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Ging-Ho Hsiue[a]; Long-Hai Wu[a]; Chang-Jyh Hsieh[a]; Ru-Jong Jeng[a]
[a] Department of Chemical Engineering, National Tsing Hua University, Taiwan, China

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Synthesis and thermal behaviour of non-linear optical materials. 1: Liquid crystals containing long conjugate and high polar terminal groups

by GING-HO HSIUE*, LONG-HAI WU, CHANG-JYH HSIEH
and RU-JONG JENG

Department of Chemical Engineering, National Tsing Hua University,
Hsinchu, Taiwan 30043, China

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A number of non-symmetrical liquid crystalline compounds with a long conjugate length (phenyltolane) and three different polar terminal groups ($-NO_2$, $-CN$, $-CF_3$) for non-linear optical applications were synthesized. These compounds are liquid crystalline and expected to exhibit a large first molecular hyperpolarizability (β). They all exhibit crystal E (CrE), smectic A (S_A), and nematic (N) phases except the compounds containing a trifluoromethyl terminal group which have CrE, S_B and S_A phases. The layer thickness and the intermolecular spacing were investigated using powder X-ray diffraction. A bilayer structure is present in the S_A phase, which disappears on going into the CrE phase. The layer thickness of the S_A phase increases as the temperature decreases. Moreover, this family of phenyltolane chromophores exhibits excellent thermal stability as shown by differential scanning calorimetry and thermogravimetric analysis. Their thermal degradation temperatures are approximately 300°C. UV–VIS absorption characteristics of all compounds show short cut-off wavelength ($\lambda_{\text{cut-off}} < 460$ nm). More polar terminal groups (polarity: $-NO_2 > -CN > -CF_3$) cause a red shift of the absorption peaks ($\lambda_{\text{cut-off}}$: $460 > 390 > 370$ nm). Such properties make these compounds potentially useful in non-linear optical applications.

1. Introduction

Organic compounds as non-linear optical (NLO) materials have attracted attention due to their large non-linearity, low dielectric constants, low switching energy, and low absorption characteristics [1]. A typical organic second order NLO species consists of electron donating and withdrawing groups separated by a π-delocalized moiety [2]. Such NLO active chromophores tend to exhibit large non-linearity. Second order NLO effects are observed when the NLO active species are aligned in a non-centrosymmetric manner in a polymer matrix. The alignment is usually achieved by a Corona poling [3]. These aligned chromophores tend to randomize when the electric field is removed. However, the ultimate applicability of polymeric materials for second order non-linear optics may depend upon the ability to produce polymers whose alignment has sufficient stability [4]. Liquid crystalline polymers are considered to be a rational approach to enhance the NLO stability because of their molecular order characteristics, i.e. self-alignment [5–7].

Tolane-based molecules are potential candidates as effective NLO chromophores because of their linearity and conjugate characteristics. 4-amino-4′-nitrolane as an NLO chromophore was covalently attached to a linear epoxy polymer backbone [8]. The poled (aligned) polymer film showed a large second harmonic coefficient ($d_{33} = 89\,\text{pm}\,\text{V}^{-1}$). This is much larger than that for lithium-niobate ($LiNbO_3$, $d_{33} = 30\,\text{pm}\,\text{V}^{-1}$). The large d_{33} value is due primarily to its long conjugate length and resonance enhancement in the tolane structure. However, the tolane-based chromophore was found to possess a low degradation temperature of approximately 170°C [9, 10]. For electro-optical (EO) applications, the NLO properties of the materials must be stable at 250°C or higher for short period of time [11], and therefore, the thermal stability of the tolane-based chromophores becomes a limiting factor in the progress toward practical applications.

The UV–VIS absorption characteristics are important the NLO applications. For frequency doubling, even a small absorption will cause damage to second order NLO materials. The cut-off wavelengths of the donor–acceptor tolane-based chromophores are shorter than 460 nm [12, 13], thus tolane-based chromophores can be utilized in frequency doubling near the blue region.

The self-aligning property of a liquid crystal phase can help to achieve homogeneous alignment induced by a d.c.

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* Author for correspondence.

