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Synthesis and thermotropic behaviour of liquid crystals containing tolane-based mesogenic units

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Tolane-based liquid crystal materials with three different terminal groups: trifluoromethyltolanes, cyanotolanes and nitrotolanes, and with different chain lengths of alkenyloxy groups, have been synthesized. The phase behaviour of these liquid crystal materials has been characterized by differential scanning calorimetry, optical polarized light microscopy and X-ray diffraction. The mesophase behaviour of the materials was shown to be significantly influenced by the polarity of the terminal groups. The trifluoromethyltolanes exhibit an enantiotropic smectic E mesophase and the cyanotolanes exhibit a monotropic nematic mesophase. The most polar among the three types of liquid crystal material; the nitrotolanes do not display any liquid crystalline phases, except for the homologue with an eleven methylene unit chain.

1. Introduction

Although Vorländer [1, 2] in 1907, reported upon the first mesogenic tolane (or diphenylacetylene) derivative, there was no further study in this area until the applications of liquid crystal displays (LCD), in the 1970s, which inspired further research [2–7]. Most of the tolane-based LCs reported possessed both low viscosity and high birefringence, properties which were known to have potential in electro-optical applications [8, 9]. In recent years, a wide range of research into tolane LC materials has been performed. Percec *et al.*, and Viney *et al.*, have reported upon new polytolane compounds [10–12]; Praefcke *et al.*, synthesized a new type of discotic tolane-based LC compound [13]. However, the correlation between chemical structure, especially that of the terminal group, and the mesophase behaviour of such compounds, is still not well established. This study aims to present the synthesis and characterization of some new unsymmetrical tolane-based LCs. This study relates to the 4-alkenyloxy-4′-trifluoromethyltolanes, 4-alkenyloxy-4′-cyanotolanes and 4-alkenyloxy-4′-nitrotolanes. The effect of the terminal groups and the alkenyl chain length on the mesomorphic properties of the LCs prepared is discussed.

2. Synthesis

The synthesis of the tolane-based compounds **1M**–**9M** is outlined in the scheme. Following the initial etherification reaction, the 4-bromo-1-(ω-alkenyloxy)benzene is coupled with 2-methyl-3-butyn-2-ol by a traditional Pd(0)/Cu(I) coupling procedure using triethylamine as base, and refluxing in THF. The resulting alkynol is then deprotected and coupled with the corresponding aryl halides. Most of the

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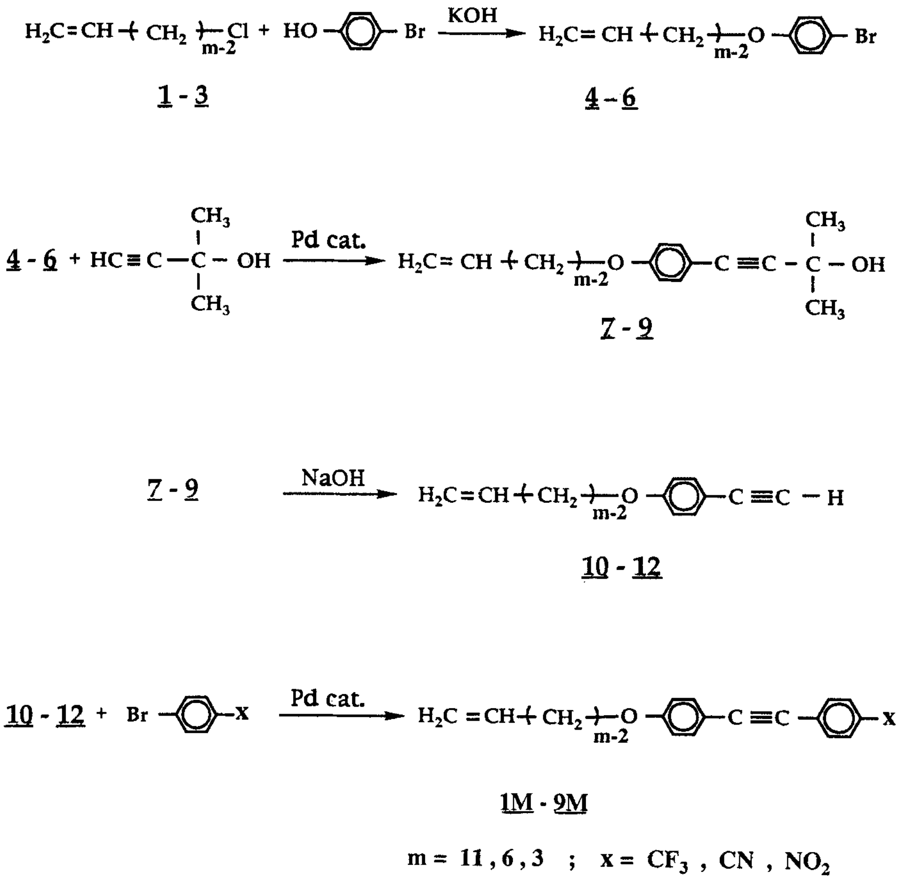

