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Columnar liquid crystals based on the lower rim functionalization on resorcin[4]arene core

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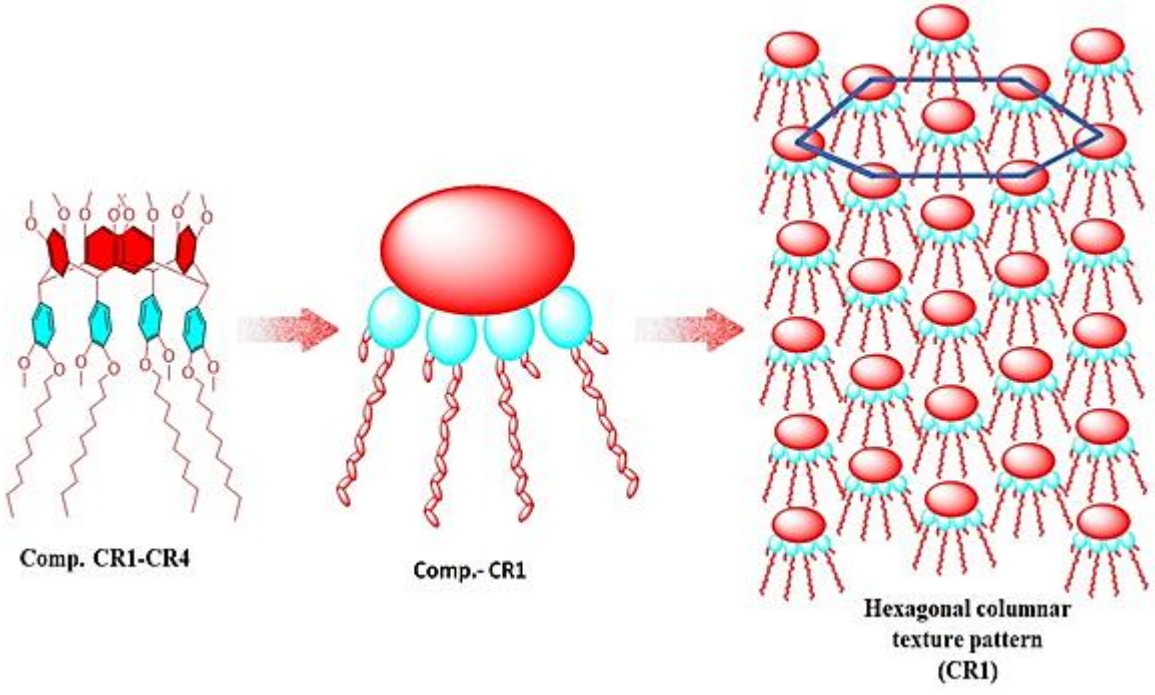
GRAPHICAL ABSTRACT



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ABSTRACT

Lower rim functionalized resorcin[4]arene derivatives were synthesized by four different n-alkyl chain spacers. All four derivatives have been characterized by using Fourier transform infrared (FT-IR) and Nuclear magnetic resonance (NMR) spectroscopic technique. The liquid crystalline properties of these synthesized compounds were studied by POM investigation. All derivatives exhibited columnar hexagonal type mesophase with broad temperature range. The mesomorphic properties were further influenced by variable side alkoxy chain (-OR). Compounds CR_1 showed higher temperature range mesophase as compared to compound CR_4.

***Keywords*:** Supramolecules, resorcin[4]arene, liquid crystal, self-assembly, columnar phase

1. INTRODUCTION

In 1888, Friedrich Reinitzer invented liquid crystal for the first time and its applications towards the optical devices. In recent decades, columnar liquid crystals have received a lot of interest among all types of liquid crystals due to its charge-transport and high hole mobility properties. Nowadays, researcher have more focus to develop optical devices from synthetic organic moieties with high temperature range.[1] Further, LCs are self-organising thermally fluctuating materials that are intermediate among isotropic liquid and crystalline solid, which is in brownian motion. [2] Moreover, in the digital era, display technologies are more emerging field for research to improve the quality of display.