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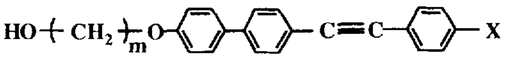
field. The second harmonic generation (SHG) of a system containing a thermotropic nematic (N) liquid crystalline copolymer doped (2 wt %) with 4-(dimethylamino)-4′-nitrostilbene (DANS) is about 100 times larger than that obtained from amorphous polymethylmethacrylate doped with 2 per cent DANS [14]. This indicates that the liquid crystalline phase can enhance the second order NLO properties of the polymer.

Mesophase stability depends on the rigidity, linearity and polarizable π-electron density of the mesogenic core [15]. Shorter tolane-based mesogenic cores tend to form only smectic A (S_A) and nematic (N) phases, and the mesophase behaviour is significantly influenced by the polarity of the terminal groups [16–19]. When a phenyltolane group is introduced into the mesogenic core, more highly ordered liquid crystal phases appear and the temperature range of the liquid crystal phases widen as a result [20]. Moreover, the increase in the number of phenyl rings in the compound tend to greatly enhance its thermal stability [21].

Based upon the considerations discussed above, NLO active non-symmetrical phenyltolane chromophores (**1 A–9 A**) exhibiting liquid crystalline phases were synthesized. The structures of compounds **1 A–9 A** are as follows:



$m = 3,6,11$ $X = NO_2$, CN, CF_3

The phenyltolane chromophores were chosen for this study due partly to the fact that the increase in the donor–acceptor strength and the conjugate length of the NLO chromophore could enhance the first molecular hyperpolarizability (β) [22, 23]. The phase behaviour, effect of temperature on the smectic layer thickness, thermal stability and UV–VIS spectra were determined.

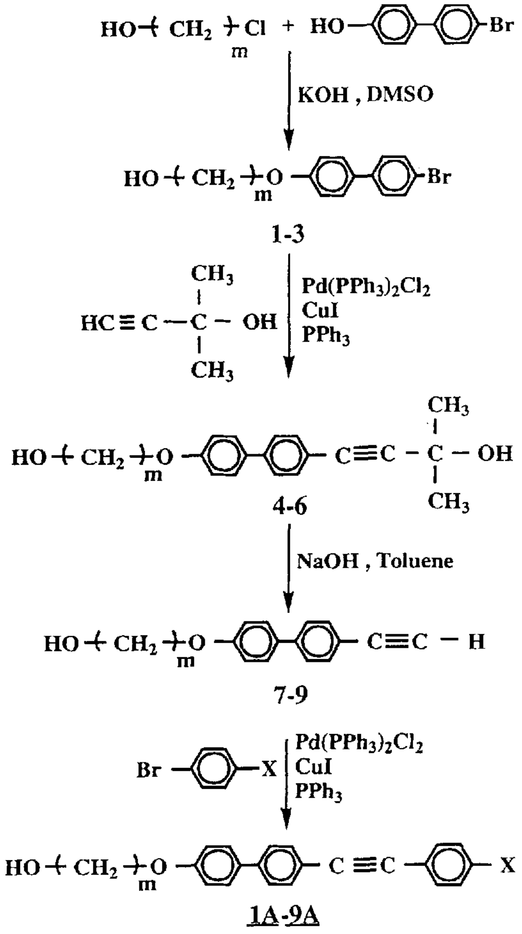
2. Experimental

2.1. *Techniques*

^{1}H NMR spectra were obtained in $CDCl_3$ with a Bruker AM-400 spectrometer using TMS as an internal standard. A Seiko SSC/5200 differential scanning calorimeter (DSC) was used for determining the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. Heating and cooling rates were 10°C min^{-1}. Thermal degradation temperatures were measured with a DuPont 951 thermogravimetric analyser (TGA) at 10°C min^{-1} under air. A Nikon Microphot-FX polarizing optical microscope (POM) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor were used for observing thermal transitions and mesomorphic textures. X-ray diffraction measurements were performed with a Rigaku powder diffractometer using a nickel-filtered CuK_α radiation. UV–VIS spectra were recorded on a Hitachi 320 spectrophotomer.

2.2. *Synthesis*

Synthesis of the compounds is outlined in the scheme.



m = 3, 6, 11; X = CF_3, CN, NO_2

Scheme. Synthesis of compounds **1 A–9 A**.

