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ORIGINAL

Three Nematogen Azobenzene-Based Stationary Phases for Capillary GC: Synthesis and Comparative Study

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Abstract In this paper, three laterally substituted liquid crystals termed LCC_1, LCC_3 and LCC_4 were synthesized. Characterization of these substances was carried out by ^1H NMR and ^{13}C NMR; they possess similar core and differ in their lateral substituents. Their thermal stability was conducted by thermogravimetric analysis and showed decomposition beginning at 212, 233 and 264 °C related to LCC_1, LCC_3 and LCC_4, respectively. Thermal properties were determined by differential scanning calorimetry, thermomicroscopy and inverse gas chromatography. The three novel compounds exhibited a nematic mesophase at a defined range of temperatures, which varied from 81 to 55 °C. Lengthening of the lateral substituent seemed to affect the nematic range by decreasing it. Fused-silica capillary columns (30 m × 0.32 mm) were employed for the analytical study. Numerous mixtures of components of various properties were injected. Particular attention was given to the selectivity towards the close-boiling isomers. These investigations indicated that lateral attached groups had considerable effect on the thermal and chromatographic properties of the liquid crystal compounds. These interesting results may guide in improving the development of new type of liquid crystals with desired properties for a widespread application.

Keywords Capillary gas chromatography · Liquid crystals · Thermal properties · Analytical properties

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Introduction

Among the various stationary phases that have been studied in gas chromatography, liquid crystal compounds remain one of the most interesting materials used as stationary phase in gas liquid chromatography (GLC). Their exceptional behavior allowed their application in the analysis of numerous mixtures of components. Applications towards the separation of isomeric phenols, naphthalene homologs, polycyclic aromatic hydrocarbons, disubstituted benzenes and volatile oil constituents [1–9] have been widely investigated. In 2005, Witkiewicz et al. [10] have reviewed their analytical applications and advancement made in both techniques of high-performance liquid chromatography and gas chromatography.

Because of the rode-like shape and the orientational order provided by the anisotropy of the liquid crystal, distinctive solvent property is revealed from this material. Separations are yielded based on variations in molecular shape (length-to-breadth ratio and planarity) independently on any specific interactions [11–14]. On conventional capillary columns, discrimination between positional or geometric isomers is difficult to achieve because of their similar physical properties. On the contrary, liquid crystal stationary phase (LCSP) enables their effective and selective separation. For two solutes with the same boiling point, the solute with the greater length-to-breadth ratio will be retained longer on the LCSP.

A better understanding of the relationship between the molecular structure of liquid crystal and its analytical properties would enable a more rational selection of the liquid crystalline stationary phase to resolve various analytical problems. For different materials, mesophases which have the same structure may display different chromatographic properties towards the same mixtures of components.

Therefore, the molecular structure of these compounds influences significantly the separation process that takes place on an LCSP. Numerous workers have been studying the effect of the presence of lateral substituents on the analytical properties of the LCSPs [15–20]. It is pointed out that compounds with higher nematic range exhibit better selectivity [21, 22]; however, the presence of lateral substituent on mesogenic structure leads to a decrease in nematic range and phase selectivity (with regard to isomers especially) by increasing the intermolecular distances in the mesophase, which reduce the steric effect responsible for the selectivity within the mesophase [23]. In other papers, it is indicated that certain lateral substituents may decrease the nematic range but may yield a higher selectivity, and thus a better separation [16, 17]. In all cases, synthesizing laterally substituted liquid crystals with higher nematic range and selectivity remains one of the principal parts in the development of these materials.

In this study, a homologous series of three mesogenic compounds termed LCC_1, LCC_3 and LCC_4 (Fig. 1) has been synthesized. The influence of the lateral substituent on the thermal and gas chromatographic properties has been examined. The three monomeric liquid crystals have the same core structure but differ by their lateral substituents (Fig. 1). The first objective of this study was to determine and compare the thermal properties of each substance by different approaches; secondly, it was to investigate and discuss the separating properties of these three mesogenic substances.