Scheme. Synthesis of tolane-based compounds 1M–9M.

reactions were accomplished with high yields [14, 15]. All products were purified by column chromatography and characterized by HPLC and ^{1}H NMR spectrometry. Synthetic details of the above reactions are described below.

2.1. *Materials*

Bis(triphenylphosphine)palladium (II)chloride, triphenylphosphine, 2-methyl-3-butyn-2-ol (all from Janssen, Belgium), copper (I) iodide (from Merck) and all other reagents (from Aldrich) were used as received. Triethylamine was distilled under nitrogen from potassium hydroxide. Tetrahydrofuran and toluene were first refluxed over sodium and then distilled under nitrogen.

2.2. *Techniques*

^{1}H NMR spectra were obtained with a Bruker AM-400 spectrometer. All spectra were recorded using $CDCl_3$ solutions with TMS as the internal standard. IR spectra were measured using a Perkin–Elmer 842 infrared spectrometer. Purity was determined by high performance liquid chromatography (HPLC) with a Spectra-Physics LC instrument. A Dupont 910 DSC equipped with a 9900 computer system was used to determine the thermal transitions that were taken at the maximum of the endothermic or exothermic peaks. In all cases, heating and cooling rates were 10°C min^{-1}. The thermal transitions were read from reproducible second or later heating scans and first or later cooling scans, unless otherwise specified. A Nikon Microphot-FX optical polarizing microscope equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was used to observe thermal transitions and anisotropic textures. X-ray diffraction measurements were performed with nickel-filtered CuKα radiation with a Rigaku powder diffractometer.

2.3. *Synthesis*

11-Chloro-1-undecene **1** and 6-chloro-1-hexene **2** were prepared by a previously published route [23].

2.3.1. *4-Bromo-1-(ω-alkenyloxy)benzenes* (**4–6**)

The three compounds were prepared by etherification of 4-bromophenol with the corresponding alkenyl halide. The synthesis of compound **4** is presented below.

A mixture of 4-bromophenol (10·0 g, 57·8 mmol), potassium hydroxide (3·2 g, 57·8 mmol) and dimethyl sulphoxide (100 ml) was heated to 65°C. Then 11-chloro-1-undecene (9·9 g, 52·5 mmol) was added dropwise. The solution was stirred at 65°C for 18 h, then cooled to room temperature. Dimethyl sulphoxide was removed under reduced pressure. The crude product was dissolved in ethyl acetate and the extract washed with dilute potassium hydroxide, water, and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure on a rotary evaporator. The residue was purified by column chromatography using silica gel with *n*-hexane as eluent to yield 14·7 g (86·1 per cent) of a colourless oily product. MS: m/z 325(M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·20–2·15 (m, 16 H, $-(CH_2)_8-$), 3·93 (t, 2 H, $-CH_2-O-$), 4·92 (m, 2 H, $H_2C=$), 5·83 (m, 1 H, $=CH-$), 6·81 and 7·34 (q, 4 H, aromatic protons).