The supramolecular chemistry is a best field for researchers due to its various applications such as self-assembly [3], cell mimicking [4], optical chemosensors[5], nano capsules [6], dendrimers in biological system [7], liquid crystals [8], HPLC stationary phases [9], photoresist [10], metal ion extraction [11], organic light emitting diode (OLED) [12], explosive sensing [13], and photovoltaic (OPV) [14]. Supramolecules is mainly classify to host guest and self-assembled supramolecules [15]. Calixarene is a third-generation class of host guest chemistry having tunable 3D-shaped hydrophobic cavities [16], that show columnar liquid crystalline property.[17] Its upper and lower rim functionalization make a suitable host and provide binding site for different guest.[18] Moreover, according to scaffold, rim modification of calixarene seeming application in various field. At present, different LC compounds were developed using calixarene core moity.[19] For example, employing long alkyl chain on calixarene core exhibiting bowl mesophase LC.[20]

Resorcin[4]arene is a subclass of calix[4]arene also known as ‘cyclic tetrameric host’ for different guest such as a sugar molecules, ions, and organic molecules.[21, 22] The core moity resorcin[4]arene and its derivative synthesized by applying various acid catalyst like molybdate sulfuric acid, tungsten sulfuric acid, Con.

HCl, trifluoracetic acid, and many more.[23-26] Various aldehyde were used as a feet in synthesis of resorcin[4]arene that have ordering of stereoisomers [27]. They are sterically hindered molecule exhibiting as different isomers like cis cone, saddle, boat and chair isomer because of hindered substitution on their rim which show number of applications such as supramolecular tectonics, host guest complexes, metal ion extraction, surface reforming agents, selective membranes, liquid crystals, nonlinear optical property in material chemistry, ion channel mimics, nano- capsules, and also used as a starting material in synthesis of different cavitands.[28]

Calix[4]resorcinarene was modify by introducing different alkyl chain and other functional group on upper/lower rim have due to their potential application in LCs devises, OLEDs, sensor, and biological activity. [29-31]

Liquid crystalline compounds based on calix[4]arene core are rarely reported in the literature while only single research article was found for the liquid crystalline application based on calix[4]resorcinarene[32-34], this motivate us to working on the study and mesomorphic behaviour of this kind of supramolecular core with 3D-bowl cavity. In the present investigation, we have reported calix[4]resorcinarene derivatives with vanillin feet and investigated their liquid crystalline and self-assembly study. Moreover, we have also study the structure-property relationship by changing the side alkyl chain on the hydroxy group of the central resorcinarene core.

2. MATERIALS AND METHOD

1,3-dimethoxybenzene, anhydrous K_2CO_3, alkyl bromides (R-Br), HCl and 4-hydroxy-3-methoxybenzaldehyde (vanillin) were purchased from Avra Chemical, India. DMF and Methanol solvents were purchased from Finar and further purified by usual established method. TLC plates (silica gel 60 F254 silica-aluminum plates) ware purchased from Merck. FT-IR spectra was carried out in KBr pellet method and further analysed in the range of 3800-560 cm^{-1} by Bruker TENSOR 27. ^1H and ^{13}C NMR spectra: The spectra were recorded on a Bruker Advance (400 MHz), in $CDCl_3$ Solvents where TMS is internal standard. The mesophase is identified by Polarizing Optical Microscope (Nikon Eclipse LV-100 POL) with temperature-controlled heating stage.

