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THERMAL AND OPTICAL STUDIES ON SOME MONOMER AND POLYMER DIACETYLENES

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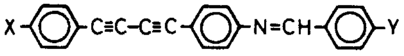
We describe the thermal and optical studies of some diacetylene molecules which were specially designed in an attempt to reduce the temperature at which the mesophase appears. Original studies were on symmetrical molecules and these were extended to include typical liquid crystal molecules with diacetylenes providing a polymeric backbone and unsymmetrically substituted diacetylenes including Schiffs bases with long alkyl chains.

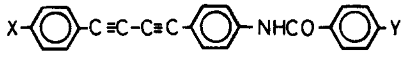
Diacetylenes and polydiacetylenes have aroused great international interest since their original investigation by Wegner [1]. Unsymmetrical conjugated polar diacetylenes have been produced and tested for potential use as non-linear optical materials and as liquid crystals since 1985 at Napier Polytechnic [2, 3]. This work has been extended and is reported below. In 1986, a parallel study of liquid crystalline symmetrical diacetylenes using side groups based on cholesterol or on long chain dicarboxylic acids commenced and many of these materials polymerised to give comb polymer liquid crystals [4, 5].

Diacetylenes of the structures:



(i)

and



(ii)

$X = -NO_2, -CN, CF_3$

$Y = OC^{n}H^{2n+1} \quad 1 \leq n \leq 12$

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have been synthesised and the results are reported below.

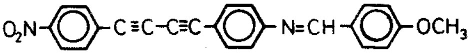
Experimental

The preparation of the diacetylenes (i) and (ii) above are reported elsewhere [3, 6]. Thermal analysis studies were first carried out on a Stanton Redcroft STA-780 thermal analyser under a nitrogen atmosphere. The thermal analyses were then repeated in both a programmed differential thermal analyser, a Mettler DSC-30 low temperature instrument with a Mettler TC-10A automatic data processor and more recently on a Perkin-Elmer DSC-7 differential scanning calorimeter. The results from these studies are described in detail below. All runs were performed under a nitrogen atmosphere. Photomicrographs of liquid crystal phases were obtained on a Nikon Optiphot Pol Microscope fitted with a Link TH-600 hot stage cell.

Characterisation of all compounds used was performed using a Carlo Erba 1106 elemental analyser and Perkin-Elmer λ7 and 278 spectrophotometers.

Results and conclusion

Liquid crystal behaviour was noticed with the compound



and other similar derivatives with the $-NO_2$ electron withdrawing group sited as shown. This electron withdrawing group was supplemented first by a $-CN$ group and more recently by a $-CF_3$ group. The $-CF_3$ group has been found to lower the transition temperature from crystal to liquid crystal and to give rise to a smectic liquid crystal phase [6].

The photomicrograph, Fig. 1 shows typical focal conic texture [7] of one of these materials.

Phase transitions are readily observed with DSC curves. Figures 2 to 5 show the transitions observed on heating two of these diacetylenes from 25° to 170° and cooling the two from 170° to 25° at 10° min^{-1}.

In Fig. 2, an endotherm (ΔH = 27 kJ mol^{-1}) from 106° to 120° is observed with another smaller endotherm centred at about 150°. The larger endotherm represents a crystal to smectic liquid crystal phase transition, the smaller endotherm represents a smectic to smectic liquid crystal phase transition. This is confined by the cooling cycle of the same compound as shown in Fig. 3 as the exotherm that first appears occurs at a temperature almost equal to that of the smaller endotherm in the heating cycle. Recrystallisation occurs at about 60° lower than the melting point.

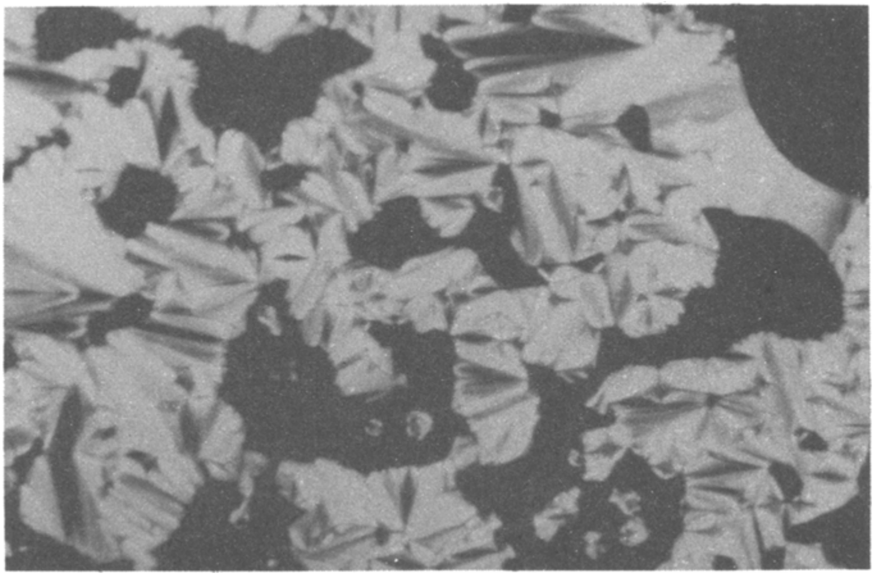
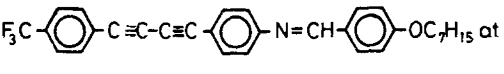


Fig. 1 Photomicrograph. Focal conics of a smectic phase



at 230.5 °C

The same pattern is observed between Figs 4 and 5 but in Fig. 4 there is an additional endotherm, preceded by a small exotherm. This endotherm is considered to be a crystal → crystal transition. The melting endotherm is thus the one occurring over the temperature range 98° →112° and again, a smectic liquid crystal is produced.