2.2.1. *Synthesis of 4-bromo-4′-(ω-hydroxyalkanyloxy)-biphenyl* (**1–3**)

All three compounds were synthesized by the etherification of 4-bromo-4′-biphenol with corresponding ω-bromoalkan-1-ol or ω-chloroalkan-1-ol. An example of this procedure is given below for $m = 6$:

A mixture of 4-bromo-4′-biphenol (10·0 g, 40·0 mmol), potassium hydroxide (4·2 g, 75·0 mmol) and dimethyl sulphoxide (100 ml) was heated to 65·0°C. 6-Chloro-1-hexanol (6·6 g, 48·3 mmol) was added dropwise, the resulting solution stirred at 65·0°C for 18 h, cooled to room temperature , and then poured into water (500 ml). The resulting white precipitate was removed by filtration, washed with dilute aqueous KOH, and then dissolved in ethylacetate. Purification was performed using flash chromatography on silica gel eluting with $CHCl_3$. The resulting solution was evaporated *in vacuo* to give the crude product. Further purification by recrystallization from EtOAc/*n*-hexane (2/1) yielded 11·2 g (79·3 per cent) of white crystals of **2**: m.p. 70·5°C; MS *m/z* 349 (M^+), and ^{1}H NMR δ 1·28–1·84 (m, 8 H, $-(\mathrm{C\underline{H}_2})_4-$). 3·68 (t, 2 H, $\mathrm{HO{-}C\underline{H}_2{-}}$), 4·00 (t, 2 H, $\mathrm{-C\underline{H}_2{-}O{-}}$), 6·93–7·53 (m, 8 H, aromatic protons).

2.2.2. *Synthesis of 4-3-hydroxy-3-methyl-1-butynyl)-4′-(ω-hydroxyalkanyloxy)biphenyl* (**4–6**)

All three compounds were synthesized by the coupling reaction of 2-methyl-3-butyn-2-ol with the corresponding aryl bromides. An example is outlined below for *m* = 6:

To a solution of 4-bromo-4′-(6-hydroxyhexanyloxy)-biphenyl (11·0 g, 32·0 mmol), 2-methyl-3-butyl-2-ol (10·0 g, 120·0 mmol), and dry triethylamine (80·0 ml) in THF (100·0 ml), the catalysts bis(triphenylphosphine)-palladium(II) chloride (0·15 g), copper(I) iodide (0·15 g) and triphenylphosphine (0·30 g) were added [24]. The mixture was heated under reflux (80°C) for 24 h, cooled to room temperature and filtered to remove precipitated material. The filtrate was evaporated under reduced pressure to give the crude product. Purification was performed using flash chromatography on silica gel eluting with $CHCl_3$ followed by recrystallization from EtOAc/*n*-hexane (2 : 1) to yield 8·0 g (72·6 per cent) of white crystals of **5**: m.p. 75·7°C; MS *m/z* 352 (M^+) and ^{1}H NMR δ 1·46–1·85 (m, 8 H, $-(\mathrm{C\underline{H}_2})_4-$), 1·63 (s, 6 H, $-(\mathrm{C\underline{H}_3})_2-$), 3·67 (t, 2 H, $\mathrm{HO{-}C\underline{H}_2{-}}$), 4·01 (t, 2 H, $\mathrm{-C\underline{H}_2{-}O{-}}$), 6·94–7·52 (m, 8 H, aromatic protons).

2.2.3. *Synthesis of [4-(ω-hydroxyalkanyloxy)biphenyl]-acetylene* (**7–9**)

These compounds were synthesized by deprotection of the protected aryl acetylides. An example is given for *m* = 6.

Sodium hydroxide (1·8 g, 40·4 mmol) was added to a solution of 4-(3-hydroxy-3-methyl-1-butynyl)-4′-(6-hydroxyhexanyloxy)biphenyl (8·0 g, 22·7 mmol). The mixture was heated under reflux (120°C) for 3 h using a Dean–Stark trap and reflux condenser, cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure purified using flash chromatography on silica gel eluting with $CHCl_3$. The crude product was further purified by recrystallization from EtOAc/*n*-hexane (2/1) to yield 5·8 g (85·1 per cent) of white crystals of **8**: m.p. 109·9°C; MS *m/z* 294 (M^+) and ^{1}H NMR δ 1·48–1·84 (m, 8 H, $-(\mathrm{C\underline{H}_2})_4-$), 3·10 (s, 1 H, $\mathrm{-C{\equiv}C{-}CH}$), 3·67 (t, 2 H, $\mathrm{HO{-}C\underline{H}_2{-}}$), 4·01 (t, 2 H, $\mathrm{-C\underline{H}_2{-}O{-}}$), 6·95 and 7·51 (m, 4 H, aromatic protons).

