The effect of terminal substituents on crystal structure, mesophase behaviour and optical property of azo-ester linked materials

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ABSTRACT

A series of azo-ester linked mesogen containing liquid crystalline acrylate compounds C1-C6 having different terminal groups (-F, -Cl, -Br, -OCH\textsubscript{3}, -OC\textsubscript{2}H\textsubscript{5} and -OC\textsubscript{3}H\textsubscript{7}) were successfully synthesised and characterised. The chemical structure, purity, thermal stability, mesophase behaviour and optical property of the synthesised compounds were investigated by different instrumental techniques. X-ray crystal structure showed that compounds C1, C4 and C5 exhibited more stable E configuration with two bulky group in the opposite side of the N=N double bond motifs. The fluoro-substituted derivative (C1) is connected by the R\textsuperscript{1}2\textsuperscript{(5)} type of C–H...O hydrogen bond motifs whereas the molecules of C4, and C5 are connected to each other by means cyclic R\textsuperscript{2}2\textsuperscript{(8)} type of C–H...O hydrogen bond motifs. Thermogravimetric study revealed that the investigated compounds exhibited excellent thermal stability. All the compounds showed enantiotropic liquid crystal (LC) phase behaviour and the mesophase formation was greatly influenced by the terminal substituents. Alkoxy (-OCH\textsubscript{3}, -OC\textsubscript{2}H\textsubscript{5} and -OC\textsubscript{3}H\textsubscript{7}) substituted compounds exhibited greater mesophase stability than those of halogen (-F, -Cl and -Br) terminated derivatives. UV-vis spectroscopic study revealed that the investigated compounds exhibited a broad absorption band around 300–420 nm with absorption maximum (\(\lambda_{\text{max}}\)) of nearly 370 nm.

1. Introduction

Liquid crystalline (LC) materials have been explored to utilise various fields of applications, such as electro-optical flat panel display devices, spectrometers, chemical and biological sensors, actuators and so on \cite{1,2}. Thermotropic LC molecules normally consist of aromatic molecular core connected by different linking groups,
e.g. azomethine (−C=N−), azo (−N=N−) and ester (−COO−). The choice of linking groups in LC compounds is very crucial because a linking group can increase the overall molecular length and the polarisable anisotropy of mesogen and hence may provide favourable geometry of the molecule [3]. For example, ester group is considered as a versatile and most commonly used linking unit in LC materials, which increases the polarisability of molecules and provides relatively stable mesophase. On the other hand, the photochromic azo group can be used to control phase behaviour and optical properties of LC materials [4,5]. Because of the rod-like rigid structure and anisotropic nature of molecular core, azo compounds can generate ideal liquid crystal mesogens with appropriate ring substitution [6]. Furthermore, the efficient and reversible photoisomerisation make azo compounds potential in a variety of applications, such as optical data storage devices, photo switching materials, nonlinear optics (NLO), liquid crystal display, self-assembly, surface relief gratings, energy transfer and so forth [7–17]. Thus, a combination of azo and ester linking groups in the mesogenic core could allow achieving an anticipated mesophase as well as multifunctional materials with improved properties. In this connection, a large number of research groups have been working with azo-ester linked LC materials with an aim to study the effect of varying alkyl chain length, lateral substituents and terminal group on the thermal and mesomorphic behaviours [18–24]. Recently, Naoum et al. synthesised, characterised and studied the exchange effect of terminal substituent, inversion effect of ester group as well as the effect of lateral methyl group of azo-ester linked LC materials [25–28]. They found that most of the synthesised compounds having terminal electron-donating substituents exhibited purely nematogenic behaviour depending on the alkoxy chain length. On the other hand, compounds bearing terminal electron-withdrawing substituents showed dimorphic and purely smectogenic (SmA) character for lower and higher homologues, respectively. However, a comparative study of the effect of the terminal halogens (−F, −Cl and −Br) with short alkoxy (−OCH₃, −OC₂H₅ and −OC₃H₇) groups among azo-ester LC materials have not been well addressed in the literature yet. To the best of our knowledge, few reports are available on single crystal structures of the azo-ester bridged LC materials. The study of the crystal structure of a compound is very crucial to know the structure–function relationships as well as systematic approach to the design of new molecules [29].

