

## **Synthesis and mesophase characterization of novel Methacrylate based thermotropic liquid crystalline monomers and their polymers**

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### **Electronic Supplementary Information (ESI)**

#### **General procedure for the synthesis of intermediates, monomers and polymers**

##### **Synthesis of benzyloxy benzoic acid (1)**

In a typical experiment, 17.5 g (130 mmol) of  $K_2CO_3$  and 15.2 g (100 mmol) of 4-hydroxymethyl benzoate were taken in 500 ml two necked round bottom (RB) flask and were dissolved in 150 ml of DMF. The mixture was stirred and heated to 90 °C, followed by the drop wise addition of 100 ml DMF solution containing 17.1 g (100 mmol) of benzylbromide. The temperature of the mixture was maintained at 90 °C for 5h. Then, the reaction mixture was poured into 1L of distilled water. The precipitate was filtered, washed with 5% KOH and it was transferred in to 500ml round bottom flask. To this, 12 g (210 mmol) of KOH, 100 ml of ethanol and 100 ml of distilled water were added and the mixture was refluxed for 1 h. Then, the solution was allowed to cool and poured into 1L of distilled water and neutralized with 1N HCL in order to obtain precipitate. The precipitate was filtered, washed with distilled water and dried under vacuum. The product was purified by recrystallization from methanol. The product was a white solid.

Yield: 87%, melting point (m.p): 190 °C, FT-IR (KBr,  $cm^{-1}$ ): 2972 (C-H<sub>str</sub>), 2665, 2547 (O-H<sub>str</sub> of carboxylic acid) 1682 (C=O<sub>str</sub> of carboxylic acid), 1603 and 1577 (C=C<sub>str</sub> aromatic), 1426 (C-H<sub>ben</sub>), 1256 and 1167 (C-O-C<sub>asym</sub> & <sub>sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (Acetone-d<sub>6</sub>): 7.97 (d, 2H), 7.47 (d, 2H), 7.38 (m, 2H), 7.32 (m, 1H) 7.10 (s, 2H), 5.16 (s, 2H); <sup>13</sup>C-NMR ppm

(Acetone- $d_6$ ):  $\delta$  166.49, 162.70, 136.69, 128.55, 128.03, 127.75, 123.05, 144.57 and 69.83. EI-MS:  $m/z$  228.2 ( $M^+$ ). Anal. Calc. for  $C_{14}H_{22}O_3$ : C 73.61, H 5.29. Found: C 73.43 and H 5.40 %.

### **Synthesis of 4-ethoxyphenyl 4-(benzyloxy)benzoate (2a)**

It was also prepared by a two step method. In a representative experiment, 22.8 g (100 mmol) 4-benzyloxy benzoic acid was placed in a 250 ml RB flask. To that, 29.7 g (250 mmol) thionyl chloride was added and refluxed for one hour. The excess thionyl chloride was removed by using a vacuum pump. 4-ethoxyphenol 13.3 g (100 mmol) and 18.3 g (180 mmol) of triethylamine were dissolved in 200 ml of MEK in a 500 ml RB flask which was cooled to 0 °C. To this 4-benzyloxybenzoylchloride was added dropwise at 0 °C and the reaction mixture was stirred for 3h at room temperature. Then, the triethylamine salt was filtered off and the solvent was evaporated. The white solid was obtained after recrystallization from methanol.

Yield: 70%, m.p: 141 °C, FT-IR (KBr,  $cm^{-1}$ ): 3060 ( aromatic C-H<sub>str</sub>), 2927, 2884 (C-H<sub>str</sub>), 1725 (C=O<sub>str</sub>), 1604, 1508 (C=C<sub>str</sub> aromatic), 1453 and 1385 (C-H<sub>ben</sub>), 1249 and 1200 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively);  $^1H$ -NMR ppm ( $CDCl_3$ ):  $\delta$  8.14 (d, 2H), 7.44 (d, 2H), 7.39 (t, 2H), 7.34 (t, 1H), 7.09 (d,2H), 7.02 (d, 2H), 6.91 (d, 2H), 5.13 (s, 2H), 4.02 (q, 2H), 0.92 (t, 3H).  $^{13}C$ -NMR ppm ( $CDCl_3$ ):  $\delta$  165.34, 163.03, 156.69, 144.48, 136.25, 132.36, 128.82, 128.37, 127.62, 122.59, 122.30, 115.15, 114.75, 70.25, 63.96 and 14.05. EI-MS:  $m/z$  348.3 ( $M^+$ ). Anal. Calc. for  $C_{22}H_{20}O_4$ : C 75.84, H 5.78. Found: C 75.63 and H 5.54 %.

### **4-butoxyphenyl 4-(benzyloxy) benzoate (2b)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (2a).

Yield: 72% m.p: 142-144 °C, FT-IR (KBr,  $cm^{-1}$ ): 3058 ( aromatic C-H<sub>str</sub>), 2933, 2870 (C-H<sub>str</sub>), 1725 (C=O<sub>str</sub>), 1604, 1508 (C=C<sub>str</sub> aromatic), 1453 and 1383 (C-H<sub>ben</sub>), 1248 and 1193 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively);  $^1H$ -NMR ppm ( $CDCl_3$ ):  $\delta$  8.13 (d, 2H), 7.43 (d, 2H), 7.40 (t, 2H),

7.31 (t, 1H), 7.09 (d, 2H), 7.03 (d, 2H), 6.91 (d, 2H), 5.11 (s, 2H), 3.93 (t, 2H), 1.77 (m, 2H), 1.47 (m, 2H) and 0.97 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 165.21, 162.90, 156.78, 144.30, 136.13, 132.23, 128.68, 128.23, 127.48, 122.43, 122.10, 115.03, 114.62, 70.11, 68.04, 31.30, 19.22 and 13.85. EI-MS: m/z 376.4 (M<sup>+</sup>). Anal. Calc. for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>: C 76.57, H 6.42. Found: C 76.68 and H 6.54 %.