2.3.2. *4-(3-Hydroxy-3-methyl-1-butynyl)-1-(ω-alkenyloxy)benzenes* (**7–9**)

Compounds **7–9** were synthesized by the coupling reaction of 2-methyl-3-butyn-2-ol with the corresponding aryl bromides **4–6** [15]. The synthesis of compounds **7** is given as follows. To a solution of 4-bromo-1-(10-undecenyloxy)benzene, **4** (10·0 g, 31·0 mmol), 2-methyl-3-butyn-2-ol (3·1 g, 37·2 mmol) and dry triethylamine (50 ml) in tetrahydrofuran (100 ml), bis(triphenylphosphine)palladium (II) chloride (0·16 g), copper (I) iodide (0·16 g) and triphenylphosphine (0·31 g) were added. The mixture was stirred at 60°C overnight. After filtration to remove precipitated material, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel with chloroform as eluent to yield 8·7 g (86·2 per cent) of white crystals. m.p. 35·8°C. MS: m/z 328(M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·25–2·07 (m, 16 H, $-(CH_2)_8-$), 1·60 (s, 6 H, $-(CH_3)_2-$), 3·94 (t, 2 H, $-CH_2-O-$), 4·95 (m, 2 H, $H_2C=$), 5·81 (m, 1 H, $=CH-$), 6·80 and 7·36 (q, 4 H, aromatic protons).

2.3.3. *[4-(ω-Alkenyloxy)phenyl]acetylenes* (**10–12**)

The three compounds were synthesized by deprotection of the alkynol **7–9** [15]. The synthesis of compound **10** is presented below.

Compound **7** (7·1 g, 21·6 mmol) was dissolved in anhydrous toluene (400 ml) in a reaction vessel equipped with a Dean–Stark trap and a reflux condenser, and then the sodium hydroxide (1·3 g, 32·5 mmol) added. The mixture was heated at reflux for

Table 1. Characterization of tolane-based compounds **1M–9M**.

Compound	Yield/per cent	400 MHz ^{1}H NMR ($CDCl_3$, TMS, δ/ppm)
1M	63	1·22–2·06 (m, 16 H, $-(CH_2)_8-$), 3·94 (t, 2 H, $-CH_2-O-$), 4·87 and 5·77 (m, 3 H, $H_2C{=}CH-$), 6·83–7·47 (q, 4 H, aromatic protons), 7·57 (s, 4 H, aromatic protons).
2M	70	1·42–2·10 (m, 6 H, $-(CH_2)_3-$), 3·95 (t, 2 H, $-CH_2-O-$), 4·95 and 5·78 (m, 3 H, $H_2C{=}CH-$), 6·85–7·47 (q, 4 H, aromatic protons), 7·56 (s, 4 H, aromatic protons).
3M	68	4·52 (d, 2 H, $-CH_2-O-$), 5·32 and 6·02 (m, 3 H, $H_2C{=}CH-$), 6·86–7·46 (q, 4 H, aromatic protons), 7·57 (s, 4 H, aromatic protons).
4M	80	1·24–2·03 (m, 16 H, $-(CH_2)_8-$), 3·93 (t, 2 H, $-CH_2-O-$), 4·91 and 5·78 (m, 3 H, $H_2C{=}CH-$), 6·82–7·60 (2q, 8 H, aromatic protons).
5M	77	1·50–2·12 (m, 6 H, $-CH_2)_3-$), 3·94 (t, 2 H, $-CH_2-O-$), 4·96 and 5·80 (m, 3 H, $H_2C{=}CH-$), 6·83–7·59 (2q, 8 H, aromatic protons).
6M	70	4·53 (d, 2 H, $-CH_2-O-$), 5·31 and 6·01 (m, 3 H, $H_2C{=}CH-$), 6·85–7·61 (2q, 8 H, aromatic protons).
7M	70	1·21–2·01 (m, 16 H, $-(CH_2)_8-$), 3·91 (t, 2 H, $-CH_2-O-$), 4·88 and 5·75 (m, 3 H, $H_2C{=}CH-$), 6·80–8·14 (2q, 8 H, aromatic protons).
8M	65	1·45–2·09 (m, 6 H, $-(CH_2)_3-$), 3·94 (t, 2 H, $-CH_2-O-$), 4·90 and 5·77 (m, 3 H, $H_2C{=}CH-$), 6·80–8·14 (2q, 8 H, aromatic protons).
9M	62	4·53 (d, 2 H, $-CH_2-O-$), 5·33 and 6·01 (m, 3 H, $H_2C{=}CH-$), 6·82–8·15 (2q, 8 H, aromatic protons).

