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Liquid Crystals

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Liquid crystal properties of novel diacetylenes having a pyridine end group

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Asymmetrical diacetylenes with a pyridine ring bonded directly to one end of the diacetylene unit and an aryl system containing a flexible alkoxy chain at the opposite end, have been synthesized and show liquid crystalline behaviour. The mesophase behaviour is shown to be dependent on the length of the flexible alkoxy chain. Incorporation of one of these diacetylenes in a polymer 'guest–host' system at a 15 wt% concentration gave a high $\chi^{(2)}$ non-linear optical susceptibility of $4{\cdot}27 \times 10^{-9}$ e.s.u.

1. Introduction

A number of organic molecules and organic polymers which have delocalized π-electron systems are being extensively studied for application in the field of non-linear optics [1–8]. Diacetylenes and polydiacetylenes have aroused considerable interest as materials exhibiting large $\chi^{(2)}$ and $\chi^{(3)}$ susceptibilities, as well as possessing other desirable properties for application, such as fast switching times, stability and optical quality [9–13]. The macroscopic non-linear optical susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ can be enhanced on the microscopic level by having extended conjugation adjacent to both ends of the diacetylene unit and particularly for the microscopic analogue of $\chi^{(2)}$, β, by creating an electronic 'push-pull' effect through the incorporation of electron donor and electron acceptor groups at opposite ends of the diacetylene moiety [1, 5, 14–20].

This has been attempted in this work by synthesizing diacetylenes with a pyridine ring bonded directly to one end of the diacetylene. The pyridine ring acts as a conjugated acceptor group and leads to greatly increased dielectric anisotropy [21]. Pyridine ring systems are also known to influence the mesomorphic behaviour of liquid crystals. For example, an unsymmetrical pyridine ring creates a lateral dipole moment within the molecules of a liquid crystalline material [22].

The aim of the syntheses was to obtain diacetylenes displaying low temperature mesophase transitions, as well as having high non-linear optical susceptibilities. The thermal polymerization of the liquid crystalline diacetylenes has also been studied to ascertain whether liquid crystalline polydiacetylenes have been produced. In this paper, we outline the synthesis used and report on the liquid crystal properties and on preliminary non-linear optical testing of two series of diacetylenes.

2. Experimental

2.1. *Synthesis*

The synthetic approach used is similar to that outlined in our previous publications and is represented in the scheme [17–18].

The bromoacetylenes and terminal acetylenes were synthesized *via* the dibromoalkenes from the corresponding aldehydes by chain extension. The bromoacetylenes were formed by heating the dibromoalkene with equimolar amounts of potassium tertiary-butoxide under reflux in toluene. The transformation of the dibromoalkenes into the corresponding terminal acetylenes was brought about by reaction with two equivalents of *n*-butyl lithium in tetrahydrofuran at −78°C for two hours, followed by stirring for another hour with water at room temperature. Aminophenylacetylene was obtained by reduction of nitrophenylacetylene with zinc in aqueous ammonia and purified by steam distillation. 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. The imine linkage was then generated from the amine and an appropriate 4-*n*-alkoxybenzaldehyde by stirring in dry ethanol.

2.2. *Instrumental*

Elemental analysis of the intermediates and diacetylenes was carried out using a Carlo–Erba 1106 elemental analyser equipped with a Spectra Physics SP 4100 computing integrator. IR and UV spectra were obtained using either a Perkin–Elmer 1760-X Fourier Transform

