $CH_3CH_2NH_2$ / EtOH

6.  / EtOH [33]

SCHEME 1 Preparation of diacetylenes.

The diacetylenes were prepared using the Cadiot–Chodkiewicz reaction, between equimolar amounts of bromo- and terminal-acetylenes in the presence of catalytic amounts of copper(I) chloride. Purification was carried out by column chromatography where necessary.[33] The imines **4** were then synthesised from the 4-aminophenyl diacetylenes by stirring with an excess of the substituted aromatic aldehyde in dry ethanol.

INSTRUMENTAL

The structures of all intermediates and diacetylenes synthesised were confirmed by elemental analyses using a Carlo–Erba 1106 elemental analyser equipped with a Spectra Physics SP 4100 computing integrator and by IR and UV spectroscopy using respectively a Perkin Elmer 1760-X FTIR Spectrometer and a Hewlett Packard Diode Array 8452A Spectrometer.

The thermal behaviour was investigated using a Perkin Elmer DSC7 differential scanning calorimeter with heating/cooling rates of 20 K min^{-1} unless otherwise stated. Thermogravimetric analysis was obtained using a Stanton–Redcroft STA780 thermal analyser. A Nikon Optiphot-Pol polarising microscope fitted with a Linkam TH600 hot stage and Nikon camera was used for polarised light microscopy studies on the mesophases formed.

Non-Linear Optical Testing

The second order nonlinear optical susceptibilities were measured by harmonic generation from submicron thin films at a fundamental wavelength of 1064 nm whereas the third order nonlinear optical susceptibilities were measured from thin films at both 1064 nm and 1579 nm.

The materials were studied in mixtures of approximately 15% by mass with a polysiloxane side chain polymer containing cyanobiphenyl side groups in order to avoid the difficult process of single crystal growth. The low molecular weight diacetylene guest molecules may then be aligned by electric fields in the polymer host matrix. The films were spin coated from solution in tetrahydrofuran onto glass substrates with interdigited electrode patterns which typically produce films of 0.2–0.5 μm thickness. The films were cured at elevated temperatures for 12 hours 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 noncentrosymmetric ordering of the molecular dipoles for second harmonic generation experiments. The highest degree of poled ordering was achieved by subjecting the guest host system to an alternat ing electric field (1000 Hz 500 V pk) at elevated temperature and storing the induced alignment by rapid cooling to the glass phase with the alternating field still applied. The poling field of about 10^6 V m^{-1} was then applied at a temperature of a few degrees above the glass transition for a period of 24 hours. Typically, the second order susceptibility was improved by a factor of three by the pre-alignment process when compared with the application of the poling field to the material with no pre-alignment history. Measurement of the χ^2 values were made immediately after the poling field had been removed. Third harmonic generation was performed simply on amorphous films of the guest-host mixtures.

The 1064 nm fundamental was obtained from a Q switched Nd^{3+}:YAG laser using a Quanta Ray DCR II, the 1579 nm fundamental was obtained by Raman shifting using a Quanta Ray RS-1 with hydrogen at 250 psi and the second harmonic of the 1064 nm fundamental produced by a commercial KDP harmonic generator.

The fundamental beam was filtered to remove lamp flash and the irradiance controlled by neutral density filters. The fundamental and harmonics were collected

and slightly focussed through a monochromating filter and detected using a Thorn EMI 9520 photomultiplier tube.

The fundamental and harmonic pulses were displayed and averaged on a fast digital oscilloscope (Hewlett Packard 54502A), triggered by a Spectraphysics 403 fast photodiode. The χ^2 or χ^3 values were then calculated from the harmonic irradiance measurements of the sample and quartz reference or sample and fused silica reference respectively.[34]

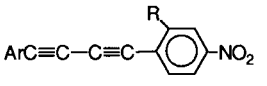
RESULTS AND DISCUSSION

The diacetylenes synthesised and analytical data are shown in Tables 1(a) and 1(b), while their thermal behaviour is summarised in Table 2.

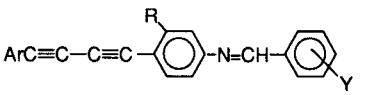
None of the compounds showed any colour change on long exposure to daylight and therefore they appear to be unreactive in the solid state. This may be due to the bulky nature of the conjugated side group.