#### **4-hexyloxyphenyl 4-(benzyloxy) benzoate (2c)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (2a).

Yield: 70%, m.p: 128-130 °C, FT-IR (KBr, cm<sup>-1</sup>): 3060 ( aromatic C-H<sub>str</sub>), 2928, 2868 (C-H<sub>str</sub>), 1725 (C=O<sub>str</sub>), 1605, 1580 and 1510(C=C<sub>str</sub> aromatic), 1455 and 1383 (C-H<sub>ben</sub>), 1193 and 1171 ( C-O-C<sub>str</sub> of ester and ether respectively) <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.14 (d, 2H), 7.43 (d, 2H), 7.39 (t, 2H), 7.33 (t, 1H), 7.09 (d, 2H), 7.04 (d, 2H), 6.91 (d, 2H), 5.12 (s, 2H), 3.94 (t, 2H), 1.80 (m, 2H), 1.45 (m, 2H), 1.33 (m, 4H), 0.92 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 165.23, 162.92, 156.80, 144.33, 136.15, 132.24, 128.70, 128.24, 127.48, 122.44, 122.20, 115.06, 114.64, 70.13, 68.40, 35.59, 29.24, 25.71, 22.61 and 14.05. EI-MS: m/z 404.4 (M<sup>+</sup>). Anal. Calc. for C<sub>26</sub>H<sub>28</sub>O<sub>4</sub>: C 77.20, H 6.97. Found: C 77.43 and H 6.74 %.

#### **4-octyloxyphenyl 4-(benzyloxy)benzoate (2d)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (2a).

Yield: 70% , m.p: 128 °C, FT-IR (KBr, cm<sup>-1</sup>): 3058 ( aromatic C-H<sub>str</sub>), 2923, 2854 (C-H<sub>str</sub>), 1725 (C=O<sub>str</sub>), 1604 and 1510 (C=C<sub>str</sub> aromatic), 1467 and 1384 (C-H<sub>ben</sub>), 1248 and 1192 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.14 (d, 2H), 7.43 (d, 2H), 7.39 (t, 2H), 7.35 (t, 1H), 7.09 (d, 2H), 7.04 (d, 2H), 6.91 (d, 2H), 5.12 (s, 2H), 3.93 (t, 2H), 1.78 (m, 2H), 1.49 (m, 2H), 1.31 (m, 8H), 0.89 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 165.22, 162.92, 156.80, 144.34, 136.16, 132.23, 128.69, 128.24, 127.48, 122.43, 122.22, 115.06, 114.64, 70.13, 68.40, 31.82, 29.36,

29.36, 29.25, 26.04, 22.66 and 14.11. EI-MS:  $m/z$  432.5 ( $M^+$ ). Anal. Calc. for  $C_{28}H_{32}O_4$ : C 77.77, H 7.45. Found: C 77.44 and H 7.27 %.

#### **4-decyloxyphenyl 4-(benzyloxy)benzoate (2e)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (2a).

Yield: 70%, m.p: 122-124 °C, FT-IR (KBr,  $cm^{-1}$ ): 3059 ( aromatic  $CH_{str}$ ), 2921, 2852 ( $C-H_{str}$ ), 1725 ( $C=O_{str}$ ), 1605 and 1509 ( $C=C_{str}$  aromatic), 1470 and 1384 ( $C-H_{ben}$ ), 1250 and 1194 (  $C-O-C_{asym \& sym}$  of ester and ether respectively);  $^1H$ -NMR ppm ( $CDCl_3$ ):  $\delta$  8.14 (d, 2H), 7.44 (d, 2H), 7.40 (t, 2H), 7.34 (t, 1H), 7.09 (d, 2H), 7.03 (d, 2H), 6.91 (d, 2H), 5.14 (s, 2H), 3.94 (t, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.27 (m, 12H), 0.87 (t, 3H).  $^{13}C$ -NMR ppm ( $CDCl_3$ ):  $\delta$  165.25, 162.92, 156.80, 144.32, 136.15, 132.24, 128.71, 128.25, 127.48, 122.43, 122.21, 115.06, 114.64, 70.15, 68.41, 31.90, 29.58, 29.56, 29.40, 29.33, 29.28, 26.04, 22.69 and 14.12. EI-MS:  $m/z$  460.6 ( $M^+$ ). Anal. Calc. for  $C_{32}H_{40}O_4$ : C 78.65, H 7.87. Found: C 78.83 and H 7.64 %.

#### **4-dodecyloxyphenyl 4-(benzyloxy)benzoate (2f)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (2a).

Yield: 70%, m.p: 120-122 °C, FT-IR (KBr,  $cm^{-1}$ ): 3058 ( aromatic  $C-H_{str}$ ), 2919, 2850 ( $CH_{str}$ ), 1725 ( $C=O_{str}$ ), 1605 and 1509( $C=C_{str}$  aromatic), 1469 and 1384 ( $CH_{ben}$ ), 1193 and 1169 (  $C-O-C_{asym \& sym}$  of ester and ether respectively);  $^1H$ -NMR ppm ( $CDCl_3$ ):  $\delta$  8.14 (d, 2H), 7.44 (d, 2H), 7.40 (t, 2H), 7.34 (t,1H), 7.09 (d,2H), 7.05 (d, 2H), 6.91 (d, 2H), 5.14 (s, 2H), 3.95 (t, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.26 (m, 16H), 0.88 (t, 3H).  $^{13}C$ -NMR ppm ( $CDCl_3$ ):  $\delta$  165.24, 162.92, 156.80, 144.32, 136.15, 132.24, 128.70, 128.25, 127.48, 122.43, 122.21, 115.06, 114.64, 70.15, 68.41, 31.92, 29.67, 29.64, 29.60, 29.40, 29.35, 29.28, 26.04, 22.70 and 14.13. EI-MS:  $m/z$  488.6 ( $M^+$ ). Anal. Calc. for  $C_{32}H_{40}O_4$ : C 78.65, H 8.25. Found: C 78.43 and H 8.54 %.