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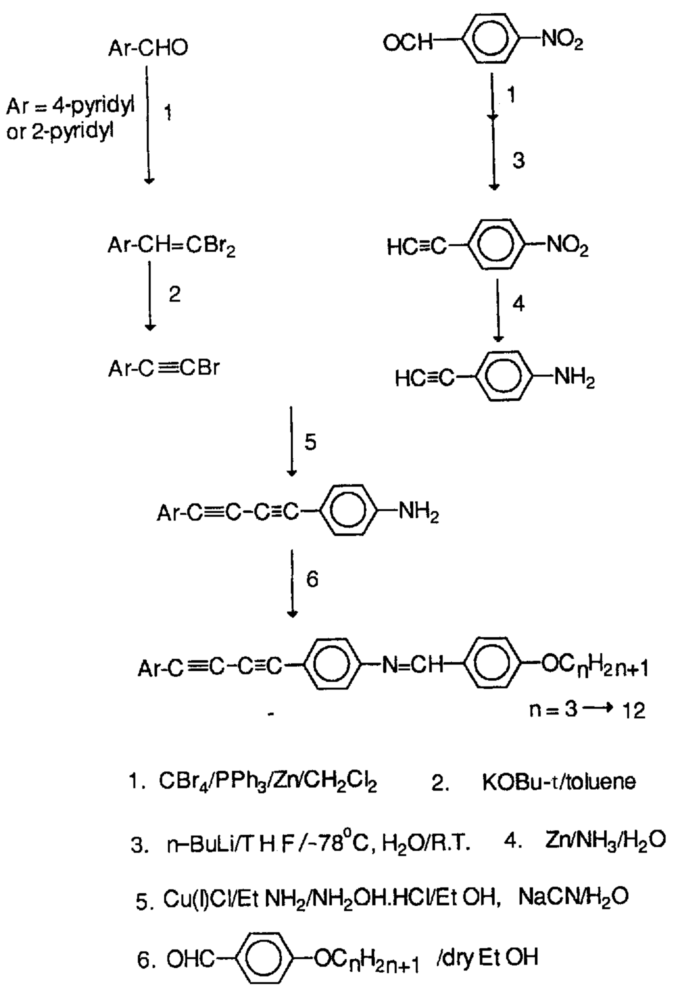


Scheme. The preparative methods employed in the synthesis of 1,4-disubstituted diacetylenes.

Spectrometer or Perkin–Elmer 881 spectrophotometer and a Perkin–Elmer Lambda 7 spectrophotometer, respectively. The thermal behaviour was investigated using a Perkin–Elmer DSC7 differential scanning calorimeter with a heating and cooling rate of 20°C min^{-1} unless otherwise stated. Results of thermogravimetric analysis were obtained using a Stanton–Redcroft STA-780 thermal analyser with a nitrogen gas atmosphere. A Nikon Optiphot-Pol polarizing microscope fitted with a Linkam TH600 hot stage and Nikon camera was used to examine the mesophases of the liquid crystalline diacetylenes.

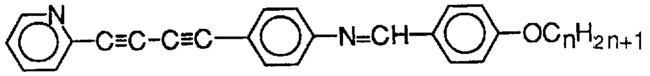
2.3. *Non-linear optical testing*

The diacetylenes were incorporated as 'guests' in a side chain liquid crystal polysiloxane and spun into thin films which were then tested for second and third harmonic generation. The technique used for this is reported in detail elsewhere [23].

3. Results and discussion

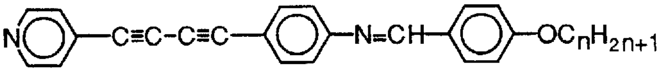
All the diacetylenes appear to be chemically stable over a 12 month period. However, after prolonged storage over 2½ years the melting behaviour changes. This may be due to some photolytically initiated conversion of monomer to

Table 1. Characterization of disubstituted diacetylenes of structure:



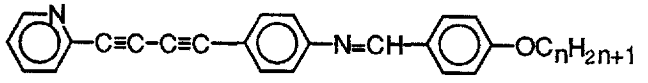
	Elemental analysis: Found (Calc.)/per cent			I.R. Bands/cm^{-1}	
n	C	H	N	ν (C≡C)	ν (C=N)
3	81·71 (82·42)	5·39 (5·49)	7·30 (7·69)	2210	1600
4	81·86 (82·54)	5·63 (5·82)	6·98 (7·40)	2200	1600
6	81·98 (82·76)	6·39 (6·40)	6·77 (6·89)	2200	1590
7	82·08 (82·85)	6·31 (6·66)	6·03 (6·66)	2190	1600
9	82·77 (83·01)	7·01 (7·14)	6·20 (6·25)	2200	1600
10	82·45 (83·11)	6·99 (7·36)	6·19 (6·06)	2200	1600
12	82·68 (83·26)	7·93 (7·76)	5·66 (5·71)	2214	1605