Experimental

Reagents

All compounds used for the synthesis of the liquid crystals as well as the chromatographic grade solvents employed (methanol, dichloromethane, and chloroform) were from Janssen Chemica (Amsterdam, The Netherlands). The analytical grade solutes of *n*-alkanes (C_9–C_{17}), 2-*n*-ketones

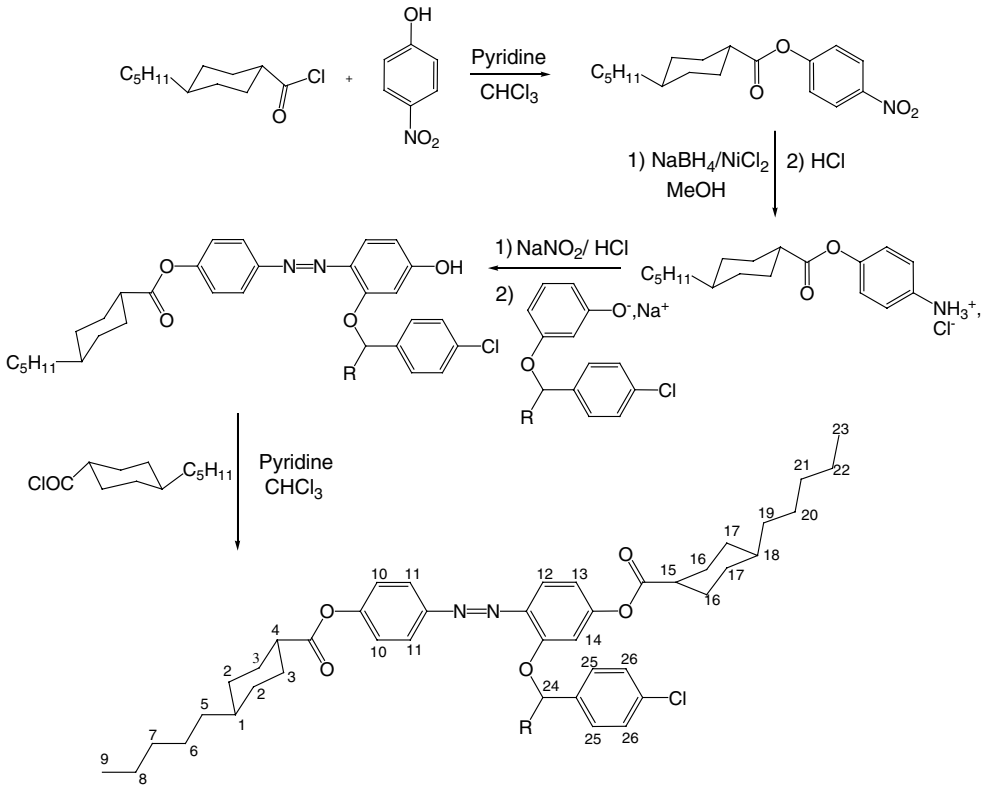

Fig. 1 Synthesis scheme of the three liquid crystals. LCC_1: 4-[(E)-[4-[[(*trans*-4-pentylcyclohexyl)carbonyl]oxy]-2-[1(*R*,*S*)-(4-chlorophenyl)ethoxy] phenyl] diazenyl] phenyl[(*trans*-4-pentylcyclohexyl) carboxylate]. LCC_3: 4-[(*E*)-[4-[[(*trans*-4-pentylcyclohexyl)carbonyl]oxy]-2-[1(*R*,*S*)-(4-chlorophenyl) butoxy] phenyl] diazenyl] phenyl[(*trans*-4-pentylcyclohexyl) carboxylate]. LCC_4: 4-[(*E*)-[4-[[(*trans*-4-pentylcyclohexyl)carbonyl]oxy]-2-[1(*R*,*S*)-(4-chlorophenyl) pentoxy] phenyl] diazenyl] phenyl [(*trans*-4-pentylcyclohexyl) carboxylate]

(C_7–C_{12}), hydrocarbon aromatics, essential oil constituents and phenol derivatives were 99 % pure or better and were supplied by Chrompack (The Netherlands) and Meyeau Boiveau (France). Prior to use, all the analytical solutes were prepared by dissolving each standard in chloroform solvent and stored into amber glass vials at 4 °C.

Liquid Crystals Synthesis

In the first step (Fig. 1), esterification occurred between one equivalent of *p*-pentylcyclohexyl chloride acid with one equivalent of *p*-nitrophenol in a mixture of pyridine/$CHCl_3$ as solvent. Afterwards, a selective reduction of the nitro group on the crude ester was obtained by means of $NaBH_4/NiCl_2$ reducing system [24]. Instead of the amine group, the solid aniline hydrochloride was used to perform the diazotization reaction. Then, coupling was carried out in PEG 200 as solvent by reacting the benzyloxyphenol with the diazonium compound. The diazotization occurs principally at the para position. The crude yield was chromatographed on silica gel (70–230 mesh) using a mixture of CH_2Cl_2/ethyl acetate (80/20) as a mobile phase, and the pure compound was collected as the ultimate fraction. In the last step, the remaining hydroxyl group was esterified with *p*-pentylcyclohexyl chloride acid in a mixture of $CHCl_3$/pyridine. Thus, it is followed by purification step on silica gel (70–230 mesh) with $CHCl_3$ as eluent; the first fraction was collected. The final product was recrystallized several times in a mixture of toluene/ethanol/4-methyl-pentan-2-one (10/80/10) until constant transition temperatures were obtained.