3 h. The mixture was then cooled to room temperature, shaken with water, and the organic layer dried over anhydrous magnesium sulphate. Toluene was removed and the resulting solid was purified by column chromatography using silica gel with 1 : 1 chloroform/*n*-hexane as eluent to yield 5·1 g (68·3 per cent) of a colourless liquid. MS: *m*/*z* 270(M^+). ^{1}H NMR ($CDCl_3$, TMS) δ 1·24–2·06 (m, 16 H, $-(CH_2)_8-$), 2·97 (s, 1 H, $\equiv C-H$), 3·94 (t, 2 H, $-CH_2-O-$), 6·80 and 7·36 (q, 4 H, aromatic protons).

2.3.4. *1-[4-(ω-Alkenyloxy)phenyl]-2-(4′-trifluoromethylphenyl)acetylenes* (**1M–3M**), *1-[4-(ω-alkenyloxy)phenyl]-2-(4′-cyanophyl)acetylenes* (**4M–6M**) *and 1-[4-(ω-alkenyloxy)phenyl]-2-(4′-nitrophenyl)acetylenes* (**7M–9M**)

All nine tolane-based compounds **1M–9M** were prepared by the coupling reaction of acetylenic compounds **10–12** with 4-bromo-1-trifluorobenzene, 4-bromobenzonitrile or 4-bromo-1-nitrobenzene [15]. The synthesis of compound **3M** is described below.

To a solution of [4-(10-undecenyloxy)phenyl]acetylene, **10** (2·5 g, 9·3 mmol) and 4-bromo-1-trifluorobenzene (2·5 g, 11·1 mmol) in dry triethylamine (10 ml) and tetrahydrofuran (50 ml), bis(triphenylphosphine)palladium (II) chloride (0·03 g), copper (I) iodide (0·03 g) and triphenylphosphine (0·06 g) were added. The mixture was heated at reflux for 5 h, then cooled to room temperature. After filtration to remove precipitated material, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel with 6 : 1 *n*-hexane/toluene as eluent to yield 2·42 g (63·2 per cent) of white crystals. The yields and ^{1}H NMR chemical shifts of compounds **1M–9M** are summarized in table 1.

3. Results and discussion

The phase transitions and thermodynamic parameters of the LCs are summarized in table 2. The compounds containing a trifluoromethyl terminal group (**1M**–**3M**) exhibit enantiotropic smectic E phases as observed by optical polarizing microscopy and confirmed by X-ray diffraction. A typical X-ray diffraction diagram of compound **1M** in different states is presented in figure 1. In the isotropic phase (curve *A*), no apparent reflection peak could be observed. When the temperature was lowered to the temperature range of the S_E phase, however, several reflections were found (curve *B*). The small angle reflections appeared at 31·53 Å (first order) and at 15·57 Å (second order) corresponding to the spacings of the smectic layers. In the wide angle range there are three sharp reflections (4·46 Å, 4·13 Å and 3·26 Å) which correspond to the orthorhombic array within the layers of a S_E mesophase [16–18]. Figure 2 shows the optical polarized micrograph of the mosaic platelet textured S_E phase of **1M** [18, 19]. As the phase changes to the crystalline state (figure 1, curve *C*) the small angle reflections disappear and a series of new wide angle reflections appear, corresponding to the diffraction of a crystalline lattice (4·49 Å, 4·36 Å and 3·93 Å).