Table 2. Characterization of disubstituted diacetylenes of structure:



	Elemental analysis: Found (Calc.)/per cent			I.R. Bands/cm^{-1}	
n	C	H	N	ν (C≡C)	ν (C=N)
3	81·80 (82·42)	5·31 (5·49)	7·27 (7·69)	2205	1605
4	81·89 (82·54)	5·74 (5·82)	7·05 (7·40)	2200	1610
6	82·01 (82·76)	6·51 (6·40)	6·86 (6·89)	2200	1605
8	82·82 (82·95)	6·40 (6·91)	6·20 (6·45)	2200	1600
9	82·34 (83·01)	7·16 (7·14)	5·76 (6·25)	2200	1600
10	82·51 (83·11)	6·98 (7·36)	6·01 (6·06)	2210	1600

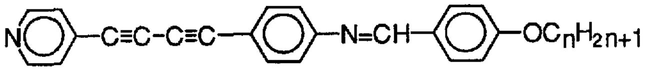
Table 3. Thermal transitions of diacetylenes of structure:



n	Phase transitions and temperature/°C
3	$\mathrm{Cr} \xrightarrow{210}$ N, polymerization
4	$\mathrm{Cr} \xrightarrow{188}$ N, polymerization
6	$\mathrm{Cr} \xrightarrow{183}$ N, polymerization
7	$\mathrm{Cr} \xrightarrow{76} \mathrm{S_B} \xrightarrow{92} \mathrm{S_A} \xrightarrow{105} \mathrm{N} \xrightarrow{112\text{–}115} \mathrm{H} \rightarrow \mathrm{I}$, polymerization
9	$\mathrm{Cr} \xrightarrow{76} \mathrm{S_B} \xrightarrow{90} \mathrm{S_A} \xrightarrow{103} \mathrm{N} \xrightarrow{114\text{–}117} \mathrm{H} \rightarrow \mathrm{I}$, polymerization
10	$\mathrm{Cr} \xrightarrow{75} \mathrm{S_B} \xrightarrow{90} \mathrm{S_A} \xrightarrow{104} \mathrm{N} \xrightarrow{112\text{–}114} \mathrm{H} \rightarrow \mathrm{I}$, polymerization
12	$\mathrm{Cr} \xrightarrow{83} \mathrm{S_B} \xrightarrow{90} \mathrm{S_A} \xrightarrow{106} \mathrm{N} \xrightarrow{112} \mathrm{H} \rightarrow \mathrm{I}$, polymerization

Cr, crystal; S, smectic; N, nematic; H, homeotropic alignment; I, isotropic.

Table 4. Thermal transitions of diacetylenes of structure:



n	Phase transitions and temperature/°C
3	$\mathrm{Cr} \xrightarrow{205}$ N, polymerization
4	$\mathrm{Cr} \xrightarrow{84} \mathrm{Cr} \xrightarrow{180}$ N, polymerization
6	$\mathrm{Cr} \xrightarrow{87} \mathrm{Cr} \xrightarrow{173}$ N, polymerization
8	$\mathrm{Cr} \xrightarrow{63} \mathrm{S_B} \xrightarrow{89} \mathrm{S_A} \xrightarrow{95} \mathrm{N} \xrightarrow{106} \mathrm{H} \rightarrow \mathrm{I}$, polymerization
9	$\mathrm{Cr} \xrightarrow{74} \mathrm{S_B} \xrightarrow{91} \mathrm{S_A} \xrightarrow{104} \mathrm{N} \xrightarrow{117\text{–}119} \mathrm{H} \rightarrow \mathrm{I}$, polymerization
10	$\mathrm{Cr} \xrightarrow{75} \mathrm{S_B} \xrightarrow{93} \mathrm{S_A} \xrightarrow{106} \mathrm{N} \xrightarrow{116} \mathrm{H} \rightarrow \mathrm{I}$, polymerization

Cr, crystal; S, smectic; N, nematic; H, homeotropic alignment; I, isotropic.

oligomer. Tables 1 and 2 show the analytical data for the diacetylenes.