In this report, we describe the synthesis and characterisation of azo-ester linked rod-like new LC compounds having polymerisable acrylate group in one terminal and different substituents in the other terminal. We have also evaluated the effect of terminal groups on single crystal structures, thermal, mesomorphic and optical properties of the synthesised materials. FT-IR, ¹H and ¹³C NMR spectroscopic techniques were made to characterise the newly synthesised compounds. TGA (Thermogravimetric Analysis), POM (Polarised Optical Microscope) and DSC (Differential Scanning Calorimetry) measurements were performed to study the thermal and mesophase behaviours. Single crystal X-ray diffraction measurements were carried out to study the crystal structure of the compounds. UV-vis spectroscopic study was done to evaluate the optical properties.

2. Experimental section
2.1. Materials and measurements

All the reagents and chemicals used in this study were of reagent grade and purchased from Merck, Acros Organics, Sigma-Aldrich, R & M Chemicals, J. T. Baker and John Kollin Corporation. N,N-dimethylformamide (DMF), dichloromethane (DCM) and tetrahydrofuran (THF) were distilled over sodium/benzophenone under an inert atmosphere prior to use. Triethylamine (TEA) was dried with anhydrous sodium sulphate (Na₂SO₄) and then distilled. All other chemicals and solvents were used as received.

¹H and ¹³C NMR spectra were recorded with a JEOL spectrometer (400 MHz) in CDCl₃ and DMSO-D₆. FT-IR spectra (4000–450 cm⁻¹) were taken on a PerkinElmer Spotlight 400 spectrometer with 16 scans using attenuated total reflectance (ATR) method and a resolution of 4 cm⁻¹. Thermal decomposition temperature data were recorded on a SDT Q600 thermogravimetric analyser under nitrogen atmosphere at a heating rate of 20°C min⁻¹. The DSC measurements were conducted to study the thermal transitions of investigated compounds using a PerkinElmer DSC6 instrument at heating and cooling rates of 10°C min⁻¹ under nitrogen atmosphere. The LC phase behaviours were investigated using an Olympus BH-2 polarised optical microscope (POM) equipped with a Mettler Toledo hot stage FP-82. UV-vis absorption spectra in dilute THF solution (5 × 10⁻⁵ M) were recorded on Cary 60 UV-vis spectrophotometer. Single crystal X-ray diffraction measurements of compounds were carried out using Bruker APEX-II CCD area detector equipped with the graphite monochromator at 140(2)K with Mo-Kα radiations (λ = 0.71073 Å). Structures were solved by the direct methods with full-matrix least-squares refinement on F².
2.2. Synthesis

Compounds ethyl 4-[(4′-hydroxy)phenylazo]benzoate (1), ethyl 4-[(4′-hydroxyhexyloxy)phenylazo]benzoate (2) and 4-[(4′-(6-hydroxyhexyloxy)phenylazo]benzoic acid (3) were synthesised according to the methods described in the literature [30,31].

Synthesis of 4-[(4′-(6-acryloyloxyhexyloxy)phenylazo]benzoic acid (4)

Compound 3 (4.5 g, 13.2 mmol) was dissolved in THF (150 mL) with slight heating and then cooled down to ambient temperature. To the red coloured solution, triethylamine (4.0 g, 39.5 mmol) was added dropwise and the obtained mixture was cooled in an ice bath. Acryloyl chloride (3.6 g, 39.5 mmol) dissolved in anhydrous THF (20 mL) was added dropwise to the cold stirred solution. Next, the temperature of the reaction mixture was maintained at 0°C for 1 h with constant stirring. After that, the stirring was continued for 24 h at ambient temperature and then the resultant yellow coloured mixture was poured into ice cold water. The obtained product was extracted with DCM and the organic layer was dried over anhydrous magnesium sulphate followed by removal of DCM under reduced pressure.