### **Synthesis of 4-ethoxyphenyl 4-hydroxybenzoate (3a)**

In a typical experiment, 18.09 g (52.5 mmol) 4-ethoxyphenyl 4-(benzyloxy) benzoate was placed in a 500 ml three necked RB flask and 100 ml of tetrahydrofuran was added. 1.8 g 10% Pd-carbon was added to the solution and hydrogen gas was purged at room temperature for 48 h to get debenzylated product.<sup>1-3</sup> Then the Pd/C catalyst was removed by filtering the reaction mixture through Celite-540 and upon evaporation of the solvent yielded the white solid which was recrystallized from Acetonitrile.

Yield: 90%, m.p: 220 °C, FT-IR (KBr, cm<sup>-1</sup>): 3395 (O-H<sub>str</sub>), 2989, 2925, 2882 (C-H<sub>str</sub>), 1704 (C=O<sub>str</sub>), 1607, 1589 and 1508 (C=C<sub>str</sub> aromatic), 1480 and 1444 (C-H<sub>ben</sub>), 1278, 1218 and 1192 (C-O-C<sub>str</sub> of ester and ether respectively)

### **4-butoxyphenyl 4-hydroxybenzoate (3b)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (3a).

Yield: 92%, m.p: 167-169 °C FT-IR (KBr, cm<sup>-1</sup>): 3373 (O-H<sub>str</sub>), 2938, 2872 (C-H<sub>str</sub>), 1701 (C=O<sub>str</sub>), 1589 and 1508 (C=C<sub>str</sub> aromatic), 1471 and 1444 (C-H<sub>ben</sub>), 1218 and 1191 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.09 (d, 2H), 7.09 (d, 2H), 6.92 (d, 2H), 6.86 (d, 2H), 6.12 (s, 1H), 3.96 (t, 2H), 1.76 (m, 2H), 1.48 (m, 2H) and 0.97 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 165.63, 160.56, 156.85, 144.26, 132.54, 122.45, 121.83, 115.41, 115.13, 68.16, 31.31, 19.23 and 14.84. EI-MS: m/z 286.3 (M<sup>+</sup>). Anal. Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>: C 71.31, H 6.33. Found: C 71.53 and H 6.54 %.

### **4-hexyloxyphenyl 4-hydroxybenzoate (3c)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (3a).

Yield: 92%, m.p: 162-164°C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3392 (O-H<sub>str</sub>), 2931, 2864 (C-H<sub>str</sub>), 1701 (C=O<sub>str</sub>), 1589 and 1509 (C=C<sub>str</sub> aromatic), 1468 (C-H<sub>ben</sub>), 1194 and 1161 (C-O-C<sub>str</sub> of ester and ether respectively) <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.08 (d, 2H), 7.09 (d, 2H), 6.90 (d, 2H), 6.87 (d, 2H), 6.24 (s, 1H), 3.95 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.33 (m, 4H) and 0.90 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  165.75, 160.66, 156.86, 144.25, 132.54, 122.45, 121.72, 115.43, 115.15, 68.50, 31.58, 29.23, 25.70, 22.60 and 14.04. EI-MS: m/z 314.3 (M<sup>+</sup>). Anal. Calc. for C<sub>19</sub>H<sub>22</sub>O<sub>4</sub>: C 72.58, H 7.05. Found: C 72.43 and H 7.34 %.

#### **4-Octyloxyphenyl 4-hydroxybenzoate (3d)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (3a).

Yield: 90%, m.p: 160-162 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3389 (O-H<sub>str</sub>), 2926, 2856 (C-H<sub>str</sub>), 1701 (C=O<sub>str</sub>), 1587 and 1509 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1219 and 1193 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.07 (d, 2H), 7.09 (d, 2H), 6.92 (d, 2H), 6.86 (d, 2H), 6.38 (s, 1H), 3.93 (t, 2H), 1.77 (m, 2H), 1.44 (m, 2H), 1.29 (m, 8H) and 0.88 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  165.86, 160.73, 156.86, 144.22, 132.54, 122.45, 121.61, 115.44, 115.14, 68.50, 31.81, 29.36, 29.24, 26.03, 22.66 and 14.11. EI-MS: m/z 342.4 (M<sup>+</sup>). Anal. Calc. for C<sub>21</sub>H<sub>26</sub>O<sub>4</sub>: C 73.65, H 7.65. Found: C 73.41 and H 7.37 %.

#### **4-Decyloxyphenyl 4-hydroxybenzoate (3e)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (3a).

Yield: 90%, m.p: 148-150 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3403 (O-H<sub>str</sub>), 2922, 2852 (C-H<sub>str</sub>), 1702 (C=O<sub>str</sub>), 1587 and 1508 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1217 and 1193 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.07 (d, 2H), 7.09 (d, 2H), 6.92 (d, 2H), 6.86 (d, 2H), 6.42 (s, 1H), 3.93 (t, 2H), 1.75 (m, 2H), 1.44 (m, 2H), 1.30 (m, 12H) and 0.88 (t, 3H). <sup>13</sup>C-NMR ppm

(CDCl<sub>3</sub>):  $\delta$  165.87, 160.75, 156.86, 144.22, 132.54, 122.45, 121.59, 115.44, 115.14, 68.50, 31.90, 29.58, 29.40, 29.33, 29.26, 26.03, 22.69 and 14.13. . EI-MS: m/z 370.4 (M<sup>+</sup>). Anal. Calc. for C<sub>23</sub>H<sub>30</sub>O<sub>4</sub>: C 74.56, H 8.16. Found: C 74.41 and H 8.33 %.