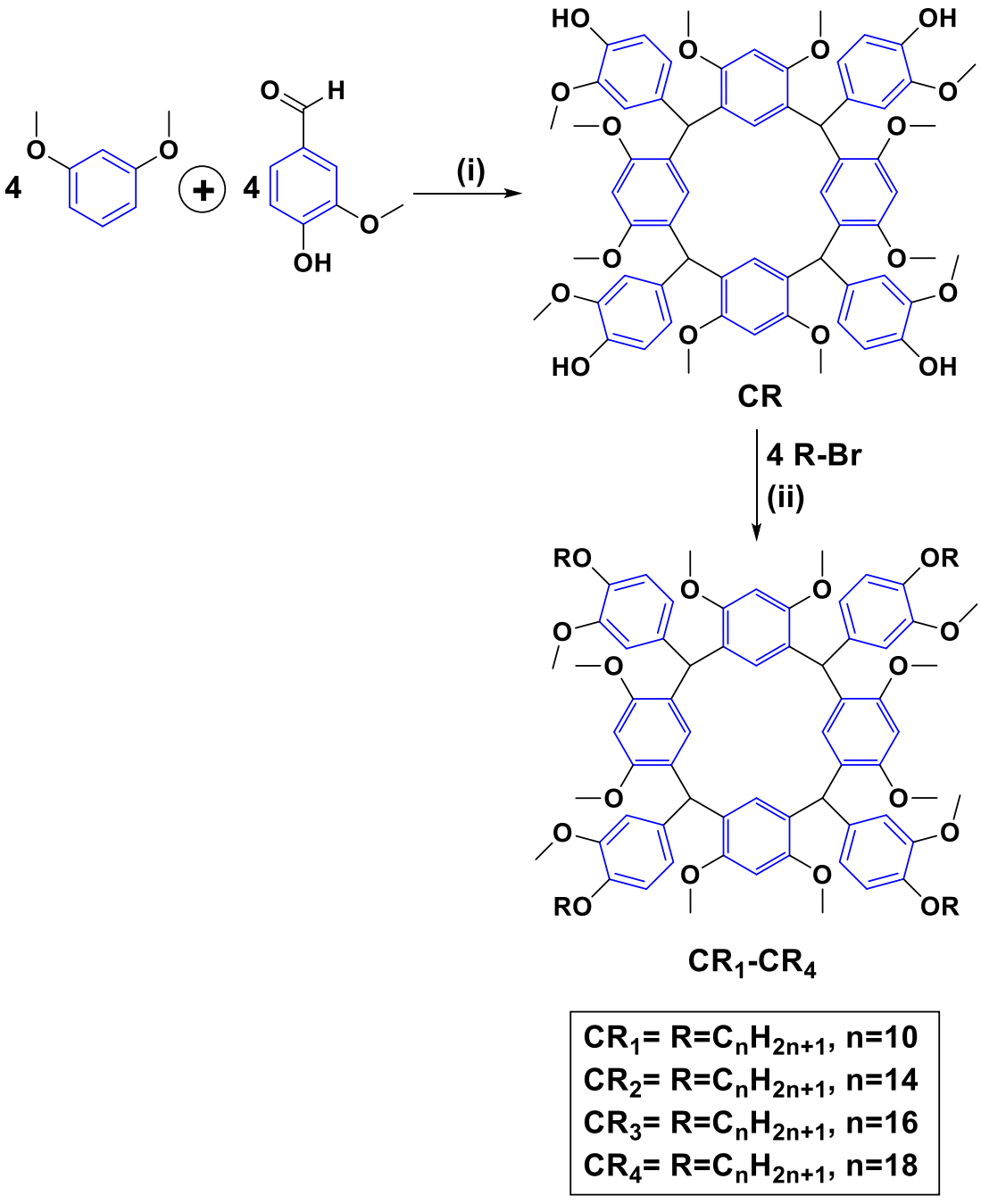
3. RESULT AND DISCUSSIONS

3. 1. Synthesis and Characterization

The synthetic routes were illustrated in Scheme 1. The mixture of 1,3-dimethoxybenzene (0.5 g: 3.6 mmol), 4-hydroxy-3-methoxybenzaldehyde (vanillin) (3.6 mmol), absolute ethanol (45 ml), and hydrochloride acid 12N (0.5 mL) was refluxed with constant stirring at 80 °C for 72 h. The reaction was monitored by thin layer chromatography (methanol: dichloromethane 0.5: 9.5).