The solid product was recrystallised twice from boiling acetic acid and hexane to get orange coloured 4-[(4′-(6-acryloyloxyhexyloxy)phenylazo]benzoic acid (4). Yield: 51%, T<sub>m</sub> = 140–142°C, FT-IR (cm<sup>-1</sup>): 2945, 2877 (C-H, aliphatic), 2657, 2569 (O-H in COOH), 1721 (C=O in acrylate), 1676 (C=O in COOCH<sub>3</sub>), 1646 (C=O in acrylate) 1603, 1585 (C=C, aromatic), 1473 (–N=N–), 1413, 1296, 1250 (C-O), 1200, 1142 (C-O-C), 1H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 12.62–12.54 (s, 1H, Ar–COOH), 8.04–7.97 (d, 2H, Ar–H), 7.83–7.66 (m, 4H, Ar–H), 6.98–6.77 (m, 2H, Ar–H), 6.23–6.16 (d, 1H, –CH=CH<sub>2</sub>), 5.98–5.87 (q, 1H, –CH=CH<sub>2</sub>), 5.66–5.57 (d, 1H, –CH=CH<sub>2</sub>), 4.07–3.93 (t, 2H, Ar–OCH<sub>2</sub>CH<sub>2</sub>–), 3.91–3.81 (t, 2H, –CH<sub>2</sub>CH<sub>2</sub>OOC–), 1.71–1.47 (m, 4H, –CH<sub>2</sub>–), 1.42–1.22 (m, 4H, –CH<sub>2</sub>–).

Synthesis of (e)-4-chlorophenyl [4′- (4′′-(6-acryloyloxyhexyloxy)phenylazo]phenylenzoate (C1)

Prepared as described for C1. Yield: 58%, T<sub>m</sub> = 115–116°C, FT-IR (cm<sup>-1</sup>): 2945, 2874 (C-H, aliphatic), 1729 (C=O in ester), 1638 (C=O, vinyl), 1602, 1573 (C=C, aromatic), 1506, 1489 (–N=N–), 1410, 1254, 1204, 1164, 1165, 1069, 1010, 842, 1H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.33–8.27 (d, 2H, Ar–H), 7.99–7.92 (d, 4H, Ar–H), 7.43–7.37 (d, 2H, Ar–H), 7.21–7.16 (d, 2H, Ar–H), 7.04–6.98 (d, 2H, Ar–H), 6.43–6.37 (d, 1H, –CH=CH<sub>2</sub>), 6.16–6.08 (q, 1H, –CH=CH<sub>2</sub>), 5.84–5.79 (d, 1H, –CH=CH<sub>2</sub>), 4.21–4.15 (t, 2H, Ar–OCH<sub>2</sub>–), 4.09–4.02 (t, 2H, –CH<sub>2</sub>–OOC–), 1.89–1.80 (m, 2H, –CH<sub>2</sub>–), 1.77–1.68 (m, 2H, –CH<sub>2</sub>–), 1.57–1.41 (m, 4H, –CH<sub>2</sub>–). 13C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 166.5 (–O–CO–), 164.6 (Ar–O–CO–Ar), 162.5, 156.0, 149.5, 146.9, 131.4, 130.7, 130.1, 129.7, 125.4, 123.2, 122.6, 116.4, 116.1, 114.9 (Ar–C), 131.3 (–CH=CH<sub>2</sub>), 128.7 (–CH=CH<sub>2</sub>), 68.3 (Ar–OCH<sub>2</sub>–), 64.6 (–H<sub>2</sub>C–OOC–) 29.1, 28.6, 25.8 (Aliphatic–C).
Synthesis of (e)-4-methoxyphenyl [4'- (4''- (6-acroyloxy)hexyloxy)phenylazo]benzoate (C6)
Prepared as described for C1. Yield: 35%, $T_m = 105-106^\circ\text{C}$, FT-IR (cm$^{-1}$): 2946, 2872 (C-H, aliphatic), 1724 (C=O in ester), 1637 (C=C, vinyl), 1509 (C=C, aromatic), 1508, 1476 (N=N), 1413, 1300, 1271, 1250, 1196, 1143, 1076, 1012, 862, 838, $^{13}$C NMR (400 MHz, CDCl$_3$) δ (ppm): 3.77-3.78 (s, 3H, OCH$_3$), 1.58-1.60 (m, 4H, CH$_2$), 1.39 (t, 3H, OCH$_3$), 0.84-0.86 (d, 6H, Ar-CH$_2$), 1.56-1.58 (s, 3H, Aliphatic-C).
spectroscopic techniques. The FT-IR spectrum and main vibrational frequencies for different functional groups of compound C1 is illustrated in Figure 1. Compound C1 exhibits different vibrational modes corresponding to the stretching and bending of various functional groups present in the molecule. Two medium intensity bands around 2945 and about 2880 cm$^{-1}$ are due to aliphatic $\nu$(C–H) asymmetric and symmetric stretching vibration of methylene (–CH$_2$–) groups of alkyl chain. The very strong absorption band at 1725 cm$^{-1}$ corresponds to $\nu$(C=O) stretching vibration of ester group. Since all the synthesised compounds bear similar structure except terminal groups, vibrational frequencies of the ester groups were slightly shifted by the influence of terminal halogen and alkoxy substituents. The medium intensity band around 1634 cm$^{-1}$ is ascribed to $\nu$(C=C) stretching vibration of the terminal acrylate functional group. The stretching vibration at 1603 and 1583 cm$^{-1}$ is attributed to $\nu$(C=C) of benzene ring. The strong and medium intensity absorption band around 1505 and 1471 cm$^{-1}$ correspond to $\nu$(N=N) stretching vibration. $^1$H NMR spectrum of compound C1 is shown in Figure 2. The signals around $\delta$ 1.89–1.34 ppm in the multiplet form are observed due to methylene (–CH$_2$–) protons of straight alkyl chain. Two triplet signals around 4.22–4.03 ppm are ascribed for –OCH$_2$– and –CH$_2$O– alkoxy protons. Characteristic vinylidene proton peaks of acrylate group are observed as doublet, quartet and another doublet around $\delta$ 6.43–5.79 ppm. The signals between $\delta$ 8.32–6.99 ppm which appeared as doublet form are assigned to aromatic ring protons. As compounds C2–C6 are structurally identical with C1 except terminal groups, their spectral results (FT-IR and $^1$H NMR) shown in Table SI1 (SI = Supporting Information) are almost similar.