TABLE 1(a)

Diacetylenes*



(3)



(4)

Compound	Ar	R	Y	Elemental Analysis: found (calc) C	H	N	IR $\bar{\nu}$ (C≡C) (cm^{-1})	$\bar{\nu}$ (N=C) (cm^{-1})
3 (a)		H	–	71.96 (72.58)	3.53 (3.26)	10.91 (11.29)	2211	–
3 (b)		CH_3	–	72.89 (73.28)	4.01 (3.82)	10.44 (10.69)	2210	–
3 (c)		CH_3	–	73.03 (73.28)	3.98 (3.82)	10.40 (10.69)	2210	–
4 (a)		H	4-NO_2	74.59 (75.21)	4.01 (3.70)	11.30 (11.96)	2212	1600
4 (b)		H	2-CF_3	73.38 (73.80)	3.56 (3.47)	7.29 (7.49)	2205	1590
4 (c)		H	4-OC_9H_{19}	82.77 (83.04)	7.01 (7.14)	6.02 (6.25)	2200	1600
4 (d)		H	4-$OC_{10}H_{21}$	76.08 (77.13)	6.68 (6.43)	2.53 (2.65)	2213	1600

* Patent pending

TABLE 1(b)

UV and ^{1}H NMR DATA

Compound	UV (nm) CH_2Cl_2		^{1}H NMR δ (Mult)							
	λ_{max}	$\lambda_{cut.\ off}$	—N=CH	Arom H	Ar—CH_3	—OCH_2	—CH_2	—CH_2	CH_2	CH_3
3(a)	314	410		8.2–7.2(8)						
3(b)	300	405		8.2–7.2(7)	2.5(3)					
3(c)	314	410		8.2–7.2(7)	2.5(3)					
4(a)	330	420	8.5(1)	8.4–6.6(12)						
4(b)	328	420	8.8(1)	8.4–6.6(12)						
4(c)	332	420	8.5(1)	8.3–6.6(12)		4.0(2)	1.8(2)	1.4(2)	1.25(10)	0.9(3)
4(d)	342	430	8.4(1)	8.3–6.9(12)		4.0(2)	1.9(2)	1.4(2)	1.25(12)	0.8(3)

TABLE 2

Thermal Behaviour of Diacetylenes

Compound	Phase Transitions, Temperature/°C
3(a)	$K \xrightarrow{113} I$, polymerisation
3(b)	$K \xrightarrow{78} I$, polymerisation
3(c)	$K \xrightarrow{77} I$, polymerisation
4(a)	$K \xrightarrow{176} I$, polymerisation
4(b)	$K \xrightarrow{53} I$, polymerisation (~ 210)
4(c)	$K \xrightarrow{76} S_B \xrightarrow{90} S_A \xrightarrow{103} N \xrightarrow{114} I$, polymerisation
4(d)	$K \xrightarrow{104} S_B \xrightarrow{144} S_A \xrightarrow{146} N$, polymerisation

K = crystal, S = smectic, N = nematic, I = isotropic.

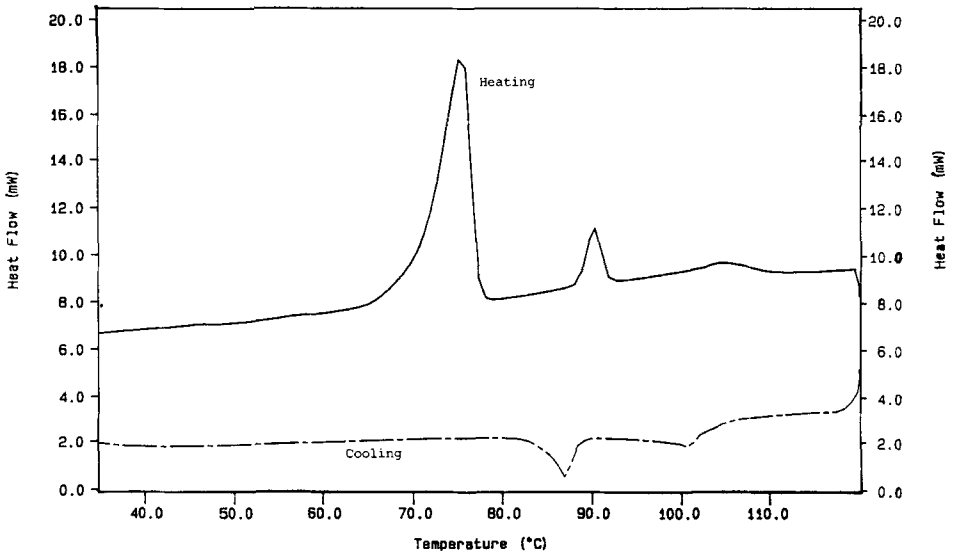


FIGURE 1 DSC thermogram of compound 4(c), heated to 120°C and cooled at 20°C/minute. The liquid–crystal transitions return on cooling, whilst the melting transition does not reappear since the smectic alignment of the molecules is retained.