After the completion of reaction, the mixture was cooled at room temperature and the product was filtered follow by washing with methanol. Product was dried to give desired compound CR as a light pink coloured compound with 81% yield, M.P.: above to 400 °C. The final targeted compound (CR_1-CR_4) were prepared from comp. CR (0.92 mmol), alkyl bromide (3.8 mmol) and K_2CO_3 (3.8 mmol) in 20 mL N,N-dimethylformamide, the solution was refluxed for 24 h. reaction was monitored by thin layer chromatograph (Ethyl acetate: Hexane 8:2).

Then the reaction mixture was dumped in ice water, The final resultant crude residue was purified by using column chromatography on silica gel eluting with ethyl acetate: hexane as eluent (1:4). The ^1H NMR, ^{13}C NMR and IR results also well supported to the corresponding structures of derivatives and final target compounds.



Scheme 1. Reaction condition: **(i)** HCl, ethanol, reflux, 72 h: **(ii)** anhydrous K_2CO_3, DMF, reflux, 24 h.

Comp. CR_1: 70% yield, FT-IR (KBr) in cm^{-1}: 843 Poly $(-CH_2-)_n$ group in $-OC_{10}H_{21}$, 889 (-C-H- def. tri-substituted on para side $-OC_{10}H_{21}$), 947 (-C-H- def. hydrocarbon), 1510 (-C-H- def. in $-CH_2$ unit in alkyl chain), 2847 and 2920 (-C-H str in aromatic ring). ^1H NMR: 0.89 (t, 12H, of $-CH_3$), 1.25–1.29 (m, 48H, n-poly $(CH_2)_n$ groups , 1.44 (m, 8H, $-CH_2-$), 1.74 (p, 8H, $-CH_2-$), 3.99 (t, 8H, $-OCH_2-$), 3.80-3.85 (s, 36H, $-OCH_3$), 5.51 (s, 4H, ArCHAr),6.80- 7.12 (s, 12H,

phenyl ring), 6.62-6.75 (dd, 8H, phenyl ring). ^{13}C NMR: 156.1, 149.9, 148.3, 145.2,136.2, 130.7,121.2 120.9, 113.0, 96.1, 68.6, 56.5, 34.5, 31.6, 29.4, 25.9, 22.7, 14.4.

Comp. CR$_2$: 70% yield, FT-IR (KBr) in cm^{-1}: 837 Poly (-CH_2-)$_n$ group in -$OC_{10}H_{21}$, 885 (-C-H- def. tri-substituted on para side -$OC_{10}H_{21}$), 952 (-C-H- def. hydrocarbon), 1516 (-C-H- def. in -CH_2 unit in alkyl chain), 2848 and 2922 (-C-H str in aromatic ring). ^{1}H NMR: 0.85 (t, 12H, of -CH_3), 1.22–1.33 (m, 80H, n-poly $(CH_2)_n$ groups , 1.47 (m, 8H, -CH_2-), 1.71 (p, 8H, -CH_2-), 3.96 (t, 8H, -OCH_2-), 3.83-3.88 (s, 36H, -OCH_3), 5.54 (s, 4H, Ar-CH-Ar),6.76- 7.14 (s, 12H, phenyl ring), 6.63-6.72 (dd, 8H, phenyl ring). ^{13}C NMR: 156.5, 150.4, 148.5, 144.8,135.9, 131.1,121.5 121.0, 113.4, 96.2, 68.8, 56.3, 34.7, 31.5, 29.8, 25.4, 22.5, 14.1.

Comp. CR$_3$: 72% yield, FT-IR (KBr) in cm^{-1}: 841 Poly (-CH_2-)$_n$ group in -$OC_{10}H_{21}$, 892 (-C-H- def. tri-substituted on para side -$OC_{10}H_{21}$), 949 (-C-H- def. hydrocarbon), 1515 (-C-H- def. in -CH_2 unit in alkyl chain), 2842 and 2924 (-C-H str in aromatic ring). ^{1}H NMR: 0.88(t, 12H, of -CH_3), 1.26–1.34 (m, 96H, n-poly $(CH_2)_n$ groups , 1.45 (m, 8H, -CH_2-), 1.76 (p, 8H, -CH_2-), 4.01 (t, 8H, -OCH_2-), 3.79-3.87 (s, 36H, -OCH_3), 5.49 (s, 4H, Ar-CH-Ar),6.83- 7.17 (s, 12H, phenyl ring), 6.60-6.73 (dd, 8H, phenyl ring).^{13}C NMR: 156.6, 150.4, 148.3, 145.3,135.9, 130.7,121.2 120.7, 113.5, 96.6, 68.3, 57.1, 34.6, 31.6, 29.3, 25.6, 22.3, 14.4.