3.2. Crystal structure

The crystal structures of compounds C1, C4 and C5 with atom-numbering scheme are illustrated in Figure 3. The crystal parameters are given in Table 1, while the selected bond distances and bond angles of the compounds are listed in Table SI2. Figure 3 reveals that the two bulky groups are situated at the opposite side of the azo N=N Scheme 1. Synthetic route for compounds C1–C6.
group and this leads to the formation of E isomer which is more stable conformation. As all the compounds (C1–C6) bear structural resemblances except terminal tail, they exhibit similar structural motif with the E configuration at the N=N double bond. As a result, the N=N and other bond distances as shown in C1, C4 and C5 do not vary significantly (Table SI2). The 1,2-diphenyldiazene fragment in all the three structures are essentially planar, with RMS deviation from planarity of 0.0314, 0.0598 and 0.0601 Å for C1, C4 and C5, respectively. Detail analysis of the crystal packing of compound C1 revealed its intriguing supramolecular sheet-like multilayer molecular packing stabilised by C–H...O interactions involving the phenyl and acryloyl hydrogen with the carbonyl oxygen and the alkoxyl oxygen atoms (Figures SI1 and SI2). As shown in Figure 4, the molecules of the fluoro-substituted derivative (C1) are connected by the R12(5) type of C–H...O hydrogen bond motifs whereas the molecules of C4 and C5 are connected to each other by means cyclic R22(8) type of C–H...O hydrogen bond motifs (Figures SI1 and SI2).