Table 1. Phase transition temperatures and associated enthalpy change (in parentheses) for the tolane-based compounds **1 A–9 A**. For each compound, the first line of data corresponds to the cooling scan, the second line to the second heating scan.

Compound	*m*†	*X*†	Phase transition data‡/°C (kJ mol^{-1})
1 A	11	NO_2	Cr 28·0 (9·2) CrE 167·3 (7·2) S_A 200·5 (0·6) N 211·7 (0·5) I Cr 102·2 (8·7) CrE 171·1 (7·6) S_A 205·6 (0·5) N 216·2 (0·7) I
2 A	6	NO_2	Cr 99·5 (12·2) CrE 170·2 (–)§ S_A 180·5 (11·6) N 265·2 (1·0) I Cr 131·5 (9·0) CrE 173·0 (–)§ S_A 185·0 (8·7) N 270·0 (0·9) I
3 A	3	NO_2	Cr 119·1 (1·0) CrE 157·0 (0·9) S_A 182·8 (7·6) N 291·3 (–)§ I Cr 123·4 (1·0) CrE 156·3 (4·6) S_A 189·3 (8·5) N 294·3 (–)§ I
4 A	11	CN	Cr 82·7 (26·0) CrE 161·9 (8·9) S_A 184·6 (–)§ N 217·9 (0·7) I Cr 132·4 (32·1) CrE 167·2 (11·4) S_A 188·2 (–)§ N 222·7 (1·5) I
5 A	6	CN	Cr 93·6 (16·6) CrE 184·6 (9·5) S_B 188·7 (2·5) S_A 201·6 (–)§ N 279·7 (0·5) I Cr 136·5 (19·3) CrE 188·8 (8·9) S_B 192·8 (3·3) S_A 209·7 (–)§ N 290·0 (0·6) I
6 A	3	CN	Cr 125·8 (0·5) CrE 208·8 (7·6) S_A 240·4 (2·3) N 307·7 (0·4) I Cr 142·5 (0·7) CrE 212·7 (7·6) S_A 245·6 (2·8) N 321·5 (0·7) I
7 A	11	CF_3	Cr 94·2 (33·9) CrE 215·1 (7·5) S_A 218·8 (15·4) I Cr 143·3 (28·4) CrE 218·0 (7·8) S_A 223·3 (12·3) I
8 A	6	CF_3	Cr 105·9 (9·8) CrE 217·7 (2·2) S_B 231·2 (6·4) S_A 240·6 (10·0) I Cr 166·1 (14·7) CrE 221·1 (2·6) S_B 234·9 (7·8) 244·3 (10·0) I
9 A	3	CF_3	Cr 202·2 (10·3) CrE 229·8 (2·2) S_B 237·5 (6·8) S_A 250·0 (8·5) I Cr 214·9 (9·8) CrE 234·2 (2·8) S_B 240·2 (6·5) S_A 253·6 (9·6) I

† *m*, *X*, according to the scheme.

‡ Cr, crystalline; CrE, crystal E; S_B, smectic B; S_A, smectic A; N, nematic; I, isotropic.

§ Could not be measured.

2.2.4. *Synthesis of 1-[4-(ω-hydroxyalkanyloxy)biphenyl]-2-(4-nitrophenyl)acetylene* (**1 A–3 A**), *1-[4-(ω-hydroxyalkanyloxy)biphenyl]-2-(4-cyanophenyl)-acetylene* (**4 A–6 A**), *and 1-[4-(ω-hydroxyalkanyloxy)biphenyl]-2-(4-trifluoromethylphenyl)acetylene* (**7 A–9 A**)

These compounds were prepared using the same method. An example of this procedure is given below for **2 A**.