Figure 3 presents the DSC traces of compounds **1M**–**3M**: several successive heating and cooling scans were performed. For **1M**, the first and subsequent heating

Table 2. Phase transition temperatures (°C) and corresponding enthalpy changes in brackets (kJ mol^{-1}) for tolane-based compounds **1M**–**9M**.

Compound	*m*†	*X*	Phase transition data‡				
1M	11	CF_3	C	66·9 (16·97)	S_E	78·3 (13·66)	I
			I	74·4 (13·21)	S_E	21·1 (18·22)	C
2M	6	CF_3	C	26·6 (1·65)	S_E	86·0 (13·42)	I
			I	82·0 (13·21)	S_E	11·5 (1·17)	C
			§C	54·1 (9·39)	S_E	86·4 (13·28)	I
3M	3	CF_3	C	−30·8 (0·45)	S_E	114·1 (15·25)	I
			I	110·3 (15·19)	S_E	−45·1 (0·73)	C
			§C	77·8 (0·79)	S_E	114·8 (15·86)	I
4M	11	CN	C	83·0 (42·96)	I		
			I	80·6 (1·78)	N	60·4 (32·39)	C
5M	6	CN	C	88·6 (37·17)	I		
			I	79·7 (0·33)	N	72·7 (34·86)	C
6M	3	CN	C	115·2 (27·56)	I		
			I	104·1 (0·93)	N	96·6 (28·05)	C
7M	11	NO_2	C	75·1 (46·84)	I		
			I	64·7 (0·90)	N	52·1 (43·01)	C
8M	6	NO_2	C	79·9 (26·50)	I		
			I	65·8 (27·73)	C		
9M	3	NO_2	C	100·6 (22·46)	I		
			I	75·5 (21·71)	C		

†*m*, *X*, according to scheme 1.

‡C, crystalline; S_E, smectic E; N, nematic; I, isotropic; first line of data obtained from second and subsequent heating scans; second line of data obtained from cooling scans.

§From first heating scan.