The behaviour of the mesophase in these materials was found to be heavily dependent on the length of the alkoxy chain as reported in some of our previous studies on similar diacetylenes and seen in the 4,4′-alkoxydiphenyldiacetylenes reported by Grant [17, 24].

The diacetylenes which have longer alkoxy chains have more complex lower temperature mesophase behaviour than that observed for the diacetylenes which have shorter alkoxy chains. Tables 3 and 4 show the dependence of the mesophase transitions on the alkoxy chain length. The information presented in tables 3 and 4 was obtained from the first heating cycle of the DSC, with supplementary

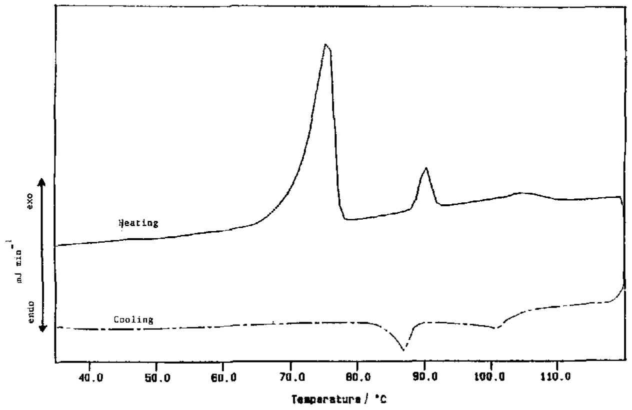
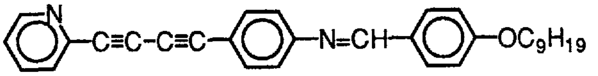


Figure 1. DSC thermogram, showing the reversible liquid crystalline behaviour of:



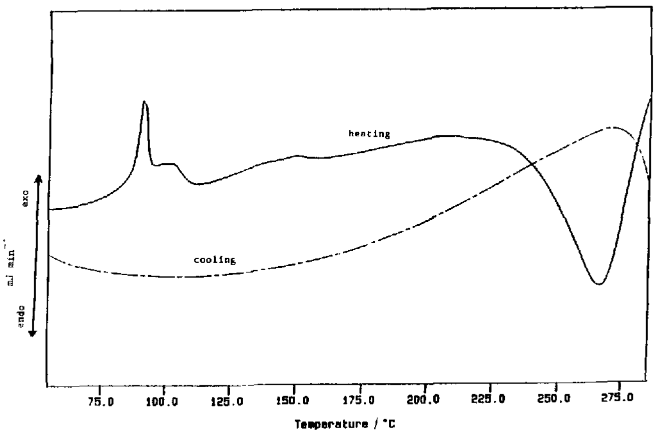
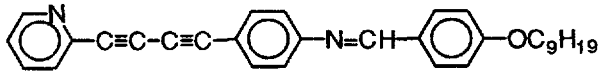
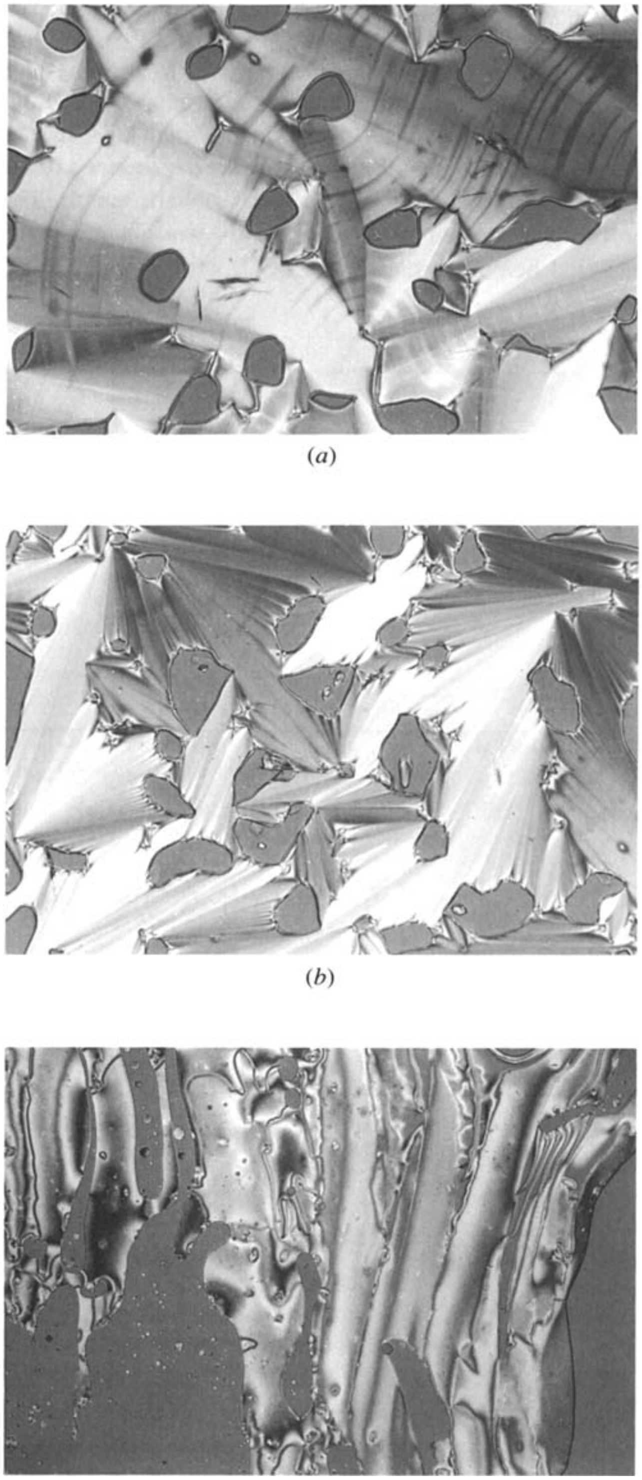