Compounds **4(c)** and **4(d)** which incorporate flexible alkoxy groups promote the appearance of liquid crystalline phases whereas those without flexible alkoxy groups simply show transitions from crystal to isotropic phases.

Figure 1 shows a DSC thermogram of **4(c)** exhibiting reversible liquid crystal phase transitions whereas Figure 2 shows the characteristically large exotherm indicative of the onset of thermal polymerisation.[22]

All the diacetylenes were found to undergo thermal polymerisation to some degree, producing brown coloured glassy polymers which were soluble, to varying degrees, in common organic solvents. It is likely that the polymers formed are less ordered than those obtained by solid state polymerisation.[19] During thermal polymerisation *cis* and *trans* 1,4- and/or 1,2-addition may be occurring[35] but no conclusions on the nature of the polymer configuration have been made.

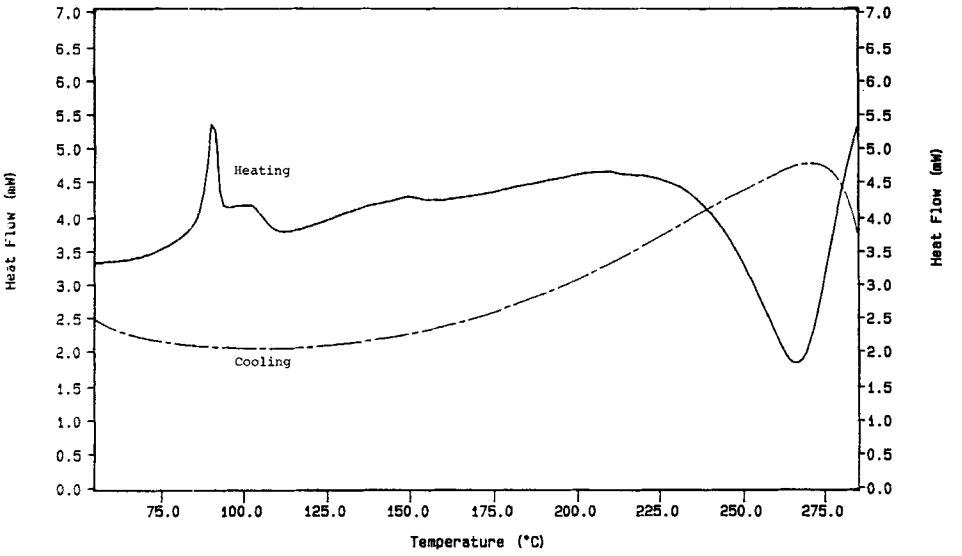


FIGURE 2 DSC thermogram of compound 4(c) heated to 290°C, resulting in polymerisation and loss of the mesophase on cooling.

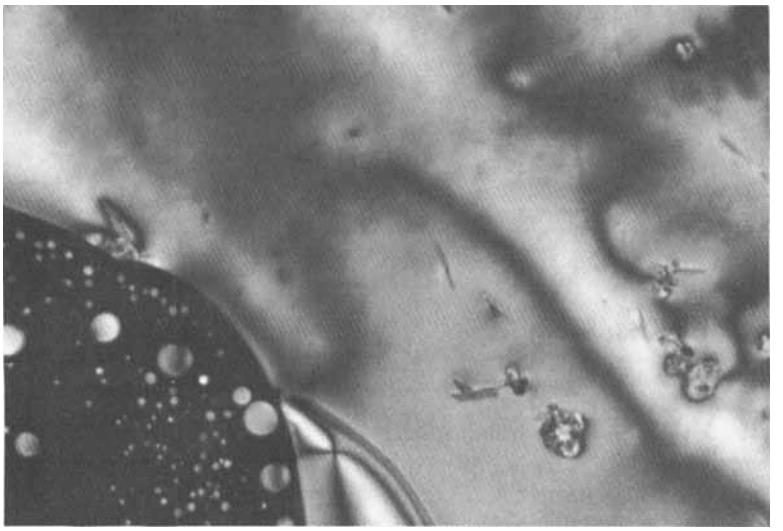


FIGURE 3 Photomicrograph of compound 4(c), recorded at 109°C, showing the mosaic texture of the nematic phase formed on cooling from the isotropic phase. See Color Plate I.