Apparatus

A TGA 4000 thermogravimetric analyzer from PerkinElmer equipped with a compact ceramic furnace was employed for the analysis of each substance. The heating run was conducted at a linear rate of 10 °C min^{-1} from 30 to 570 °C under condition of dynamic nitrogen gas.

Transition temperature measurements of the mesogenic compounds were carried out by means of Differential Scanning Calorimetry (DSC), Diamond PerkinElmer Technology. Transition points were determined during a heating run at a rate of 10 °C min^{-1} from 40 °C up to 200 °C.

Recognition of the different phase states of LCC_1, LCC_3 and LCC_4 was achieved by means of a Polarizing Microscope, Olympus, fitted with a heated turntable during a heating run of 10 °C min^{-1}.

The gas chromatograph utilized for this work was a Clarus®500 from PerkinElmer designed with an automated pressure control (PPC) and equipped with a split/splitless injector and a flame ionization detector (FID). Raw data were acquired using a TotalChrome software. High-purity nitrogen 99.995 % was used as a carrier gas. Fused-silica columns of intermediate polarity 30 m × 0.32 mm were provided by Supelco (Bellafonte, PA, USA). The treatment and the deactivation process of the inner surface by methylphenyl silylating reagent were performed by the manufacturer.

Column Preparation and IGC Setup

Prior to the dynamic coating, the treated fused-silica capillary columns were washed with dichloromethane, methanol and dichloromethane again (~10 mL each), respectively, and then dried with nitrogen flow for about 6 h. The solution of coating contained 10 % of the liquid crystal in dichloromethane solvent (3 mL). A plug of this solution was pushed through the column by means of nitrogen flow by keeping its linear velocity at 1–2 cm s^{-1}. After the exit of the coating solution from the column, a purge step was followed by nitrogen gas (40 psi) for 8 h to evaporate the remaining solvent into the column. Subsequently, the column was conditioned into the gas chromatograph oven under nitrogen flow, the oven temperature was set from 60 °C up to the second transition temperature related to the nematic–isotropic liquid transition for each liquid crystal stationary phase and kept overnight constant at this final temperature. The thickness (d_f, μm) of the stationary phases of the coated capillary columns was 1.1, 0.9 and 1.0 for LCC_1, LCC_3 and LCC_4, respectively.

To conduct the IGC study, the GC apparatus was set as follows: split ratio mode at 60:1, injector chamber at 250 °C, FID temperature at 280 °C and carrier gas flow rate at 1 mL min^{-1}. Different standard mixtures were prepared in chloroform, the first one included propylbenzene, 1,3,5-trimethylbenzene, *n*-butylbenzene, and 1,2,4,5-tetramethylbenzene as solute probes and was injected isothermally between 60 and 140 °C for plotting ln *k* vs. 1/*T*. For the selectivity study, four other test mixtures of couple of isomers were prepared individually: α/β pinene, *n*-propylbenzene/1,3,5-trimethylbenzene, nerol/geraniol and *cis*/*trans*-decaline. The reactions were carried out separately at the isotherm conditions of 80, 100, 120 and 140 °C, respectively, with the three columns. Manual injections of 0.2 μL of diluted solutions were carried out by a Hamilton syringe 5 μL. The gas hold-up time was obtained from the injection of the methane gas.

Results and Discussion

Liquid Crystals Structures

The cores of the three mesogenic compounds are similar (Fig. 1); however, the main difference between them stems

Table 1 Chemical shifts obtained by ^{1}H NMR of the liquid crystal LCC_4

H position	δ (ppm)	H position	δ (ppm)
1	1.33	16 ax	1.95
2 ax	0.9	16 eq	2.2
2 eq	1.75	17 ax	0.9
3 ax	1.95	17 eq	1.75
3 eq	2.2	18	1.33
4	2.5	19	1.30
5	1.30	20	1.35
6	1.35	21	1.35
7	1.35	22	1.39
8	1.39	23	1.1
9	1.1	24	5.3
10	7.30	25	7.30
11	7.95	26	7.35
12	7.85	27	1.85
13	6.90	28	1.35
14	6.85	29	1.39
15	2.4	30	1.6

from the number of carbons on the lateral substituent. The elucidation of the molecular structure was performed with ^{1}H NMR and ^{13}C NMR; the liquid crystal shifts (ppm) are given in Table 1.