Bis(triphenylphosphine)palladium(II) chloride (0·026 g), copper(I) iodide (0·026 g) and triphenylphosphine (0·052 g) were added to a solution of [4-(6-hydroxyalkanyloxy)biphenyl]acetylene (1·8 g, 5·1 mmol) and 4-bromobenzonitrile (1·1 g, 6·2 mmol) in dry triethylamine (20·0 ml) and THF (50·0 ml). The mixture was heated under reflux (80°C) for 24 h, cooled to room temperature and filtered to remove any precipitated material. The filtrate was evaporated under reduced pressure to obtain the crude product. Purification was performed using flash chromatography on silica gel eluting with $CHCl_3$, and was further purified by recrystallization from EtOAc/*n*-hexane (2/1) to yield 1·5 g (62·4 per cent) of white crystals of **2 A**: m.p. 290·8°C; MS m/z 395(M^+). ^{1}H NMR δ 1·29–1·79 (m, 8 H, $-(C\underline{H}_2)_4-$), 3·62 (t, 2 H, $HO-C\underline{H}_2$), 3·99 (t, 2 H, $Ph-O-C\underline{H}_2-$), 6·92–8·22 (m, 12 H, aromatic protons). Yields for compounds **1 A–9 A** ranged from 59 to 90 per cent.

3. Results and discussion

The phase behaviour of the compounds **1 A–9 A** was determined by DSC, POM, and powder X-ray diffraction. The thermal transition behaviour of all the compounds is summarized in table 1.

All these compounds exhibited enantiotropic mesophases. Those with either a nitro (**1 A–3 A**) or a cyano terminal group (**4 A–6 A**) exhibited CrE S_A, and N phases. Compounds with a trifluoromethyl terminal group (**7 A–9 A**), all possessed CrE and S_A phases but no N phase due to the presence of the less polar trifluoromethyl group. Compounds **8 A** and **9 A** exhibited an additional S_B phase below the S_A phase. Furthermore, the melting and clearing transition temperatures decreased with increasing length of the hydroxyalkanyloxy chains.

The compounds with high polar terminal groups ($-NO_2$, $-CN$) tended to form homeotropic N, S_A or S_B textures as observed by POM on cooling. This could possibly have been induced by the interaction between the polar terminal groups and the cover slip. As the temperature was further lowered into the crystal E (CrE) phase, a mosaic texture was observed. Figure 1 shows the texture of the S_A, S_B and CrE phases exhibited by compound **8 A**. Focal-conic fans could be clearly observed for the S_A phase (see figure 1 (*a*)), across which transition bars appeared over the S_A–S_B transition (cooling process). After cooling into


(*a*)

(*b*)

(*c*)

Figure 1. Optical polarizing micrograph (400 ×) of compound **8 A**. (*a*) S_A at 237·4°C; (*b*) S_B at 230°C; (*c*) CrE at 93°C.

the S_B phase, the focal-conic fan texture disappeared and paramorphic grain boundaries emerged. As the temperature was further lowered into the CrE phase, a mosaic texture with concentric arcs was observed (see figure 1 (*c*)).

Further identification of the mesophases was achieved by X-ray diffraction (see figure 2). The peak in the wide angle ($2\theta \sim 20°$) is broad, indicating random centres of mass within the smectic layer, and is assigned as smectic A (see figure 2, curve A). On cooling into the S_B phase, the wide angle sharpened significantly (see curve B) indicating increased positional order within the smectic layers. This sharp outer ring (200, 110) is centred at 4·47 Å corresponding to the distance between hexagonal packing mesogens within the same smectic layer [25]. When the temperature was lowered into the CrE phase, the hexagonal packing became distorted, the outer single ring separating into three different rings centred at 4·40 Å (110, 111), 4·19 Å (200, 201), 3·30 Å (210, 211) (see curve C). This phenomenon is similar to the results reported by Doucet *et al.* [25]. On further cooling many diffraction peaks appeared corresponding to a crystal lattice, i.e. below the CrE–crystal transition (see curve D).

The smectic layer spacing for **4 A** as a function of the temperature is shown in figure 3. In the vicinity of the N–S_A phase transition (182·5°C), the layer spacing was 36·6 Å (the calculated fully extended molecular length is 36·1 Å), but increased to 39·9 Å at 180·2°C, well below the N–S_A transition. It is postulated that a gradual formation of the bilayer structure occurs in the vicinity of N–S_A phase transition [26, 27]. When the temperature was lowered further, the layer thickness increased. This is possibly due to the suppressed vibrations of the flexible hydroxyalkanyloxy chains at lower temperatures, which would improve the orientational order of the mesogens and lead to the increase in S_A layer spacing. As soon as the mesophase changed from the S_A to the CrE phase, the layer thickness decreased gradually to 36·7 Å (154·2°C) suggesting that the bilayer structure no longer exists for the CrE phase. This may have been due to the fact that the highly ordered packing of the CrE phase hindered the formation of the bilayer structure. The layer spacing