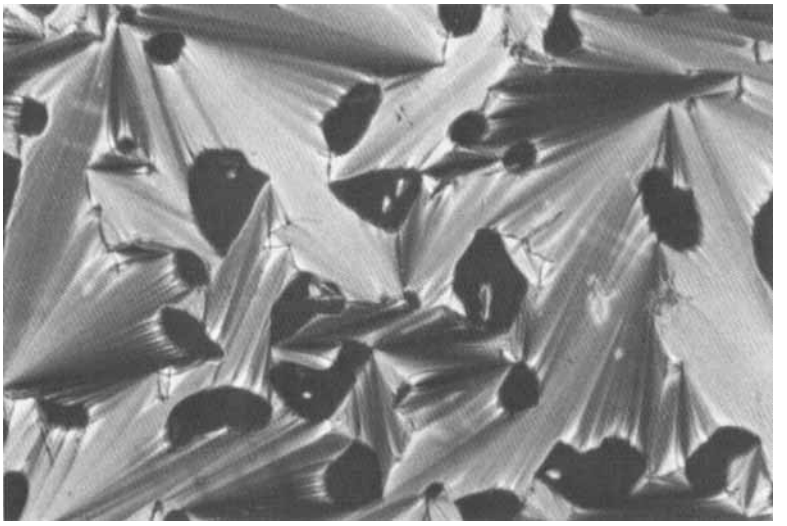


FIGURE 4 Photomicrograph of compound 4(c), recorded at 100°C, showing the focal conic fan texture of the smectic A phase formed on cooling from the nematic phase. See Color Plate II.

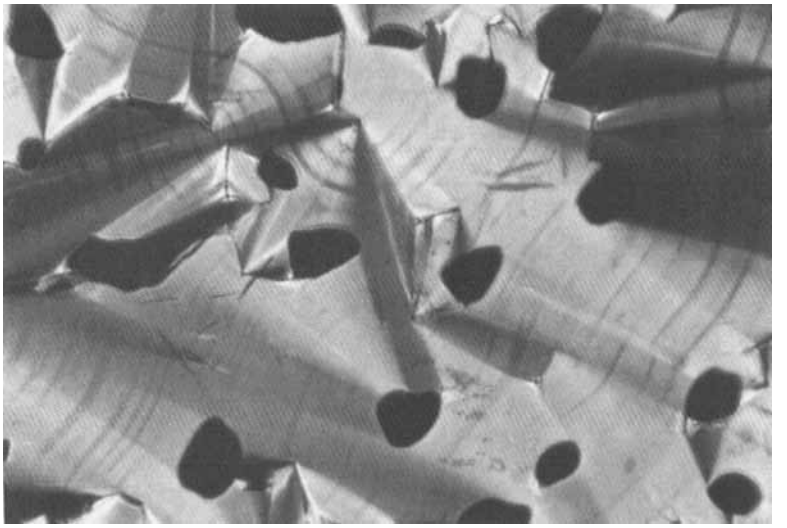


FIGURE 5 Photomicrograph of compound 4(c), recorded at 89°C, showing the paramorphotic focal conic texture of the smectic B phase formed on cooling from the smectic A phase. The fans exhibit transition lines near the temperature of the smectic A, smectic B phase boundary. On further cooling, the transition lines disappear. See Color Plate III.

Photomicrographs showing the liquid crystalline phase textures of compound **4(c)** are shown in Figures 3–5 while Figure 6 shows the appearance of the polymer.

The results of non-linear optical testing are given in Table III.