Thermal Stability of the Three Liquid Crystal Compounds

As it can be seen from Fig. 2, the resulting weight-change versus temperature plot exhibited different decomposition temperatures. LCC_1, LCC_3 and LCC_4 compounds begun to manifest mass losses at 212, 233 and 264 °C, respectively. It was clear to notice that thermal stability differences of

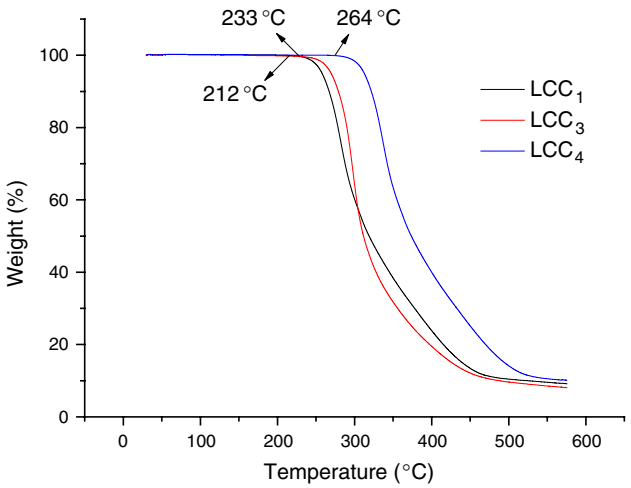

Fig. 2 Thermogravimetric curves of LCC_1, LCC_3 and LCC_4

the three synthesized mesogenic compounds were mainly affected by the length of the lateral chain substituted to the main core. The liquid crystal with the longest one (LCC_4) exhibited better stability conversely to LCC_1 which revealed the least stability feature as a function of temperature.

Thermal Characteristics of the Mesogenic Compounds

The transition temperatures related to the three liquid crystals were investigated by different approaches. The transitions obtained by DSC are listed in Fig. 3. The transition points observed by thermomicroscopy are given in Table 2. Inverse Gas Chromatography (IGC) which is recognized as a reliable source of physicochemical data for various substances [25, 26] was used to determine the phase transitions of these materials. By choosing the suitable analytes and injecting them at different isothermal temperatures, many parameters can be obtained by applying the following Van't Hoff equation:

$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \varphi \quad (1)$$

where k is the retention factor, ΔH and ΔS are the enthalpy and entropy of transfer, R is the ideal gas constant, T is

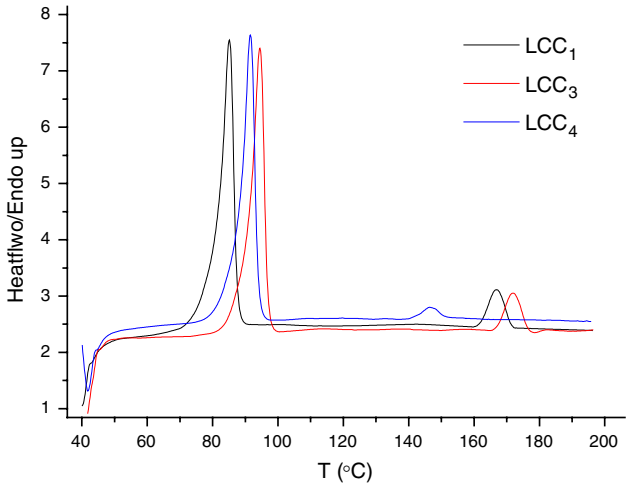

Fig. 3 DSC thermograms for LCC_1, LCC_3 and LCC_4

Table 2 Transition temperatures obtained from the various approaches

	Solide → nematic			Nematic → liquid	
	IGC	DSC	Microscopy	DSC	Microscopy
LCC_1	80	85.1	84.4	166.1	165.8
LCC_3	94	94.4	91.5	171.9	172.1
LCC_4	89	91.5	92.4	146.4	145.2