3.3. Thermal properties

The thermal studies were carried out to give more insight into structures of the synthesised compounds and the measurements were performed in a temperature range of 50–900°C in nitrogen atmosphere. The TG curves of the compounds C1–C6 are depicted in Figure 5 and relevant data are presented in Table SI3. The thermal
decomposition temperatures correspond to 5% \( (T_d) \) weight loss for all the compounds are above 316°C and these results indicate that the thermal stability of the synthesised compounds are very high [32,33]. All the synthesised compounds (C1–C6) exhibited two-staged thermal decomposition. The first stage decomposition of C1–C6 started around 264–284°C and completed about 352–400°C with estimated mass loss of 36–51%. These cleavages may be due to the thermal decomposition of azo group, long alkyl chain and terminal substituents located in the mesogen [34,35]. On the other hand, the second stage decomposition of C1–C6 was around 352–556°C and a mass loss of 13–35% was observed in this stage. This decomposition may be ascribed to the thermal degradation of the heat resistant aromatic moiety [36]. No significant effect of terminal substituents was observed on decomposition pattern of the studied compounds. However, percent of degradation was influenced by the terminal substituents. For example, bromo substituted compound lost around 51% weight in the first decomposition step because of the heavier size of bromine atom.

### 3.4. Mesomorphic behaviour

The mesophase behaviour of compounds C1–C6 was studied by DSC and POM. Phase transition temperatures and associated enthalpy changes of the synthesised compounds are summarised in Table 3. The thermal transition traces studied by DSC of compounds C1–C6 are illustrated in Figure 6. The synthesised compounds exhibited enantiotropic thermal transitions during DSC measurements and all the thermograms are very clear-cut. The optical micrographs of C1–C6 are presented in Figure 7. The identification of nematic and smectic phases was made by comparing the observed textures with those reported in the literature [37,38]. The POM observations revealed that all the compounds exhibited enantiotropic nematic and smectic phase transitions during heating and cooling cycles. On cooling from isotropic liquid compound C1 revealed schlieren texture of nematic phase with fourfold brush at 176.8°C and fan-shaped texture of SmA phase at 154.4°C (Figure 7(a,b)). Compound C2 showed schlieren texture of nematic phase with fourfold brush at 196.2°C and focal conic texture characteristic of SmA mesophase at 173.0°C (Figure 7(c,d)) upon cooling from isotropic melt. Similarly, compound C3 displayed schlieren texture of nematic phase at 191.3°C and fan-shaped SmA phase at 174.1°C (Figure 7(e,f)). Likewise, C4 exhibited schlieren texture of nematic phase with fourfold brush at 204.2°C and fan-shaped textures of SmA phase at 141.0°C (Figure 7(g,h)). Compound C5 also showed schlieren texture of nematic phase with fourfold brush at 209.1°C and fan-shaped textures of SmA phase at 154.8°C (Figure 7(i,j)). Finally, compound C6 exhibited schlieren texture of nematic phase at 199.1°C and fan-shaped textures of SmA phase at 156.8°C (Figure 7(k,l)) during cooling scan from isotropic liquid. The mesophase transitions according to POM observation are in good agreement with the corresponding DSC thermal transition temperatures. It can be envisaged form Table 3 that the mesophase stability of compounds C1–C6 was greatly influenced by the terminal substituents (-OCH₃, -OC₂H₅, -OC₃H₇, -F, -Cl and -Br). The alkoxyl (-OCH₃, -OC₂H₅ and -OC₃H₇) terminated compounds (C4–C6) exhibited greater mesophase stability than...
Table 1. Crystal, experimental and refinement data for compounds C1, C4 and C5.