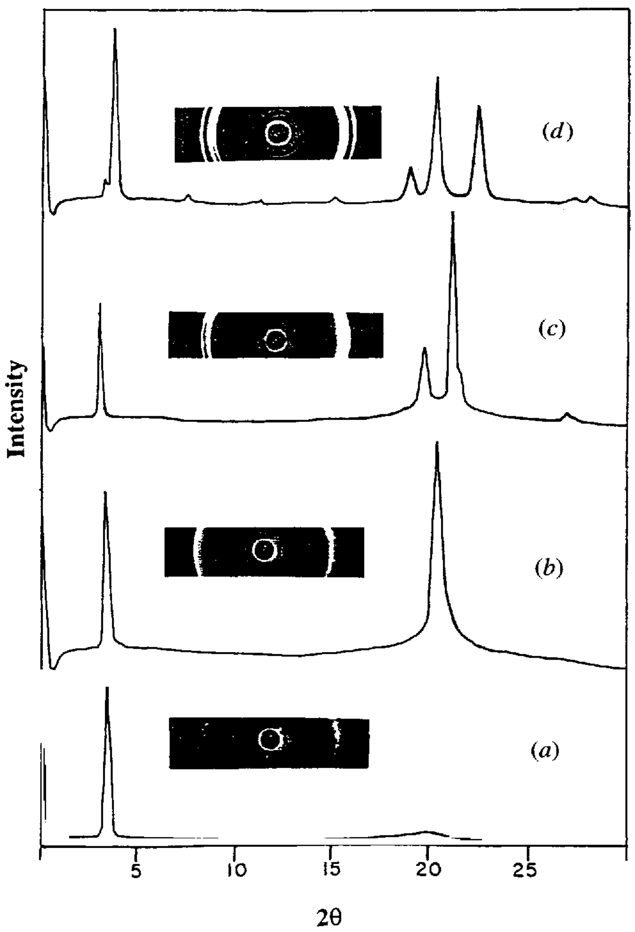


Figure 2. Temperature dependent X-ray diffraction of compound **5 A** at (*a*) S_A (186°C), (*b*) S_B (182°C), (*c*) CrE (175°C), and (*d*) crystal (80°C).

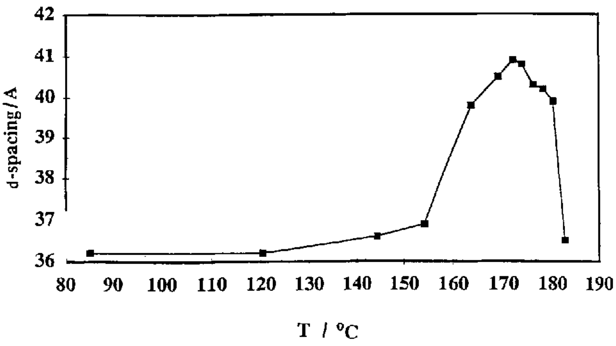


Figure 3. The smectic layer *d*-spacings for compounds **4 A** as a function of temperature.

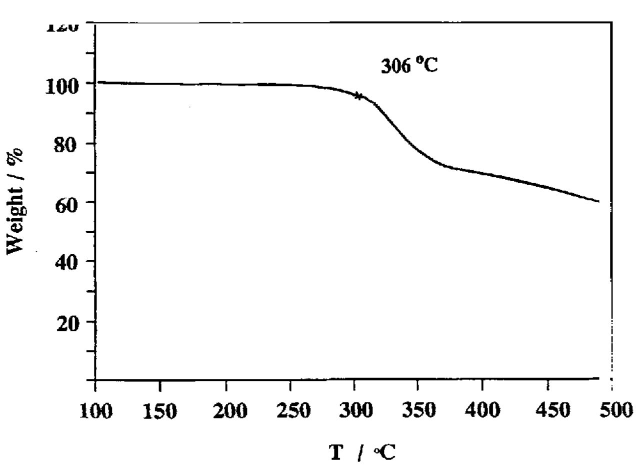


Figure 4. Thermogravimetric thermogram of compound **2 A**.

remained almost unchanged as the temperature dropped further to 82·7°C.