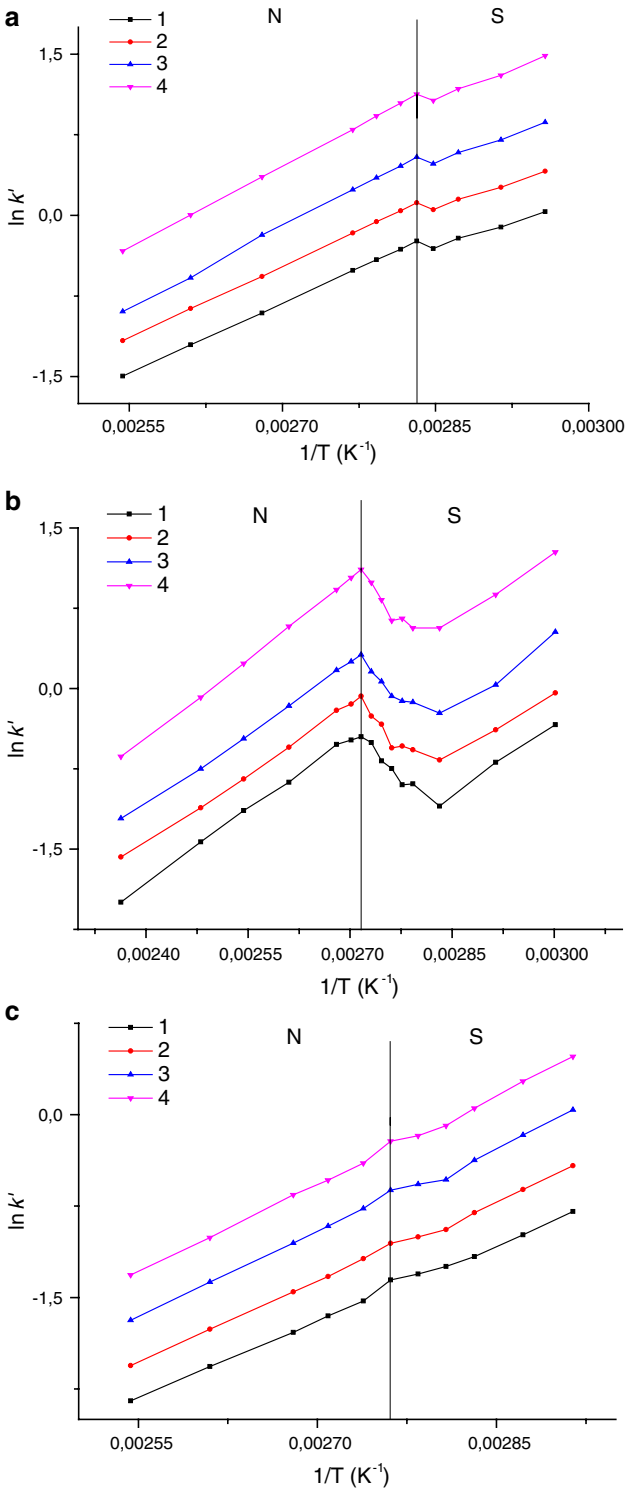

Fig. 4 Van't Hoff Plots (ln *k*vs. $1/T$) related to LCC_1 (**a**), LCC_3 (**b**) and LCC_4 (**c**). *1* propylbenzene, *2* 1,3,5-trimethylbenzene, *3* *n*-butylbenzene, *4* 1,2,4,5-tetramethylbenzene

the absolute temperature and φ represents the phase ratio (that is the volume of the stationary phase, V_s, divided by the volume of the mobile phase, V_m). ΔH and ΔS parameters depend on the physical state of the mesogenic stationary phase [27], by shifting to a different state, e.g., solid to nematic, a variation in retention mechanism occurs which results in discontinuities on the curve. These breaks represent the melting and clearing points, respectively. Figure 4a–c exhibits the resulting Van't Hoff plots ($\ln k$ vs. $1/T$) related to the three stationary phases. The transition points obtained by the different approaches are summarized in Table 2. From these results, some observations can be drawn:

1. The transition points observed by IGC are close to the measurements obtained by either DSC or thermomicroscopy;
2. Polarizing optical microscope reveals that nematic mesophase is present for each liquid crystal at a definite temperature range;
3. The differences in nematic range observed by DSC (81.3, 77.5 and 54.9 °C corresponding to LCC_1, LCC_3 and LCC_4, respectively) appear to depend on the lateral substituent. The liquid crystal with the longest lateral group (LCC_4) owns the narrowest nematic range;
4. A marked increase in the retention time of solutes probes was observed around the solid-nematic transition for LCC_1 and LCC_3 (Fig. 4a, b). The maximum retention time noticed around this transition is assumed to correspond to the melting point. However, with LCC_4 stationary phase, the melting point was less pronounced (Fig. 4c). For the second transition, i.e., nematic to liquid isotropic state, the breaks were not obviously noticed with the three substances.