| Compound | C1 | C4 | C5 |
|----------|----|----|----|
| Empirical formula | C28H27FN2O5 | C29H30N2O6 | C30H32N2O6 |
| Formula weight | 490.52 | 502.55 | 516.58 |
| Temperature (K) | 296(2) | 296(2) | 296(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Unit cell parameters: | | | |
| a/Å | 5.65420(10) | 7.4299(2) | 8.6125(5) |
| b/Å | 8.4324(2) | 42.3953(10) | 12.4755(7) |
| c/Å | 26.5979(6) | 8.1742(2) | 13.2435(8) |
| α (°) | 86.855(2) | 90 | 87.625(5) |
| β (°) | 88.753(2) | 101.1890(10) | 77.087(4) |
| γ (°) | 73.313(2) | 90 | 75.192(4) |
| Volume (Å³) | 1212.89(5) | 1018.90(10) | 1342.77(11) |
| Z, Calculated density (mg/m³) | 2, 1.343 | 4, 1.322 | 2, 1.280 |
| μ (Mo/Kα) mm⁻¹ | 0.098 | 0.093 | 0.089 |
| 2θ range for data collection(deg.) | 0.77–26.50 | 0.96–26.50 | 1.58–26.50 |
| Limiting indices | −7 ≤ h ≤ 7,−10 ≤ k ≤ 10,−33 ≤ l ≤ 33 | −9 ≤ h ≤ 9,−50 ≤ k ≤ 53,−10 ≤ l ≤ 10 | −10 ≤ h ≤ 10,−15 ≤ k ≤ 15,−16 ≤ l ≤ 16 |
| Reflections collected/unique | 10887/4993[R(int) = 0.0357] | 18370/5146[R(int) = 0.0259] | 11942/5553[R(int) = 0.0298] |
| Completeness to θ = 26.50% | 99.6% | 98.2% | 99.8% |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data/restraints/parameters | 4993/0/325 | 5146/0/335 | 5553/0/344 |
| Goodness-of-fit on F² | 1.022 | 1.128 | 1.008 |
| Final R indices [I > 2σ(I)] | 0.0486, 0.1222 | 0.0414, 0.1005 | 0.0484, 0.1072 |
| R indices [all data] | 0.0891, 0.1610 | 0.0571, 0.1170 | 0.0936, 0.1315 |
| (R1, wR2) | 0.239 and −0.256 | 0.198 and −0.219 | 0.185 and −0.224 |
those of halogen (–F, –Cl and –Br) terminated compounds (C1–C3). This outcome may be explained on the basis that the lone pair electrons of oxygen in –OCH₃, –OC₂H₅ and –OC₃H₇ groups are shielded by an insulator-like methyl, ethyl and propyl groups. The repulsive forces between the lone pairs of oxygen in different molecules are thereby significantly reduced and allow a close approach of the neighbouring molecules, increasing bonding forces. As a result, total mesophase stability of compounds C4–C6 increases substantially [39]. Compound C5 (–OC₂H₅ terminated) showed highest mesophase stability than those of C4 (–OCH₃)
terminated) and C6 (–OC\textsubscript{3}H\textsubscript{7} terminated). The mesophase stability order of compounds C4–C6 is C5 > C4 > C6, i.e. 151.8°C > 148.5°C > 127.8°C. This consequence may be due to the odd-even effect of the terminal alkoxyl substituent [40,41]. Among the halogen terminated derivatives fluoro compound (C1) showed higher mesophase stability (101.6°C) than chloro (C2) (95.9°C) and bromo (C3) (80.0°C) derivatives. This result may be due to the highest electron-withdrawing capacity of fluorine atom which causes greater polarity or polarisability in the mesogenic part of the molecule and may enhance mesophase stability. The clearing temperature of compound C3 was higher than those of compounds C2 and C1, i.e. 203.7°C > 202.5°C > 180.1°C. This order in clearing temperatures may be due to the size of the halogen atoms attached to one end of the terminals of the mesogenic core. On the other hand, the temperature range of the mesophase was also lower for compound C3 than those of compounds C2 and C1, i.e. 80.0°C < 95.9°C < 101.6°C on cooling. The lowest mesophase stability of compound C3 may be the heavier size and lesser polarising power of bromine atom than fluorine and chlorine atoms.