#### **4-Dodecyloxyphenyl 4-hydroxybenzoate (3f)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (3a).

Yield: 85%, m.p: 140-142 °C, FT-IR (KBr, cm<sup>-1</sup>): 3401 (O-H<sub>str</sub>), 2921, 2851 (C-H<sub>str</sub>), 1704 (C=O<sub>str</sub>), 1587 and 1509 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1194 and 1161 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.08 (d, 2H), 7.10 (d, 2H), 6.92 (d, 2H), 6.86 (d, 2H), 6.34 (s, 1H), 3.95 (t, 2H), 1.77 (m, 2H), 1.42 (m, 2H), 1.29 (m, 4H) and 0.88 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  165.73, 160.61, 156.94, 144.33, 132.64, 122.53, 121.93, 115.49, 115.21, 68.57, 32.02, 29.76, 29.74, 29.71, 29.50, 29.45, 29.35, 26.13, 22.79 and 14.23. . EI-MS: m/z 398.53 (M<sup>+</sup>). Anal. Calc. for C<sub>25</sub>H<sub>34</sub>O<sub>4</sub>: C 75.34, H 8.59. Found: C 75.49 and H 8.39 %.

#### **Synthesis of 4-[(6-hydroxyhexyl)oxy]benzoic acid (5)**

In a 500 ml three necked RB flask 15.2 g (100mmol) of 4-hydroxy methyl benzoate and 20g (150mmol) of K<sub>2</sub>CO<sub>3</sub> were taken and were dissolved in 200 ml of DMF. The mixture was stirred and heated to 90 °C, followed by the drop wise addition of 100 ml DMF solution containing 13.6 g (100 mmol) of 6-chlorohexanol. The temperature of the mixture was maintained at 90 °C for 5 h. Then, the reaction mixture was poured into 1L of distilled water and transferred to a separating funnel and extracted with diethyl ether. The ether layer was washed using 10% sodium hydroxide solution and distilled water and the organic layer was dried with anhydrous sodium sulfate. Upon evaporation of ether, a light brown liquid 4-hydroxy hexyloxy methyl benzoate resulted (4).

4-hydroxy hexyloxy methyl benzoate (4) was placed in a one-liter single necked round bottom flask equipped with double wall water condenser. Ethanol (150 ml) and 14 g (250 mmol) of potassium

hydroxide dissolved in distilled water (150 ml) were added to the flask. The solution was refluxed for 1 hour and allowed to cool to room temperature. It was then neutralized with 1N HCL in order to obtain a white precipitate. The compound was purified by recrystallization from toluene.

Yield: 80%, m.p: 142 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3338 ( $\text{O-H}_{\text{str}}$ ), 2947, 2862 ( $\text{C-H}_{\text{str}}$ ), 2531 ( $\text{O-H}_{\text{str}}$  of carboxylic acid) 1671 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1604 and 1511 ( $\text{C=C}_{\text{str}}$  aromatic), 1420 ( $\text{CH}_{\text{ben}}$ ), 1283, 1254 and 1169 ( $\text{C-O-C}_{\text{asym \& sym str}}$  of ester and ether respectively);  $^1\text{H-NMR}$  ppm ( $\text{DMSO-d}_6$ ):  $\delta$  7.83 (d, 2H), 6.94 (d, 2H), 3.95 (t, 2H), 3.33(t, 2H), 1.64 (m, 2H), 1.34 (m, 6H).  $^{13}\text{C-NMR}$  ppm ( $\text{DMSO-d}_6$ ):  $\delta$  167.59, 162.83, 131.88, 123.23, 114.71, 68.25, 61.17, 32.92, 29.09, 25.86 and 25.74. . EI-MS: m/z 238.2 ( $\text{M}^+$ ). Anal. Calc. for  $\text{C}_{13}\text{H}_{18}\text{O}_4$ : C 65.52, H 7.61. Found: C 65.52 and H 7.88 %.

#### **Synthesis of 4-((6-[(2-methylacryloyl)oxy]hexyl)oxy)benzoic acid (6)**

In a representative experiment, 250 ml double neck round bottom flask equipped with a stirrer and a dropping funnel, is placed in a thermostat water bath at 0 °C. 12 g (50 mmol). 4-[(6-hydroxyhexyl)oxy]benzoic acid 8.5ml of triethylamine (60 mmol and 0.6 g (5 mmol) of 4-dimethylaminopyridine were placed in RB flask. 20 ml of dichloromethane is added to the flask and 7.5 g (50 mmol) of methacrylic anhydride is added through a dropping funnel over a period of 30 minutes. The contents were stirred for five hours at 0 °C. Then, the solution was transferred to a separating funnel and extracted with 50 ml (10%) hydrochloric acid and a white solid obtained by evaporating dichloromethane is purified with a 2:4 mixture of ethyl acetate and hexane as a eluent by column chromatography.

Yield: 60%, m.p: 86 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2938, 2858 ( $\text{C-H}_{\text{str}}$ ), 2679, 2566 ( $\text{O-H}_{\text{str}}$  of carboxylic acid) 1714 ( $\text{C=O}_{\text{str}}$ ), 1685 ( $\text{C=O}_{\text{str}}$  of carboxylic acid) 1606 and 1513 ( $\text{C=C}_{\text{str}}$  aromatic), 1468 ( $\text{C-H}_{\text{ben}}$ ), 1255 and 1172 ( $\text{C-O-C}_{\text{asym \& sym str}}$  of ester and ether respectively);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  8.05 (d, 2H), 6.90 (d, 2H), 6.80 (s, 1H), 5.53 (s, 1H), 4.15 (t, 2H), 4.01 (t, 2H), 1.93 (s, 3H), 1.81 (m, 2H), 1.71 (m, 2H) and 1.48 (m, 4H).  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  172.12, 167.67, 163.67, 144.33,



132.52, 132.42 125.40, 121.58, 114.25, 68.13, 64.71, 29.07, 28.62, 25.86, 25.78, 29.45 and 18.42. .