The third order non-linear susceptibilities for mixtures of the diacetylenes with the polymer host are not as high as those reported for polydiacetylenes[9] which have more

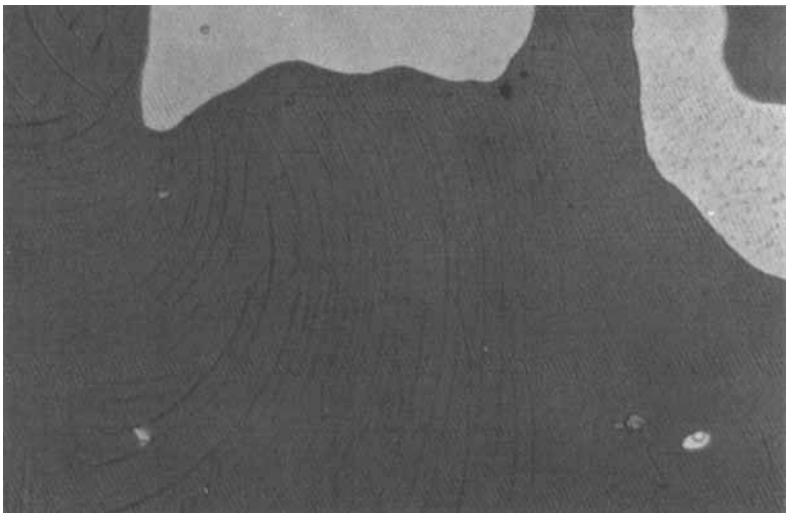


FIGURE 6 Photomicrograph of compound 4(c), recorded at 85°C, after heating sample to 300°C to induce polymerisation. On cooling, no liquid crystal textures are observed. See Color Plate IV.

TABLE III

Non-Linear Optical Testing of Diacetylenes

Material	Mass % in polymer host	Wavelength 1064 nm $\chi^{(2)}_{33}/\text{pm V}^{-1}$	Wavelength 1064 nm $\chi^{(3)}_{film}/10^{-21}\text{m}^2\text{V}^{-2}$	Wavelength 1579 nm $\chi^{(3)}_{film}/10^{-21}\text{m}^2\text{V}^{-1}$
Polymer host	100.0	0.23 ± 0.06	30.0 ± 4.5	10.0 ± 1.5
3(a)	15.0	2.02 ± 0.50	104.0 ± 16.0	252.0 ± 38.0
3(b)	13.8		79.0 ± 7.6	122.3 ± 3.3
3(c)	20.0	1.02 ± 0.25	98.3 ± 14.6	216.0 ± 32.0
4(a)	14.7	0.78 ± 0.20	75.4 ± 11.8	100.0 ± 15.0
4(b)	17.5	1.01 ± 0.25	42.5 ± 6.4	98.0 ± 14.7
4(c)	14.0	1.80 ± 0.45	28.2 ± 4.2	56.1 ± 8.4
4(d)	13.0	0.19 ± 0.05	82.5 ± 12.4	161.0 ± 24.0

extensive conjugation. For this reason, thermally polymerised diacetylenes in these guest-host systems would presumably produce even higher χ^3 values. This assumption will be experimentally tested as part of our ongoing research programme.

The magnitude of the second order non-linear optical susceptibility relative to the concentration of dopant **3(a)** in the polymer host displayed a similar relationship to those observed in other polymer guest-host systems.[36–38]

A linear proportionality was observed at low concentration (Figure 7) but the magnitude of the second order non-linear optical susceptibility increased more rapidly with higher concentrations of dopant (Figure 8). This is attributed to dopant–dopant interaction which may be electrostatic in nature, possibly occurring between the lone pair of the nitrogen atom of the pyridine ring and the electron deficient nitrogen atom

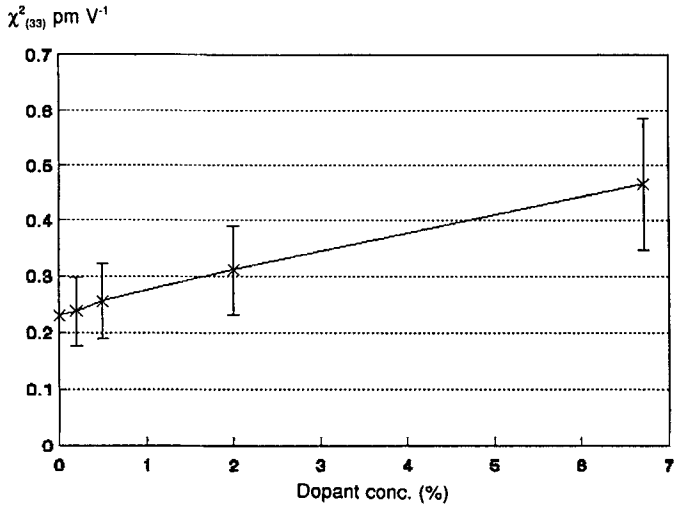


FIGURE 7 Linear response of the second order susceptibility coefficient of compound **3(a)** in polymer host at low concentrations.