Figure 2. DSC thermogram showing the polymerization and absence of liquid crystalline transitions on cooling cycle of:



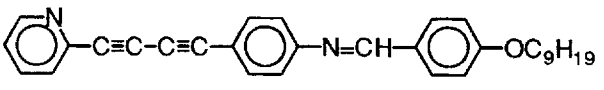


(*a*)

(*b*)

(*c*)

Figure 3. The texture of (*a*) the smectic B mesophase (taken at 89°C, (*b*) the smectic A mesophase (taken at 91°C) and (*c*) the nematic mesophase (taken at 109°C) for:



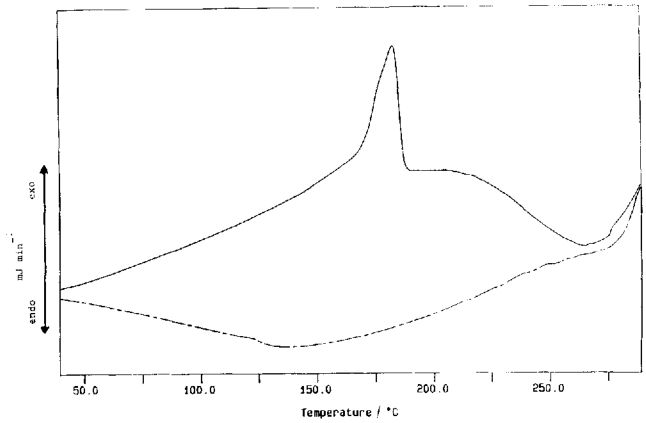
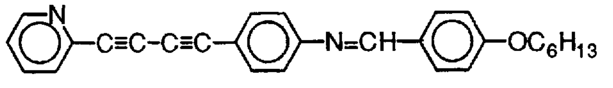
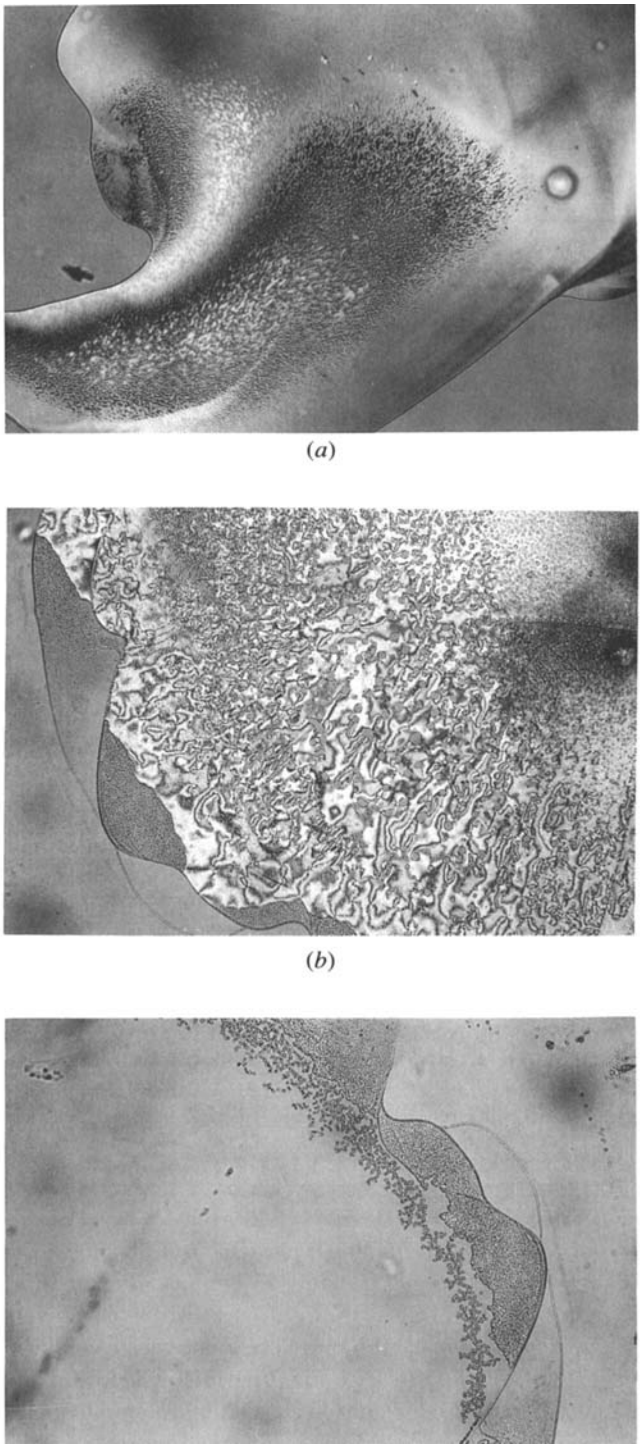


Figure 4. DSC thermogram, showing the heating, polymerization and cooling of:



information on the nature of the transitions being obtained from polarized optical microscopy. When the alkoxy chain length, OC_nH_{2n+1} has $n \geq 7$, the diacetylenes exhibit smectic and nematic phases. In all cases when $n \geq 7$, polarizing microscopy showed a loss of nematic texture, but no corresponding transition to the isotropic phase was observable in the DSC results. When the microscopic samples were subjected to shearing, a 'flashing' effect was observed which implies a homeotropic alignment of the nematic phase. This effect has been confirmed by high temperature X-ray diffraction studies of one of the compounds, see table 3, $n = 9$ [25]. Polymerization occurs at much higher temperatures, presumably in the isotropic phase, and is accompanied by an exothermic transition in the DSC studies. Typical DSC thermograms showing this behaviour are given in figures 1 and 2. The polymeric material showed no liquid crystalline phase behaviour on cooling (see figure 2), had a brown glassy appearance and was soluble in common organic solvents (chloroform, tetrahydrofuran). This type of polymer is likely to be less ordered than that formed by solid state polymerization of diacetylenes [14] and of lower relative molar mass. During thermal polymerization, *cis*- and *trans*-1,4-addition and/or 1,2-addition may be occurring [26]. Copolymers which contain diacetylene moieties in the main chain may undergo a random crosslinking in the molten state [27]. This can be effected thermally or by photopolymerization and produces highly transparent materials in which the polydiacetylene structure is mainly linked by 1,4 diacetylene units [28–30]. Studies of the polymerization processes are still ongoing. Figure 3(*a*)–(*c*) show the