Comparison of the Liquid Crystal Stationary Phases

From the Van't Hoff equation (Eq. 1), the enthalpy of interaction of the analyte-stationary phase system can be evaluated to compare between the three liquid crystal stationary phases. However, a previous study [26] demonstrates the variation of the phase ratio parameter between columns whose deviation influences on the thermodynamic measurements. This parameter dependence can be removed to compare directly between columns by considering the ratio of retention factor of each solute instead of the solutes themselves [28, 29]. The resulting selectivity Van't Hoff plots (α vs. $\frac{1}{T}$) were rather employed to compare between the three columns.

Figure 5 displays the selectivity revealed from each liquid crystal stationary phase towards some couples of isomers: α-pinene/β-pinene, 1,3,5-trimethylpropylbenzene/*n*-propylbenzene, nerol/geraniol and *cis*-decaline/*trans*-decaline. The pairs of isomers were chosen to assess the shape selectivity of the mesogenic stationary phases over the nematic range as they were injected at different isothermal

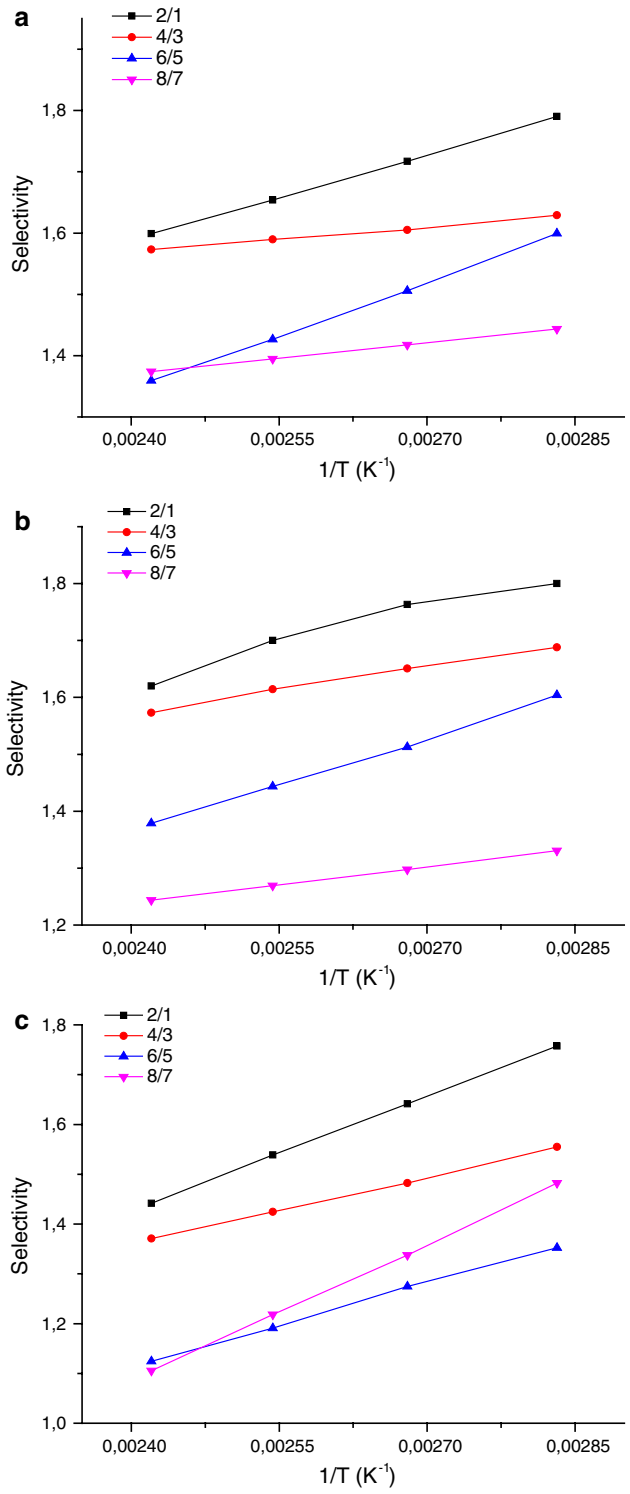

Fig. 5 Selectivity plots of LCC_1 (**a**), LCC_3 (**b**) and LCC_4 (**c**). *1* α-pinene, *2* β-pinene, *3* *n*-propylbenzene, *4* 1,3,5-trimethylbenzene, *5* nerol, *6* geraniol, *7* *cis*-decaline, *8* *trans*-decaline

temperatures (80, 100, 120 and 140 °C). The first two pairs are regarded as positional isomers whereas the second two couples are considered as geometric isomers. With the three columns, higher selectivity was noticed over the melting point and a subsequent decrease of this factor was noticed by increasing the oven temperature. Indeed Witkiewicz et al. [10] mentioned the case of the nematic stationary phases where the best separations are obtained slightly above the melting point and below it. In overall, LCC_1 and LCC_3 appeared to show better selectivity towards these analytes over the nematic range (Fig. 5a, b). On the other hand, LCC_4 stationary phase revealed the least selectivity towards the pairs of isomers as a marked decline of its curves was noticed (Fig. 5c) by approaching the clearing point (140 °C).

