THERMAL AND OPTICAL STUDIES ON SOME MONOMER AND POLYMER DIACTYLENES

G. H. W. Milburn, C. Campbell, A. J. Shand, A. R. Werninck, J. Varga*, K. Belina* and G. Baksay*

NAPIER POLYTECHNIC, 10 COLINTON ROAD, EDINBURGH EH10 5DT, SCOTLAND
*THE TECHNICAL UNIVERSITY OF BUDAPEST, DEPARTMENT OF PLASTICS AND RUBBER, BUDAPEST 1521, HUNGARY

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:

\[
\text{(i) } \text{X} - \text{C\equiv C\equiv C\equiv C - \text{N}=\text{C}-\text{H} - \text{O}} \nonumber \\
\text{and } \text{X} - \text{C\equiv C\equiv C\equiv C - \text{N=CH-O}} \nonumber \\
\text{X = -NO}_2, -\text{CN, CF}_3 \\
\text{Y = OCH}_2\text{H}_2\text{n} \quad 1 \leq n \leq 12
\]
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 27 and 278 spectrophotometers.

**Results and conclusion**

Liquid crystal behaviour was noticed with the compound

\[ \text{O}_2\text{N}-\begin{array}{c}
\text{C} \equiv \text{C} \equiv \\
\text{N} \equiv \text{C} \equiv \text{C} \equiv \\
\text{N} \equiv \text{CH} - \end{array} \text{OCH}_3 \]

and other similar derivatives with the \(-\text{NO}_2\) electron withdrawing group sited as shown. This electron withdrawing group was supplemented first by a \(-\text{CN}\) group and more recently by a \(-\text{CF}_3\) group. The \(-\text{CF}_3\) 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 \((\Delta H = 27 \text{ kJ mol}^{-1})\) 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