Comp. CR$_4$: 68% yield, FT-IR (KBr) in cm^{-1}: 844 Poly (-CH_2-)$_n$ group in -$OC_{10}H_{21}$, 890 (-C-H- def. tri-substituted on para side -$OC_{10}H_{21}$), 951 (-C-H- def. hydrocarbon), 1513 (-C-H- def. in -CH_2 unit in alkyl chain), 2853 and 2927 (-C-H str in aromatic ring). ^{1}H NMR: 0.84 (t, 12H, of -CH_3), 1.22–1.27 (m, 112H, n-poly $(CH_2)_n$ groups , 1.50 (m, 8H, -CH_2-), 1.70 (p, 8H, -CH_2-), 3.97 (t, 8H, -OCH_2-), 3.84-3.89 (s, 36H, -OCH_3), 5.53 (s, 4H, Ar-CH-Ar),6.84- 7.15 (s, 12H, phenyl ring), 6.58-6.67 (dd, 8H, phenyl ring).^{13}C NMR: 156.3, 150.2, 148.0, 145.1,135.8, 130.9,121.4 121.1, 113.2, 96.4, 68.7, 56.2, 34.3, 31.7, 29.7, 25.8, 22.8, 14.2.

3. 2. POM investigation

The transition temperatures of our synthesised lower rim functionalized calix[4]resorcinarene derivatives (**CR$_1$-CR$_4$**) were confirmed by using polarizing optical microscope (POM) equipped with hot plate and digital camera, by observing the textures of thin film of sample at various temperatures on heating and cooling conditions. POM was cross-polarized to obtain dark field and to better evaluate the LCs phases of compounds in the present study. All the target materials showed defect type texture pattern of columnar hexagonal mesophase (Colh) which is basically appeared in bowl or disk-shaped compounds.[36-37] The POM texture of compounds **CR$_1$**, **CR$_2$, CR$_3$,** and **CR$_4$** are showed in Figure 4 and the corresponding data were summarized in Table 1. Compound **CR$_1$**, **CR$_2$, CR$_3$,** and **CR$_4$** showed similar texture pattern of hexagonal columnar phase at 160.2 °C, 153.2 °C, 142.4 °C, and 134 °C on heating (Figure 1) and 157.9 °C, 152.5 °C, 139.2 °C, and 130.9 °C on cooling condition (Figure 2), respectively. The isotropic liquid transition temperatures of **CR$_1$**, **CR$_2$, CR$_3$,** and **CR$_4$** were 198.1 °C, 189.7 °C, 176.4 °C and 165.1 °C on heating. Compound **CR$_1$** show higher mesophase temperature range compare to other 3 compounds **CR$_2$, CR$_3$** and **CR$_4$**. Figure 3 exhibited the phase diagram of comp. **CR$_1$-CR$_4$** on heating and cooling. This is due to short alkoxy side chain substitutes on lower rim which is stabilized the columnar mesophase in resorcinarene core, which is dependent on the functionalization of periphery alkyl chain in lower or upper rim of resorcinarene with various linking group. On cooling condition, the same textural pattern of hexagonal columnar phase was observed before solidifying to solid crystal.

Thus, an enantiotropic mesomorphic behaviour over a broad thermal range of mesophase was seen for the synthesized vase-shaped resorcinarene materials.

Table 1. Phase transition temperature (°C) and corresponding enthalpies (kJ/mol) of comp. **CR_1-CR_4**.