EI-MS: m/z 306.3 ( $M^+$ ). Anal. Calc. for  $C_{17}H_{22}O_5$ : C 66.64, H 7.23. Found: C 66.41 and H 7.03 %.

### Synthesis of Monomers

#### 4-[(ethoxyphenoxy)carbonyl] phenyl 4-[(2-methylacryloyloxy)hexyloxy]benzoate (7a)

In a typical experiment, 6.45 g (25mmol) 3a and 7.65 g (25mmol) compound 6 were placed in a 500 ml conical flask and were dissolved in 100 ml THF. To this stirred solution, 6.18g (30 mmol) N,N-dicyclohexylcarbodiimide (DCC) dissolved in 50 ml dichloromethane was added, followed by the addition of 4-dimethylaminopyridine (2.5 mmol) and stirring was continued overnight at room temperature. Filtration of solid dicyclohexyl urea and subsequent evaporation of the solvent yielded a semi solid which was purified, by column chromatography, using 2:4 mixture of ethyl acetate and hexane as a eluent in order to obtain colourless solid.

Yield: 60%, m.p: Nematic, Smectic [94.3-225 °C], FT-IR (KBr,  $cm^{-1}$ ): 3071 (aromatic C-H<sub>str</sub>), 2946, 2870 (C-H<sub>str</sub>), 1725 (C=O<sub>str</sub>), 1634 (C=C of methacrylic unit) 1606 and 1513 (C=C<sub>str</sub> aromatic), 1476 (C-H<sub>ben</sub>), 1245 and 1190 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively);  $^1H$ -NMR ppm ( $CDCl_3$ ):  $\delta$  8.26 (d, 2H), 8.15 (d, 2H), 7.36 (d, 2H), 7.11 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.16 (t, 2H), 4.04 (t, 2H), 4.04 (q, 2H) 1.94 (s, 3H), 1.84 (m, 2H), 1.71 (m, 2H) and 1.48 (m, 4H), 1.40 (t, 3H).  $^{13}C$ -NMR ppm ( $CDCl_3$ ):  $\delta$  167.62 164.94, 164.43, 163.80, 156.81, 155.36, 144.31, 136.56, 132.52, 131.84, 127.12, 125.39, 122.50, 122.15, 121.13, 115.19, 114.48, 68.23, 64.68, 63.94, 29.08, 28.64, 25.87, 25.79, 18.42 and 14.95. EI-MS: m/z 546.6 ( $M^+$ ). Anal. Calc. for  $C_{32}H_{34}O_8$ : C 70.31, H 6.26. Found: C 70.57 and H 6.44 %.

#### 4-[(butoxyphenoxy)carbonyl] phenyl 4-[(2-methylacryloyloxy)hexyloxy]benzoate (7b)

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (7a).

Yield: 58%, m.p: Nematic, Smectic [66.4-206 °C], FT-IR (KBr,  $\text{cm}^{-1}$ ): 3071 (aromatic C-H<sub>str</sub>), 2942, 2869 (C-H<sub>str</sub>), 1733 (C=O<sub>str</sub>), 1634 (C=C of methacrylic unit) 1604 and 1508 (C=C<sub>str</sub> aromatic), 1471 (C-H<sub>ben</sub>), 1193 and 1162 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.27 (d, 2H), 8.15 (d, 2H), 7.34 (d, 2H), 7.11 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.17 (t, 2H), 4.05 (t, 2H), 3.96 (t, 2H), 1.94 (s, 3H), 1.83 (m, 2H), 1.75 (m, 4H) and 1.52 (m, 6H), 0.98 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  167.64, 164.97, 164.44, 163.80, 157.03, 155.35, 144.25, 136.56, 132.52, 131.85, 127.13, 125.40, 122.47, 122.14, 121.12, 115.20, 114.47, 68.23, 68.18, 64.68, 31.40, 29.08, 28.63, 25.87, 25.79, 19.34, 18.45 and 13.96. EI-MS: m/z 574.6 (M<sup>+</sup>). Anal. Calc. for C<sub>34</sub>H<sub>38</sub>O<sub>8</sub>: C 71.06, H 6.66. Found: C 71.29 and H 6.47 %.

#### **4-[(hexyloxyphenoxy)carbonyl]phenyl 4-[(2-methylacryloyloxy)hexyloxy]benzoate (7c)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (7a)

Yield: 60%, m.p: Nematic, Smectic [66-182°C], FT-IR (KBr,  $\text{cm}^{-1}$ ): 3071 (aromatic C-H<sub>str</sub>), 2951, 2865 (C-H<sub>str</sub>), 1739 (C=O<sub>str</sub>), 1634 (C=C of methacrylic unit) 1601 and 1507 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1190 and 1160 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.25 (d, 2H), 8.15 (d, 2H), 7.34 (d, 2H), 7.12 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.16 (t, 2H), 4.04 (t, 2H), 3.95 (t, 2H), 1.94 (s, 3H), 1.84 (m, 2H), 1.78 (m, 2H), 1.72 (m, 2H), 1.50 (m, 6H), 1.32 (m, 4H) 0.91 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  167.61, 164.94, 164.42, 163.81, 157.02, 155.35, 144.25, 136.56, 132.52, 131.84, 127.12, 125.40, 122.47, 122.14, 121.12, 115.19, 114.48, 68.50, 68.22, 64.68, 31.69, 29.34, 29.08, 28.64, 25.82, 25.80, 22.72, 18.45 and 14.16. EI-MS: m/z 602.7 (M<sup>+</sup>). Anal. Calc. for C<sub>36</sub>H<sub>42</sub>O<sub>8</sub>: C 71.73, H 7.02. Found: C 71.51 and H 7.18 %.

#### **4-[(octyloxyphenoxy)carbonyl]phenyl 4-[(2-methylacryloyloxy)hexyloxy]benzoate (7d)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (7a).