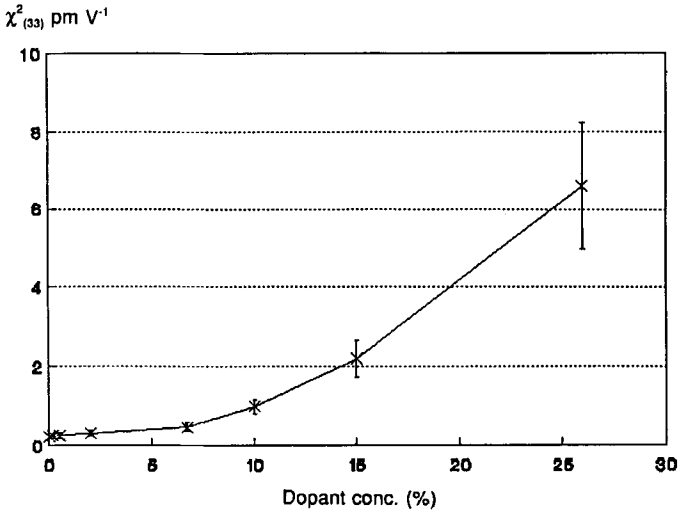


FIGURE 8 Deviation from linear behaviour of second order susceptibility coefficient of compound **3(a)** in polymer host at higher concentrations.

of the nitro group. Dopant-host interaction does not appear to contribute to this non-linear relationship since changing the host from polysiloxane to polymethyl methacrylate yielded similar results.

The predicted χ^2 value for 100% concentration of dopant, based on this relationship, is 8.5 pm V^{-1}. This correlates well with the value of 8.0 pm V^{-1} obtained in a separate study on a microcrystalline sample of **3(a)** and is therefore marginally superior to that of lithium niobate.[34]

The results indicate that large values of χ^2 in the diacetylenes are dependent on the inclusion of a pyridine ring, rather than merely the presence of a strong acceptor group since replacement of the pyridine ring in **4(c)** by a 2-trifluoromethylphenyl group, **4(d)**, did not show this increase in susceptibility.

However, it was noted that **4(d)** showed an enhanced χ^3 susceptibility value which confirms the common view that the criteria for χ^3 and χ^2 effects are different.[1] The relative χ^2 values of compounds **3(a)**, **(c)** and **4(a)–(c)** suggest that **3(a)** may be worthy of further study. This molecule differs from those previously studied in having two electron acceptor groups separated by the conjugated diacetylenic system.[22–27]

The presence of the two electron withdrawing groups may cause an electron deficiency in the centre of the diacetylene unit, giving rise to a continuous oscillation about the positive hole formed and therefore increased hyperpolarisability within the molecule.

The values obtained for compounds **3(a)** and **4(a)–(c)** shows that extension of conjugation in the diacetylene does not necessarily lead to increased χ^2 susceptibility and it is possible that the imine group has a disruptive effect on the electronic motion. Nevertheless, extended conjugation through unsaturated non-polar entities may be worthy of further investigation.[39] Compounds **4(a)** and **4(b)** have similar structures and properties and show the expected comparable χ^2 values.

CONCLUSIONS

The results show that a pyridine ring in conjugation with the diacetylene moiety in diacetylenes leads to increased second order non-linear optical susceptibilities while the highest values of χ^3 are obtained with the lesser conjugated diacetylenes.

The non-centrosymmetric diacetylene **3(a)** containing two different electron withdrawing groups displayed the highest χ^2 value similar to that of lithium niobate and its use in optical devices is currently under investigation.

This result contradicts the accepted view that both donor and acceptor groups, which provide electronic push-pull effects, are necessary for high χ^2 values. Further investigations to confirm this finding are in progress.

The use of a polymer guest-host system leads to easier effective application of these materials, overcoming the difficulties associated with single crystal growth.[40]

Acknowledgements

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