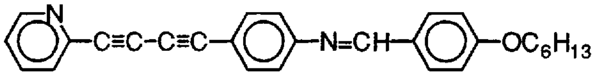


(*a*)

(*b*)

(*c*)

Figure 5. The textures of the structure below. (*a*) The nematic texture observed at 189°C; (*b*) on shearing the sample, the nematic texture still observable at 286°C; (*c*) The sample shows no birefringence, after annealing for 5 min, at 299°C.



typical phase textures of the diacetylenes with longer alkoxy chains.

For diacetylenes with shorter alkoxy chains, tables 3 and 4 when $n \leq 6$, higher temperature nematic phases are exhibited, from which the monomers polymerize. A nematic texture can be observed in sheared samples at temperatures well above that of the minimum of the polymerization exotherm observed in the DSC thermogram, figure 4. Prolonged annealing at these temperatures resulted in the loss of the observed texture. This may indicate that the polymerization proceeds via a liquid crystalline oligomer or that disorder grows steadily within the monomer mesophase, which after prolonged annealing converts completely to a non-liquid crystalline polymer. These observations are shown in figure 5 (*a*)–(*c*) which correspond with the DSC thermogram given in figure 4.

As polymerization (or oligomerization) has occurred from the nematic phase, it may be possible to achieve the same from the lower temperature mesophases of the diacetylenes having longer alkoxy chains by longer periods of thermal annealing, in a similar manner to that described in the work of Schen [26].

Comparisons between tables 3 and 4 for similar values of *n*, show that the position of the nitrogen atom within the pyridine ring has had very little effect on the transition temperatures.

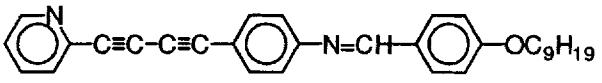
The non-linear optical susceptibilities of a range of these disubstituted diacetylenes have been measured and are reported elsewhere [23]. One of those tested is listed in table 3 where $n = 9$. The results of evaluations of $\chi^{(2)}$ and $\chi^{(3)}$ are given in table 5, with results for the polymer host and a low molar mass standard, 2-methyl-4-nitroaniline shown for comparison. High values of $\chi^{(2)}$ were obtained for all the diacetylenes tested which had a pyridine group directly bonded to the diacetylene unit. ($\chi^{(2)} = 4{\cdot}29 \times 10^{-9}$ e.s.u. at 15 wt%; 1×10^{-8} e.s.u. on 100 per cent microcrystalline samples).

4. Conclusions

Two series of liquid crystalline diacetylenes have been synthesized, some of which exhibit mesophases at temperatures lower than those reported in previous studies [17, 18]. The number of mesophases formed and transition temperatures depend on the length of the flexible part of the molecule and this has a significant effect on the thermal polymerization.

Diacetylenes containing a pyridine ring showed large enhancements of the second order non-linear susceptibilities under the test conditions and therefore these materials may be particularly useful for device applications involving second order processes.

Table 5. Results of non-linear optical testing of:



Material	Concentration	$\chi^{(2)}_{33} \times 10^{-9}$ e.s.u. at 1064 nm	$\chi^{(3)} \times 10^{-13}$ e.s.u. at 1064 nm	$\chi^{(3)} \times 10^{-13}$ e.s.u. at 1579 nm
Polymer host	100	$0{\cdot}55 \pm 0{\cdot}14$	$2{\cdot}10 \pm 0{\cdot}32$	$0{\cdot}64 \pm 0{\cdot}09$
Diacetylene	14·0	$4{\cdot}29 \pm 1{\cdot}10$	$1{\cdot}61 \pm 0{\cdot}24$	$3{\cdot}20 \pm 0{\cdot}48$
2-Methyl-4-nitroaniline	15·5	$3{\cdot}87 \pm 0{\cdot}97$	$5{\cdot}80 \pm 0{\cdot}97$	$13{\cdot}90 \pm 2{\cdot}10$

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