Yield: 58%, m.p: Nematic, Smectic [67-165 °C], FT-IR (KBr, cm<sup>-1</sup>): 3074 (aromatic C-H<sub>str</sub>), 2931, 2860 (C-H<sub>str</sub>), 1734 (C=O<sub>str</sub>), 1642 (C=C of methacrylic unit) 1604 and 1508 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1194 and 1163 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.25 (d, 2H), 8.15 (d, 2H), 7.34 (d, 2H), 7.12 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.17 (t, 2H), 4.05 (t, 2H), 3.95 (t, 2H), 1.94 (s, 3H), 1.84 (m, 2H), 1.78 (m, 2H), 1.74 (m, 2H), 1.50 (m, 6H), 1.30 (m, 8H) 0.89 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 167.60, 164.93, 164.42, 163.81, 157.03, 155.36, 144.27, 136.57, 132.52, 131.83, 127.14, 125.37, 122.46, 122.13, 121.14, 115.20, 114.48, 68.52, 68.23, 64.67, 31.92, 29.46, 29.34, 29.08, 28.64, 26.14, 25.87, 25.79, 22.76, 18.44 and 14.22. EI-MS: m/z 630.76 (M<sup>+</sup>). Anal. Calc. for C<sub>38</sub>H<sub>46</sub>O<sub>8</sub>: C 72.35, H 7.35. Found: C 72.49 and H 7.15 %.

#### **4-[(decyloxyphenoxy)carbonyl]phenyl 4-[(2-methylacloyloxy)hexyloxy]benzoate (7e)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (7a).

Yield: 55%, m.p: Nematic, Smectic [59-160 °C], IR (KBr, cm<sup>-1</sup>): 3071 (aromatic C-H<sub>str</sub>), 2926, 2856 (C-H<sub>str</sub>), 1730 (C=O<sub>str</sub>), 1634 (C=C of methacrylic unit) 1604 and 1510 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1196 and 1165 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.26 (d, 2H), 8.15 (d, 2H), 7.34 (d, 2H), 7.12 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.17 (t, 2H), 4.04 (t, 2H), 3.95 (t, 2H), 1.94 (s, 3H), 1.84 (m, 2H), 1.76 (m, 2H), 1.73 (m, 2H), 1.50 (m, 2H), 1.47 (m, 2H), 1.30 (m, 12H) 0.88 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 167.58, 164.92, 164.39, 163.81, 157.03, 155.36, 144.26, 136.56, 132.52, 131.83, 127.13, 125.38, 122.46, 122.14, 121.13, 115.19, 114.48, 68.50, 68.22, 64.67, 32.01, 29.70, 29.68, 29.51, 29.44, 29.38, 29.08, 28.64, 26.15, 25.87, 25.80, 22.79, 18.45 and 14.25. EI-MS: m/z 658.8 (M<sup>+</sup>). Anal. Calc. for C<sub>40</sub>H<sub>50</sub>O<sub>8</sub>: C 72.92, H 7.64. Found: C 72.81 and H 7.88 %.

#### **4-[(dodecyloxyphenoxy)carbonyl] phenyl 4-[(2-methylacloyloxy)hexyloxy]benzoate (7f)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (7a).

Yield: 60%, m.p: Nematic, Smectic [61-155 °C] FT-IR (KBr,  $\text{cm}^{-1}$ ): 3071 (aromatic C-H<sub>str</sub>), 2920, 2852 (C-H<sub>str</sub>), 1728 (C=O<sub>str</sub>), 1634 (C=C of methacrylic unit) 1604 and 1510 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1197 and 1164 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.26 (d, 2H), 8.15 (d, 2H), 7.34 (d, 2H), 7.10 (d, 2H), 6.98 (d, 2H), 6.91 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.16 (t, 2H), 4.04 (t, 2H), 3.94 (t, 2H), 1.94 (s, 3H), 1.84 (m, 2H), 1.74 (m, 2H), 1.71 (m, 2H), 1.47 (m, 6H), 1.30 (m, 18H) 0.88 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  167.63, 164.97, 164.44, 163.80, 157.02, 155.34, 144.23, 136.56, 132.52, 131.85, 127.12, 125.41, 122.47, 122.15, 121.11, 115.19, 114.47, 68.51, 68.22, 64.69, 32.02, 29.77, 29.75, 29.72, 29.70, 29.51, 29.47, 29.37, 29.08, 28.64, 26.14, 25.87, 25.80, 22.80, 18.46 and 14.26. EI-MS: m/z 686.53 (M<sup>+</sup>). Anal. Calc. for C<sub>42</sub>H<sub>54</sub>O<sub>8</sub>: C 73.44, H 7.92. Found: C 73.59 and H 8.07 %.

## Synthesis of Polymers

### Synthesis of poly{4-[(ethoxyphenoxy)carbonyl] phenyl 4-[(2-methylacyloxy)hexyloxy]benzoate} (8a)

In a typical experiment, 1g of 4-[(ethoxyphenoxy)carbonyl] phenyl 4-[(2-methylacyloxy)hexyloxy]benzoate was placed in a polymerization tube. To that, 1, 4- dioxan (30 ml) and 0.01g of benzoylperoxide were added. The solution was flushed with nitrogen gas for few minutes, tightly closed and kept in thermostated water bath at 70±1 °C. The polymerization was continued for 24 h. The viscous polymer, thus formed, was precipitated by pouring into methanol. The white polymer solid obtained was further purified by redissolving it in chloroform and precipitated using methanol.