	Phase transition temperature (°C)	
Compound	Heating	Cooling
CR_1	Cr 160.2 Col_h 198.1 I	I 192.4 Col_h 157.9
CR_2	Cr 153.2 Col_h 189.7 I	I 184.5 Col_h 152.5
CR_3	Cr 142.4 Col_h 176.4 I	I 168.2 Col_h 139.2
CR_4	Cr 134.0 Col_h 165.1 I	I 160.9 Col_h 130.9

[a]Peak temperature obtained in POM investigation during heating and cooling condition; Cr= crystalline; I= Isotropic Col_h= columnar hexagonal phase.

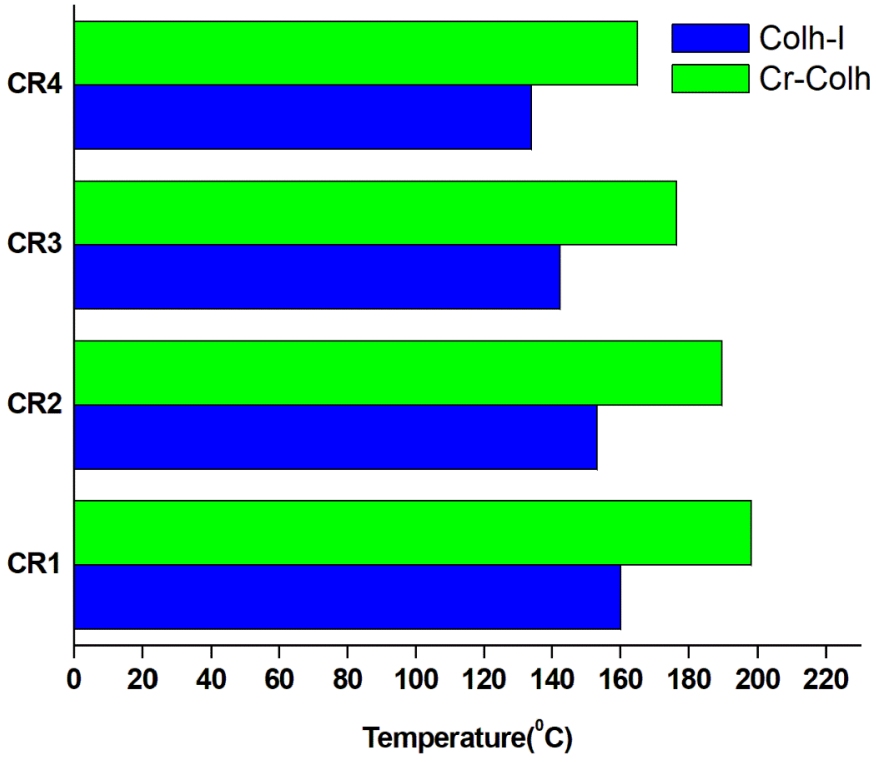


Figure 1. Bargraph showing the thermal behaviour of compounds **CR_1-CR_4** (heating condition)