### 3.5. Optical properties

The UV-vis absorption spectra of compounds C1–C6 in dilute chloroform solutions are presented in Figure 8. As all the compounds bear structural similarity except one end of the terminals, the absorption spectra are very similar in shape. A shoulder like absorption band appeared around 250–260 nm and this band may be attributed to a π–π* transition of the phenyl rings [42]. The broad absorption band of the investigated compounds was found about 300–420 nm with absorption maximum (\(\lambda_{\text{max}}\)) of nearly 370 nm. This band can be regarded as a π–π* transition involving the π-electronic system throughout the whole molecule with a considerable charge transfer (CT) character [43,44]. However, a little effect of terminal substituent was observed on the absorption maxima (\(\lambda_{\text{max}}\)) of the studied compounds.

| Phase transition (°C) (enthalpy changes, J g\textsuperscript{−1}) | Mesophase range (°C) |
|---------------------------------------------------------------|----------------------|
| **C1** Heating Cr 102.9 (70.4) SmA 160.6 (1.3) N 180.1 (0.5) | 79.5 22.1 |
| Cooling Cr 75.4 (−65.4) SmA 154.9 (−1.1) N 177.0 (−0.6) | 72.6 23.3 |
| **C2** Heating Cr 115.8 (60.1) SmA 184.7 (1.6) N 202.5 (0.5) | 62.7 17.3 |
| Cooling Cr 100.8 (−28.4) SmA 173.4 (−0.9) N 196.7 (−0.6) | 85.4 63.1 |
| **C3** Heating Cr 123.7 (30.9) SmA 192.2 (2.2) N 203.7 (0.5) | 97.3 54.5 |
| Cooling Cr 111.7 (−25.7) SmA 174.4 (−0.6) N 191.7 (−0.4) | 85.3 42.5 |
| **C4** Heating Cr 103.9 (79.3) SmA 159.5 (0.6) N 213.4 (0.8) | 85.3 42.5 |
| Cooling Cr 56.1 (−33.1) SmA 141.5 (−0.3) N 204.6 (−0.6) | 85.3 42.5 |
| **C5** Heating Cr 105.6 (76.1) SmA 163.8 (0.5) N 212.3 (0.8) | 85.3 42.5 |
| Cooling Cr 57.7 (−24.2) SmA 155.0 (−0.4) N 209.5 (−1.0) | 85.3 42.5 |
| **C6** Heating Cr 106.2 (75.4) SmA 168.8 (0.6) N 206.3 (0.9) | 85.3 42.5 |
| Cooling Cr 71.7 (−11.1) SmA 157.0 (−0.5) N 199.5 (−0.9) | 85.3 42.5 |

*Second heating and first cooling; †First heating and first cooling; Transition temperatures (°C) and enthalpy changes (in parentheses, J g\textsuperscript{−1}) were measured by DSC (at a heating and cooling rates of 10°C min\textsuperscript{−1}); Cr = Crystalline phase; SmA = Smectic A phase; N = Nematic phase; I = Isotropic liquid.

Figure 6. DSC thermograms of compounds (a) C1–C3 and (b) C4–C6 upon heating and cooling scans at the rate of ± 10°C min\textsuperscript{−1}.
4. Conclusions

In the present study, a series of new azo-ester linked LC acrylate compounds C1–C6 having different terminal groups were successfully synthesised and characterised. X-ray crystal structure revealed that compounds C1, C4 and C5 exhibited E configuration.
at the N = N double bond motifs. The fluoro-substituted derivative (C1) are connected by the R^1_3(5) type of C–H...O hydrogen bond motifs, whereas the alkoxy substituted molecules of C4, and C5 are connected to each other by means cyclic R^2_2(8) type of C–H...O hydrogen bond motifs. All the investigated compounds exhibited excellent thermal stability under TGA observations. The mesophase behaviour investigated by DSC and POM was greatly influenced by the terminal substituents. Alkoxy terminated (–OCH3, –OC2H5 and –OC3H7) compounds exhibited greater mesophase stability than those of halogen (–F, –Cl and –Br) terminated derivatives. The UV-vis study revealed a shoulder-like absorption band around 250–260 nm and a broad band about 300–420 nm with absorption maximum (λ_max) of nearly 370 nm. The newly synthesized LC monomers would be utilised to prepare new side chain liquid crystalline polymers (SCLCPs).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors would like to thank University of Malaya for the research grant PV041-2012A and BK066-2014.

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