A smectic to smectic liquid crystal phase transition is assigned to the smaller endotherm in the range 133° to 150°. The results obtained on cooling the compound are displayed in Fig. 5 and fit the assignments described. The nematic to smectic liquid crystal transition occurs over the range 144° to 127° and the recrystallisation is lowered again by 60° relative to melting.

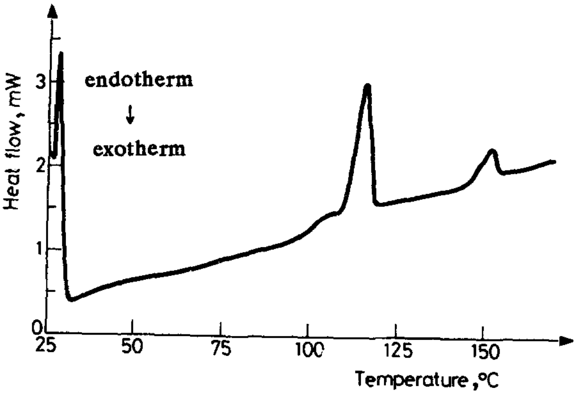
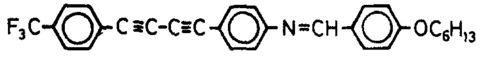


Fig. 2 Thermal curve. Heating at 10 deg min^{-1} from 25°C to 170°C for



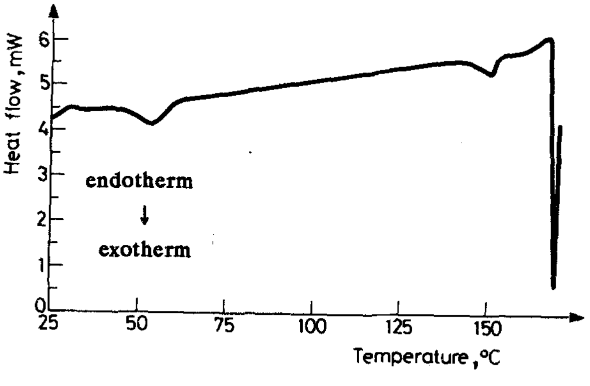
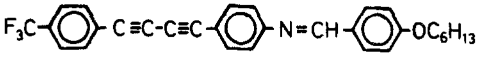


Fig. 3 Thermal curve. Cooling at 10 deg min^{-1} from 170°C to 25°C for



Figures 2 to 5 also show that as the hydrocarbon chain length increases, the crystal to smectic liquid crystal phase transition temperature is lowered whereas the temperature of smectic to smectic liquid crystal phase transition is hardly changed, thus the temperature range of existence of smectic liquid crystal is increased. The results for a series of these compounds is shown in Table 1.

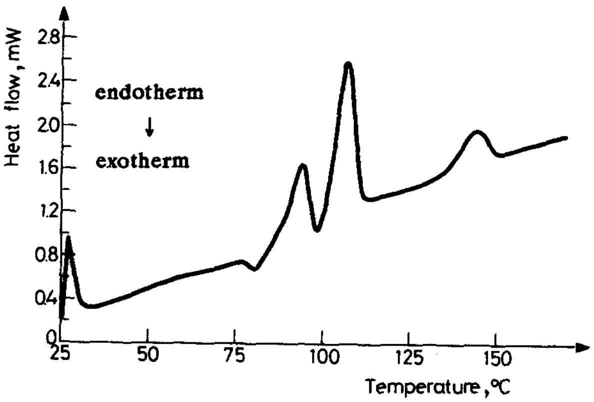
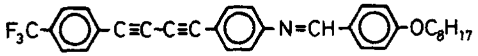


Fig. 4 Thermal curve, Heating at 10 deg min^{-1} from 25°C to 170°C for



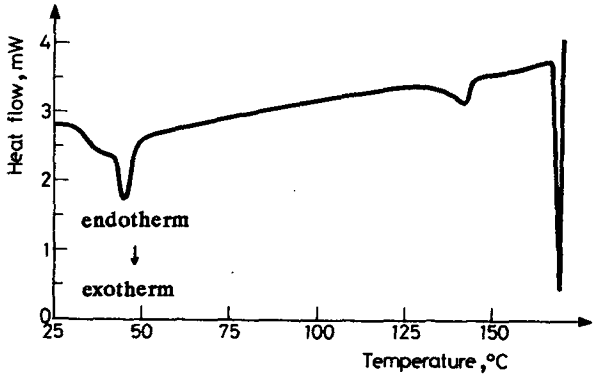


Fig. 5 Thermal curve. Cooling at 10 deg min^{-1} from 170°C to 25°C for

By contrast, results for compounds of type (ii) do not show these changes and are not discussed further.

Table 1 Phase transition temperatures of compounds of type (i) X = $-CF_3$

Y	OCH_3	OC_4H_9	OC_6H_{13}	OC_7H_{15}	C_8H_{17}	$C_{10}H_{21}$
Melting temperature/°C	222	140	115	100	96	90
Smectic to smectic liquid crystal temperature		160	140	140	140	140

Large exothermic changes occur in all compounds from about 250°. This phenomenon is currently under investigation.

References

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Zusammenfassung — Es werden thermische und optische Studien einiger Diacethylene beschrieben, die zwecks der Senkung der Temperatur für das Auftreten von Mesophasen eigens gestaltet wurden. Ursprüngliche Untersuchungen an symmetrischen Molekülen wurden erweitert, um auch typische Flüssigkeitskristallmoleküle mit Diacethylenen mit Polymerhauptketten und unsymmetrisch substituierte Diacethylene wie Schiff-Basen mit langen Alkylketten einzubeziehen.