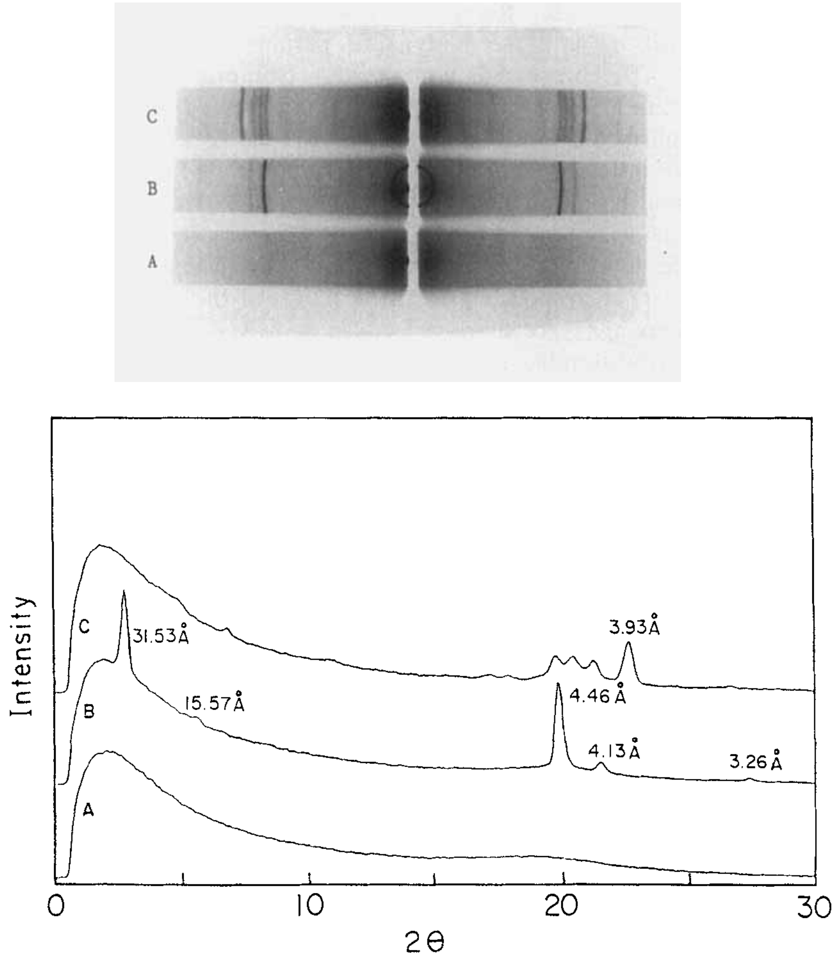

Figure 1. Temperature dependent X-ray diffraction of the compound **1M** at: (*A*) 85°C; (*B*) 60°C and (*C*) 20°C.

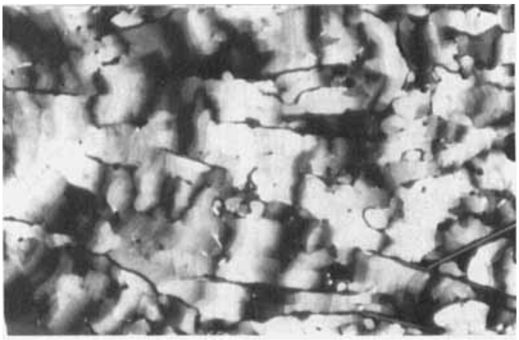

Figure 2. Optical polarizing micrograph (magnification ×80) displayed by **1M**: smectic E texture obtained at 60°C on cooling.

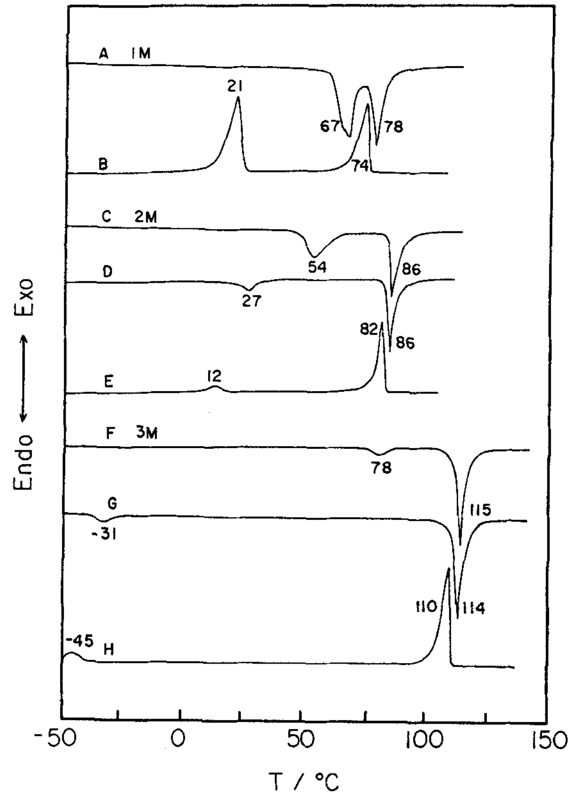

Figure 3. Normalized DSC traces ($10^{\circ}\mathrm{C\,min}^{-1}$) of (*A*) **1M**, heating scans; (*B*) **1M**, cooling scans; (*C*) **2M**, first heating scan; (*D*) **2M**, second and subsequent heating scans; (*E*) **2M**, cooling scans; (*F*) **3M**, first heating scan; (*G*) **3M**, second and subsequent heating scans; (*H*) **3M**, cooling scans.