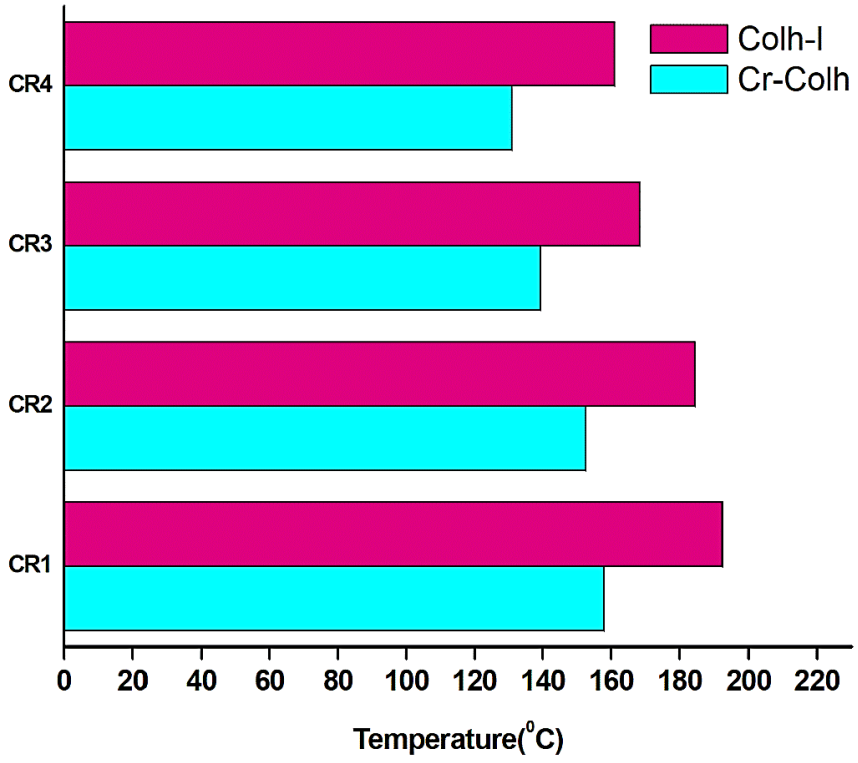


Figure 2. Bargraph showing the thermal behaviour of compounds **CR1-CR4** (Cooling condition)

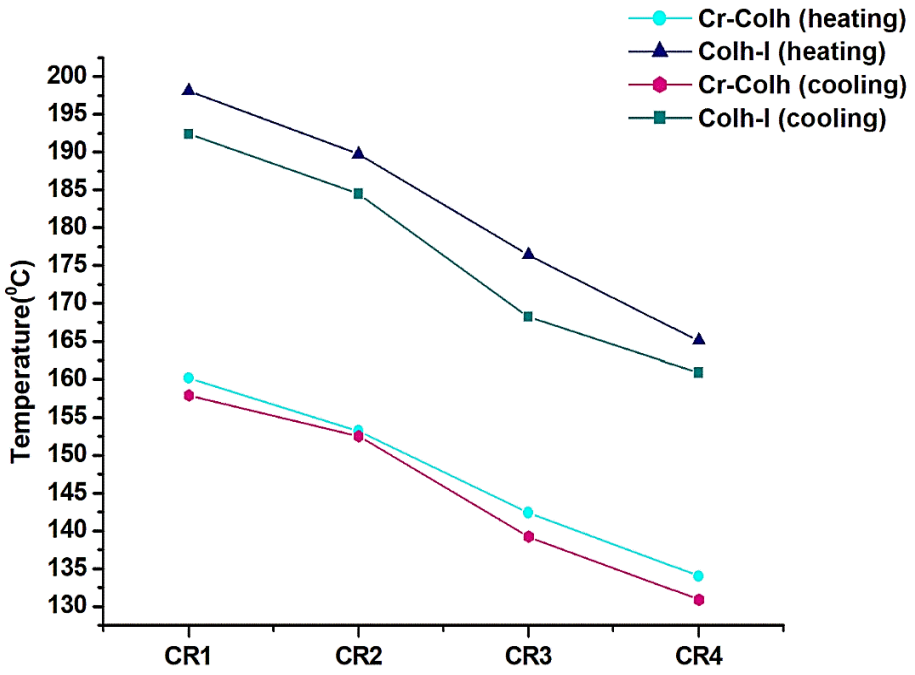


Figure 3. Phase diagram of comp. **CR1-CR4** (heating and cooling) by POM.