Yield: 65%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3079 (aromatic C-H<sub>str</sub>), 2939, 2865 (C-H<sub>str</sub>), 1733 (C=O<sub>str</sub>), 1604 and 1508 (C=C<sub>str</sub> aromatic), 1475 (C-H<sub>ben</sub>), 1192 and 1161 ( C-O-C<sub>asym & sym str</sub> of ester and ether

respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.15 (d, 2H), 8.04 (d, 2H), 7.24 (d, 2H), 7.04 (d, 2H), 6.85 (d, 4H), 3.97 (t, 6H), 1.79 (m, 2H), 1.84 (m, 2H), 1.64 (m, 2H), 1.39 (m, 8H), 0.91 (t, 3H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 164.80, 164.22, 163.62, 156.80, 155.16, 144.21, 132.47, 131.76, 127.13, 122.49, 122.09, 121.25, 115.10, 114.39, 68.19, 65.12, 63.87, 45.28, 44.95, 29.16, 28.21, 26.06, 25.88 and 14.95.

**Poly-{4-[(butoxyphenoxy)carbonyl] phenyl 4-[(2-ethylacyloyloxy)hexyloxy]benzoate} (8b)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (8a).

Yield: 68%, FT-IR (KBr, cm<sup>-1</sup>): 3079 (aromatic C-H<sub>str</sub>), 2924, 2854 (C-H<sub>str</sub>), 1732 (C=O<sub>str</sub>), 1604 and 1509 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1194 and 1162 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.17 (d, 2H), 8.07 (d, 2H), 7.26 (d, 2H), 7.04 (d, 2H), 6.88 (d, 4H), 3.96 (t, 6H), 1.77 (m, 8H), 1.48 (m, 6H), 0.96 (t, 6H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 177.56, 176.91, 164.78, 164.19, 163.61, 157.02, 155.17, 144.18, 132.47, 131.75, 127.17, 122.45, 122.05, 121.28, 115.12, 114.39, 68.15, 65.08, 45.20, 44.98, 31.41, 29.16, 28.21, 26.06, 25.88, 19.33 and 14.95.

**Poly-{4-[(hexyloxyphenoxy)carbonyl]phenyl4-[(2-methylacyloyloxy)hexyloxy] benzoate} (8c)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (8a).

Yield: 63%, FT-IR (KBr, cm<sup>-1</sup>): 2933, 2861 (C-H<sub>str</sub>), 1732 (C=O<sub>str</sub>), 1603 and 1508 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1252, 1193 and 1163 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 8.14 (d, 2H), 8.05 (d, 2H), 7.25 (d, 2H), 7.04 (d, 2H), 6.86 (d, 4H), 3.95 (t, 6H), 1.75 (m, 6H), 1.64 (m, 4H), 1.49 (m, 6H), 1.31 (m, 4H), 0.88 (t, 6H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 164.78, 164.19, 163.60, 157.01, 155.16, 144.15, 142.47, 131.75, 127.14, 122.43, 122.05, 121.26, 115.10, 114.39, 68.46, 68.19, 44.94, 44.89, 31.69, 29.34, 29.15, 26.06, 25.88, 25.81, 22.70 and 14.15.

**Poly-{4-[(octyloxyphenoxy)carbonyl]phenyl4-[(2-methylacyloyloxy)hexyloxy] benzoate} (8d)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (8a).

Yield: 60%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3074 (aromatic C-H<sub>str</sub>), 2929, 2858 (C-H<sub>str</sub>), 1733 (C=O<sub>str</sub>), 1604 and 1508 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1194 and 1161 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.15 (d, 2H), 8.05 (d, 2H), 7.25 (d, 2H), 7.04 (d, 2H), 6.86 (d, 4H), 3.95 (t, 6H), 1.75 (m, 6H), 1.65 (m, 2H), 1.42 (m, 6H), 1.29 (m, 8H), 0.88 (t, 6H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  177.54, 176.92, 164.67, 164.08, 163.49, 156.89, 155.03, 144.04, 132.35, 131.63, 127.04, 122.33, 121.94, 121.15, 114.98, 114.27, 68.35, 68.07, 64.86, 45.17, 44.83, 31.82, 29.38, 29.27, 29.25, 29.05 28.10, 26.03, 25.95, 25.77, 22.66 and 14.95.

**Poly-{4-[(decyloxyphenoxy)carbonyl]phenyl4-[(2-methylacyloyloxy)hexyloxy] benzoate} (8e)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (8a).

Yield: 63%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3074 (aromatic C-H<sub>str</sub>), 2925, 2854 (C-H<sub>str</sub>), 1733 (C=O<sub>str</sub>), 1603 and 1508 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1193 and 1161 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.16 (d, 2H), 8.06 (d, 2H), 7.25 (d, 2H), 7.04 (d, 2H), 6.87 (d, 4H), 3.96 (t, 6H), 1.77 (m, 8H), 1.44 (m, 6H), 1.27 (m, 12H), 0.88 (t, 6H). <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  164.79, 164.20, 163.60, 157.01, 155.14, 144.15, 132.47, 131.75, 127.15, 122.45, 122.05, 121.25, 115.09, 114.37, 68.46, 68.18, 65.04, 44.97, 44.92, 31.01, 29.70, 29.55, 29.44, 29.40, 29.17, 26.15, 26.07, 25.89, 22.80 and 14.25.

**Poly-{4-[(dodecyloxyphenoxy)carbonyl] phenyl 4-[(2methylacyloyloxy)hexyloxy] benzoate} (8f)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (8a).

Yield: 62%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3074 (aromatic C-H<sub>str</sub>), 2924, 2853 (C-H<sub>str</sub>), 1733 (C=O<sub>str</sub>), 1604 and 1508 (C=C<sub>str</sub> aromatic), 1470 (-C-H<sub>ben</sub>), 1193 and 1162 ( C-O-C<sub>asym & sym str</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.16 (d, 2H), 8.07 (d, 2H), 7.25 (d, 2H), 7.05 (d, 2H), 6.90

(d, 4H), 3.94 (t, 6H), 1.77 (m, 8H), 1.44 (m, 6H), 1.27 (m, 16H), 0.88 (t, 6H).  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ):  $\delta$  164.80, 164.39, 163.64, 157.02, 155.18, 144.20, 132.53, 131.84, 127.15, 122.46, 122.12, 121.25, 115.17, 114.44, 68.49, 68.20, 64.95, 44.19, 44.80, 32.03, 29.78, 29.76, 29.71, 29.53, 29.48, 29.39, 29.16, 26.15, 25.89, 25.83, 22.81 and 14.26.