scans exhibit the same melting temperature and melting enthalpy of the crystalline phase (curve *A*). Different behaviour, however, was observed in the cases of **2M** and **3M**. The melting temperatures and enthalpies of the second scans (or subsequent scans) were much lower than those found on the first scans. The result indicated that once **2M** and **3M** were melted they could not easily recrystallize and, therefore, a lower degree crystallinity and a lower melting point were obtained. If, however, **2M** and **3M** were stored at ambient temperature for a long time (about 2 days), the same crystallinity as that on the first scan could be obtained. The clearing temperatures did not exhibit the same behaviour, possibly because crystallization is a mainly kinetically controlled process whereas liquid crystalline phase transitions are thermodynamically controlled. It is noteworthy that among the compounds with the same alkenyl chain length, for those with the more polar terminal groups (for example **5M**, **6M**, **8M** and **9M**), crystallization is easily attained without depression of the melting temperature for the second successive heating scan. This suggests that the ease of crystallization is associated with the nature of the mesophase formed. (This may, in turn, eventually relate to the molecular structure.) The more ordered the mesophase, the lower is the tendency towards crystallization.

When replacing the terminal trifluoromethyl group with a more polar cyano group, the compounds exhibit only a monotropic nematic liquid crystalline phase. A typical schlieren texture of the nematic phase of **4M** is shown in figure 4. For the most polar nitrotolane compounds, it is found that only the longer alkenyl chain homologue (eleven methylene units) possesses a liquid crystalline phase. It is seen that the polarity of the terminal groups has a profound effect on the nature of the resulting mesophase. These results are in good agreement with results for LCs containing a diphenyldiacetylene moiety with the same terminal groups [20], in that replacement of a cyano or a nitro group by a trifluoromethyl group resulted in smectic phase formation rather than a nematic phase.

The influence of terminal groups and chain lengths of the alkenyloxy group on phase transitions is illustrated in figure 5. The clearing transition temperatures are

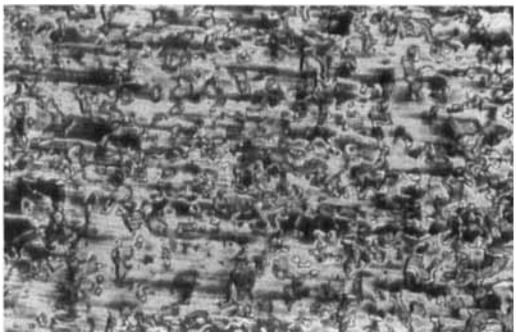

Figure 4. Optical polarizing micrograph (magnification ×80) displayed by **4M**: nematic texture obtained at 69°C on cooling.

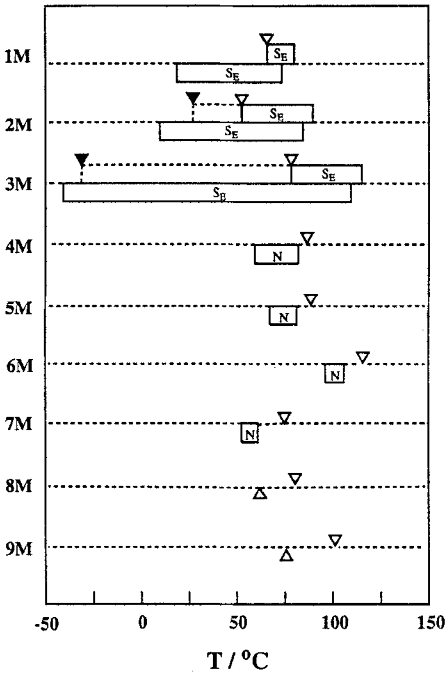

Figure 5. The mesophase ranges for the compounds **1M**–**9M**. (▽) melting temperatures, (△) crystallization temperatures, (▼) melting temperatures obtained from second and subsequent heating scans.

decreased by increasing the length of the alkenyloxy chains. For the same chain length, the cyanotolanes have the highest clearing temperatures. This could be due to a conjugation effect induced by the cyano group with the tolane-based moiety leading to a longer mesogenic core. The same behaviour is commonly reported in the literature [21, 22].

4. Conclusion

Three types of tolane-based compound containing trifluoromethyl, cyano and nitro terminal groups have been prepared. The polarity of the terminal groups has a profound effect on the nature of the mesophases formed. According to the results obtained in this study, it seems that introducing a terminal group of lower polarity into the structural unit of the LCs, increases the degree of order of the resulting mesophase.

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