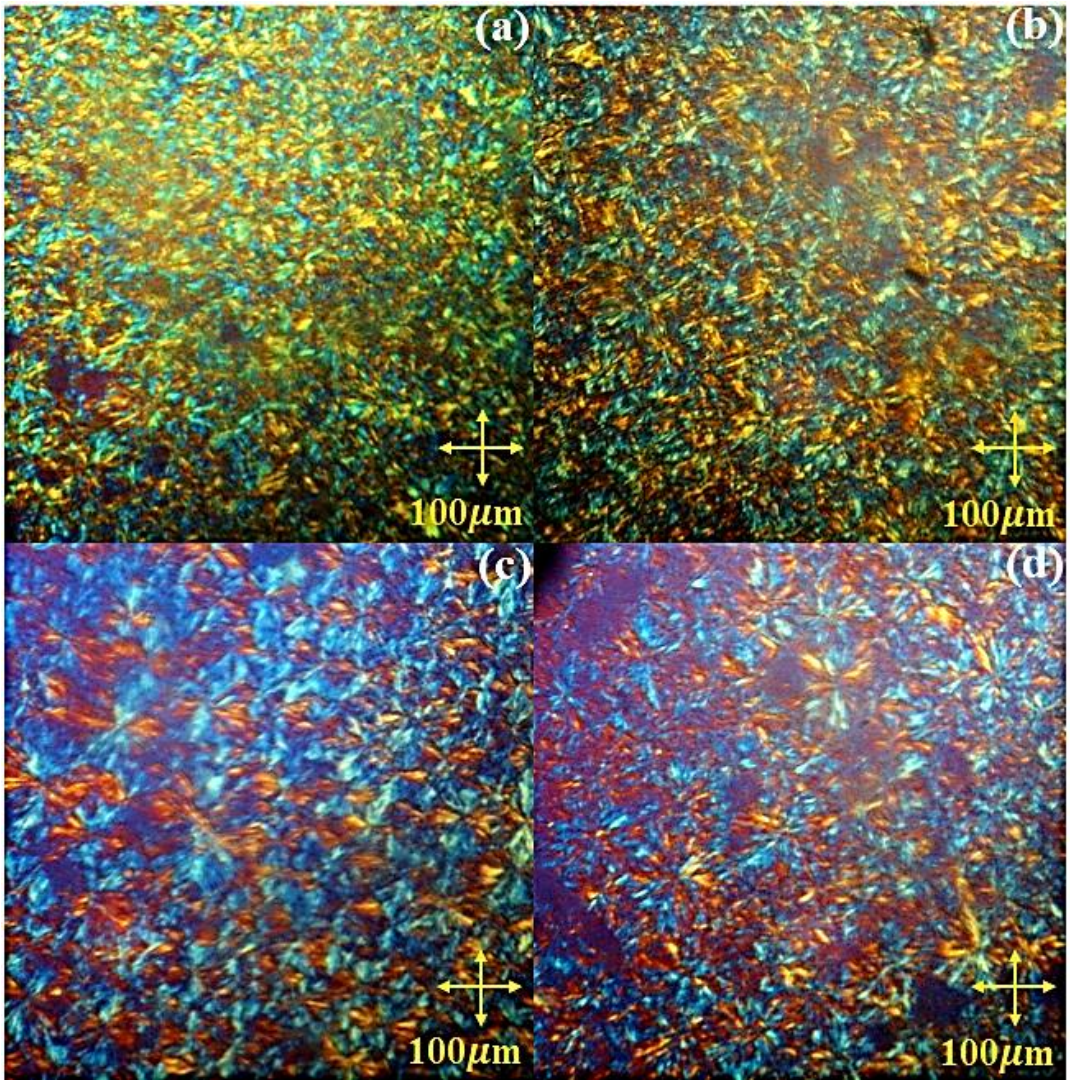


Figure 4. POM texture images: comp. **CR1** at 160.2 °C on crossed polarizers, 1 K/min **(a)**; comp. comp. **CR2** at 153.2 °C on crossed polarizers **(b)** comp. **CR3** at 142.4 °C on crossed polarizers **(c)**; comp. **CR4** at 134.0 °C on crossed polarizer **(d)**.

4. CONCLUSIONS

In summary, we have synthesised tetrameric resorcinarene core moiety by reacting 1,3-dimethoxybenzene and vanillin and furthermore four derivatives **(CR1-CR4)** prepared with 67-72% yield using different alkyl chain. All four derivative were confirmed by FTIR and NMR. Their liquid crystalline behaviour was examined by POM. Tetrameric resorcinearene derivatives show the hexagonal columnar liquid crystals. Compounds **CR1** showed higher temperature range mesophase as compared to other three. The POM study of lower rim functionalized resorcin[4]arene suggested that this kind of molecules could be used as a building block for columnar LC and many different substitution on lower rim of resorcin[4]arene influenced to the mesomorphic properties.

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