Chromatographic Behavior of LCC_1, LCC_3 and LCC_4 Stationary Phases

Column Efficiency

The efficiency of the stationary phases was assessed by injecting isothermally n-undecane solute at 120 °C (nematic state) with each column. The obtained results were as follows: 3,025, 2,955 and 2,660 plates/m corresponding to LCC_3, LCC_4 and LCC_1, respectively.

Analytical Performances

Analytes of different polarities belonging to different families were tested. The interesting analytical abilities of the mesogenic compounds are discussed below. The relative retention times as well as the column temperature conditions for each chromatographed family are listed in Table 3. The solid, nematic and liquid isotropic states were involved and displayed good separations with the different chromatographed compounds; however, the nematic state was mostly involved as it offered better efficiencies. This liquid crystal behavior is well known due to the elevated molecular arrangement that characterizes the liquid crystal stationary phase. With conventional stationary phases, the separation processes are mainly achieved thanks to the difference in volatility or polarity between the chromatographed analytes; whereas with mesogenic stationary phases, shape difference is the chief factor that influences the separation mechanism. In this table, the peaks are characterized by the relative retention time *r* obtained via the Eq. (2):

$$r = (t_{ri} - t_m)/(t_{ref} - t_m) \quad (2)$$

where t_m, t_{ri} and t_{ref} are, respectively, the gas hold-up time, the retention time of the analyte of interest and the retention time of the reference analyte, i.e., the compound that is eluted near the center of the complex mixture of the related chromatographed substances. Thus, every *r* that equals unity corresponds to the chosen reference peak.

Table 3 Relative retention times of the various test mixtures chromatographed with the three liquid crystal stationary phases

Analyte	LCC_1		LCC_3		LCC_4	
	State	r	State	r	State	r
n-Alkanes	90 °C (3 min) then $R = 5$ °C min^{-1}		100 °C (3 min) then $R = 7$ °C min^{-1}		100 °C $R = 7$ °C min^{-1}	
n-Nonane	N	0.11	N	0.11	N	0.17
n-Decane	N	0.26	N	0.24	N	0.32
n-Undecane	N	0.55	N	0.50	N	0.58
n-Dodecane	N	1	N	1	N	1
n-Tridecane	N	1.57	N	1.78	N	1.61
n-Tetradecane	N	2.21	I	2.82	I	2.45
n-Pentadecane	I	2.85	I	3.95	I	3.38
n-Hexadecane	I	3.45	I	5.10	I	4.44
n-Heptadecane	I	4.18	I	6.43	I	5.53
Analyte	LCC_1		LCC_3		LCC_4	
	State	r	State	r	State	r
2-Ketones	100 °C (3 min) then $R = 7$ °C min^{-1}		100 °C $R = 7$ °C min^{-1}		110 °C $R = 5$ °C min^{-1}	
2-Heptanone	N	0.26	N	0.21	N	0.25
2-Octanone	N	0.54	N	0.51	N	0.51
2-Nonanone	N	1	N	1	N	1
2-Decanone	N	1.61	N	1.71	N	1.83
2-Undecanone	I	2.29	N	2.69	N	3.15
2-Dodecanone	I	3.01	N	3.86	N	5.03
Analyte	LCC_1		LCC_3		LCC_4	
	State	r	State	r	State	r
Volatile aroma compounds	100 °C (10 min) then $R = 5$ °C min^{-1}		80 °C $R = 5$ °C min^{-1}		90 °C (6 min) then $R = 3$ °C min^{-1}	
α–Pinene	N	0.10	S	0.11	N	0.10
β–Pinene	N	0.15	S	0.17	N	0.17
(−)-Limonene	N	0.22	S	0.29	N	0.28
Eucalyptol	N	0.28	S	0.33	N	0.31
(+)-Fenchone	N	0.59	S	0.65	N	0.59
(−)-Linalool	N	0.59	S	0.73	N	0.67
Camphore	N	1	N	1	N	1
Linalyl acetate	N	1.09	N	1.18	N	1.26
Borneol	N	1.19	N	1.18	N	1.41
Menthol	N	1.32	N	1.29	N	1.40
α-Terpineol	N	1.59	N	1.44	N	1.75
β-Citreonellol	N	1.73	N	1.63	N	1.88
Nerol	N	1.82	N	1.63	N	1.88
Geraniol	N	2.14	N	1.82	N	2.25
Anethol	N	2.65	N	2.00	N	2.62
Carvone	N	2.81	N	2.09	N	2.88
Thymol	N	3.01	N	2.25	N	3.30
Carvacrol	N	3.24	N	2.50	N	3.57
Eugenol	N	3.46	N	2.56	N	3.57
cis-Jasmone	I	4.03	N	2.89	N	3.95
cis-Isoeugenol	I	4.03	N	2.95	N	3.95
trans-Isoeugenol	I	4.83	N	3.38	N	4.43