The thermal stability of these compounds was determined by DSC and TGA with degradation temperatures being approximately 300°C (see figure 4). No exothermic peaks (other than recrystallization peaks at approximately 100°C) were observed at temperatures below 300°C for these compounds during the DSC heating scans. For E–O application, the NLO properties must be stable for temperatures up to 250°C for at least short periods of time [11]. With such excellent thermal stability, these phenyltolane chromophores could be considered for E-O modulation applications.

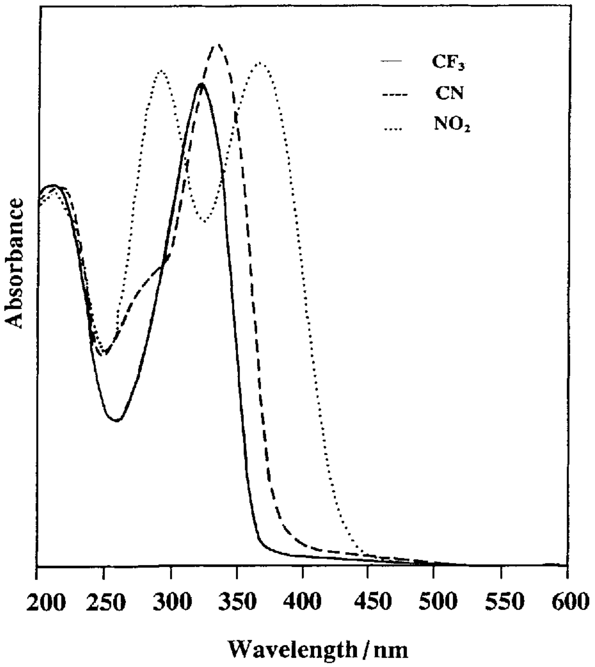


Figure 5. UV–VIS spectra of phenyltolane-based compounds with different terminal groups (*a*) nitro (*b*) cyano (*c*) trifluoromethyl.

Table 2. UV–VIS absorption characteristics of the phenyltolane-based compounds **1 A–9 A**.

Compound	*m*†	*X*	λ_{max}/nm	$\lambda_{cut\text{-}off}$/nm
1 A	11	NO_2	362	460
2 A	6	NO_2	362	460
3 A	3	NO_2	362	460
4 A	11	CN	330	390
5 A	6	CN	330	390
6 A	3	CN	330	390
7 A	11	CF_3	315	370
8 A	6	CF_3	315	370
9 A	3	CF_3	315	370

† *m*, *X*, according to the scheme.

It has been reported that compounds possessing more than two rings would be insoluble in most common organic solvents [28]. However, these phenyltolane compounds (three phenyl rings) could be dissolved in common organic solvents such as chloroform, THF, ethylacetate, etc. UV–VIS spectra of the compounds with three different terminal groups were measured separately in dilute solution. Different absorption characteristic were obtained due to the polarizability of the terminal groups, and conjugate lengths of the NLO active chromophores. Figure 5 shows the UV–VIS spectra of three different terminal groups with the same hydroxyhexanyloxy group. Cut-off wavelengths were 460 nm (λ_{max}: 362 nm), 390 nm (λ_{max}: 330 nm) and 370 nm (λ_{max}: 315 nm) for the terminal nitro, cyano and trifluoromethyl groups, respectively. The absorption characteristics of all the compounds are summarized in table 2. These indicate that the hydroxyalkanyloxy chain does not influence the UV–VIS absorption behaviour of the chromophores. When the wavelength was longer than 460 nm, there was no absorption peak in the UV–VIS spectra for all the chromophores. With this characteristic, this series of chromphores could be utilized in frequency doubling applications in the blue region, especially the chromophores with the cyano or trifluoromethyl terminal groups.

4. Conclusions

In conclusion, this study had demonstrated the effect on the thermal behaviour of the trifluoromethyl, cyano, and nitro terminal groups of the phenyltolane compounds. Not only can the biphenyl structure of a mesogenic core enhance the formation of mesophases, but it also greatly improves the thermal stability of the tolane-based chromophores. The increase in smectic layer spacing with decreasing temperature in the S_A phase, and subsequent decrease in layer spacing in the CrE phase, indicates the presence of a bilayer structure in the S_A phase. These phenyltolane-based chromophores possess high thermal stability and short cut-off wavelengths, which make them potentially useful for NLO applications. This series of chromophores can be covalently attached to a polymer to form an NLO side chain liquid crystalline polymer and will be reported elsewhere.

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