#### **Synthesis of 4-[(4-hexyloxyphenoxy) carbonyl] phenyl 4-hexyloxybenzoate (9a)**

In a typical experiment, 15.7 g (50 mmol) 4-hexyloxyphenyl 4-hydroxybenzoate (3c) and 8.67 g (85 mmol) of triethylamine were dissolved in 100 ml MEK. To this, a 50 ml MEK solution containing 11.1 g (50 mmol) 4-hexyloxybenzoylchloride (prepared from 4-hexyloxy benzoic acid and thionyl chloride) was added drop wise at 0 °C. Then the reaction mixture was stirred for 3 h at room temperature and then the triethylamine salt thus formed was filtered off and solvent was evaporated. The solid obtained was purified by recrystallization from isopropanol to yield a white solid.

Yield: 73% m.p-95 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3076 (aromatic C-H<sub>str</sub>), 2930, 2860 (C-H<sub>str</sub>), 1739 (C=O<sub>str</sub>), 1605 and 1512 (C=C<sub>str</sub> aromatic), 1469 (C-H<sub>ben</sub>), 1275, 1194 and 1166 (C-O-C<sub>asym & sym str</sub> of ester and ether respectively);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ ):  $\delta$  8.27 (d, 2H), 8.16 (d, 2H), 7.36 (d, 2H), 7.13 (d, 2H), 6.99 (d, 2H), 6.94 (d, 2H), 4.05 (t, 2H), 3.96 (t, 2H), 1.81 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H) and 0.93 (t, 6H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ):  $\delta$  164.87, 164.35, 163.81, 156.94, 155.27, 144.18, 132.41, 131.74, 127.03, 122.36, 122.05, 120.09, 115.11, 114.41, 68.42, 68.38, 31.59, 31.54, 29.24, 29.05, 25.72, 25.65, 22.61, 22.59 and 14.05. EI-MS: m/z 518.78 ( $\text{M}^+$ ). Anal. Calc. for  $\text{C}_{32}\text{H}_{38}\text{O}_6$ : C 74.31, H 7.26 Found: C 74.52 and H 7.13 %.

#### **4-[(4-dodecyloxyphenoxy) carbonyl] phenyl 4-hexyloxybenzoate (9b)**

The procedure adopted for the synthesis of this compound was identical to that adopted for Compound (9a)

Yield: 70% m.p-100 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3076 (aromatic C-H<sub>str</sub>), 2918, 2852 (C-H<sub>str</sub>), 1737 (C=O<sub>str</sub>), 1606 and 1510 (C=C<sub>str</sub> aromatic), 1470 (C-H<sub>ben</sub>), 1277, 1247 1196 and 1166 (C-O-C<sub>asym</sub> & <sub>sym str</sub> of ester and ether respectively) <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$  8.27 (d, 2H), 8.15 (d, 2H), 7.36 (d, 2H), 7.12 (d, 2H), 6.99 (d, 2H), 6.93 (d, 2H), 4.06 (t, 2H), 3.97 (t, 2H), 1.81 (m, 4H), 1.46 (m, 4H), 1.34 (m, 20H) and 0.89 (t, 3H), 0.87 (t, 3H) <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$  164.85, 164.33, 163.82, 156.94, 155.28, 144.19, 132.41, 131.74, 127.04, 122.36, 122.05, 120.96, 115.10, 114.41, 68.42, 68.38, 31.94, 31.56, 29.68, 29.66, 29.62 29.42, 29.37, 29.29, 29.06, 26.05, 25.66, 22.71, 22.61, 14.14 and 14.04. EI-MS: m/z 602.89 (M<sup>+</sup>). Anal. Calc. for C<sub>38</sub>H<sub>50</sub>O<sub>6</sub>: C 75.71, H 8.36 Found: C 75.56 and H 8.19 %.

## References

1. G. Buchi, S. M. Weinreb, *J. Am. Chem. Soc.*, 1971, 93, 746.
2. W. Greene, *Protecting Groups in Organic Synthesis*, John Wiley & Sons. New York, 1999.
3. M. P. Denieul, B. Laursen, R. Hazell, T. Skrdstrup, *J. Org. Chem.*, 2000, 65, 6052.



**Table 1 HOPM and DSC data of model mesogens**

Sample Code	Transitions observed by DSC	Transition temperature (°C)	$\Delta H$ (kJ/mole)	Phases observed by HOPM
9a (Heating)	Cr-S <sub>C</sub>	92.0	23.07	Smectic C
	S <sub>C</sub> -S <sub>A</sub>	115.1	0.008	Smectic A
	S <sub>A</sub> -N	116.4	0.006	Nematic
	N-I	209.6	1.45	Isotropic
9a (Cooling)	I-N	208.8	1.30	Nematic
	N-S <sub>A</sub>	119.7	0.011	Smectic A
	S <sub>A</sub> -S <sub>C</sub>	115.3	0.006	Smectic C
	S <sub>C</sub> -Cr	64.2	19.6	Crystallization
9b (Heating)	Cr-S <sub>C</sub>	99.58	41.95	Smectic C
	S <sub>C</sub> -S <sub>A</sub>	126.0	0.004	Smectic A
	S <sub>A</sub> -N	166.1	0.15	Nematic
	N-I	183.4	0.68	Isotropic
9b (Cooling)	I-N	182.5	0.655	Nematic
	N-S <sub>A</sub>	165.6	0.233	Smectic A
	S <sub>A</sub> -S <sub>C</sub>	126.1	0.002	Smectic C
	S <sub>C</sub> -Cr	76.3	41.290	Crystallization