Table 3 continued

Analyte	LCC_1		LCC_3		LCC_4	
	State	r	State	r	State	r
Phenols	120 °C $R = 3$ °C min^{-1}		100 °C $R = 3$ °C min^{-1}		110 °C (5 min) then $R = 3$ °C min^{-1}	
Phenol	N	0.53	N	0.55	N	0.43
o-Cresol	N	0.71	N	0.72	N	0.64
m-Cresol	N	0.80	N	0.79	N	0.77
p-Cresol	N	0.80	N	0.79	N	0.77
2,6-Dimethylphenol	N	0.90	N	0.89	N	0.82
2-Ethylphenol	N	1	N	1	N	1
2,5-Dimethylephenol	N	1.16	N	1.14	N	1.18
2,3-Dimethylephenol	N	1.28	N	1.24	N	1.39
2,4,6-Trimethylephenol	N	1.28	N	1.28	N	1.39
3,5-Dimethylephenol	N	1.39	N	1.34	N	1.68
3,4-Dimethylephenol	N	1.57	N	1.49	N	1.94
2,3,5-Trimethylephenol	I	1.93	N	1.81	N	2.26
2,4,5-Trimethylephenol	I	1.93	N	1.81	N	2.26
Analyte	LCC_1		LCC_3		LCC_4	
	State	r	State	r	State	r
Halogenophenols	140 °C $R = 3$ °C min^{-1}		120 °C $R = 5$ °C min^{-1}		130 °C $R = 5$ °C min^{-1}	
2-Chlorophenol	N	0.30	N	0.28	N	0.28
2-Bromophenol	N	0.50	N	0.48	I	0.47
2,6-Dichlorophenol	I	1.01	N	0.91	I	0.94
2,4-Dichlorophenol	I	1	N	1	I	1
3-Chlorophenol	I	1.49	N	1.53	I	1.39
4-Chlorophenol	I	1.49	N	1.53	I	1.39
3-Bromophenol	I	2.19	I	2.17	I	2.21
4-Bromophenol	I	2.19	I	2.17	I	2.21
2,6-Dibromophenol	–	–	–	–	I	2.35
3,5-Dichlorophenol	–	–	–	–	I	3.54
3,4-Dichlorophenol	–	–	–	–	I	3.85

S solid, *N* nematic, *I* isotropic, *R* rate of the programmed-temperature (°C min^{-1})

With non-polar compounds of n-alkanes as well as with polar 2-ketones (Fig. 6), both homologous series were completely resolved with the three stationary phases (Table 3).

Very interesting features were observed with the three columns for the chromatography of the constituent of essential oils (Table 3). With respect to the shape selectivity and polarity, better separations were obtained with LCC_1 and LCC_3, whereas a decline in separation quality was observed with the third stationary phase (LCC_4). α-pinene/β-pinene, fenchone/camphore and eugenol/isoeugenol positional isomers were separated with the three stationary phases. On LCC_1, good separations were obtained for the close-boiling molecules such as β-citronellol (bp = 224 °C)/nerol (bp = 225 °C) and linalyl acetate (bp = 220 °C)/borneol (bp = 214 °C), respectively; whereas on LCC_3 better resolutions were displayed for higher boiling solutes as observed with *cis*-jasmon/*cis*-isoeugenol. With PEG (classical phase), it is found that anethol is eluted before thymol and Carvacrol [30]; similar results were reported with the three columns. Carvacrol and thymol own a polar oxygen atom on their aromatic ring which is strongly retained by the stationary phase than the double bond and aromatic ring pertaining to the anethol, and this is particular to the intermediate polarity and polar stationary phases [31]. The difficult pair of limonene/eucalyptol (eucalyptus oil) which is resolved on the classical polar phase (Carbowax 20M) is unresolved on the apolar classical phase (SE30); only partial separation was achieved on LCC_3. Linalool/linalyl acetate (fingerprints of lavender oil) is discriminated on apolar phase (SE30) and partially separated on polar phase

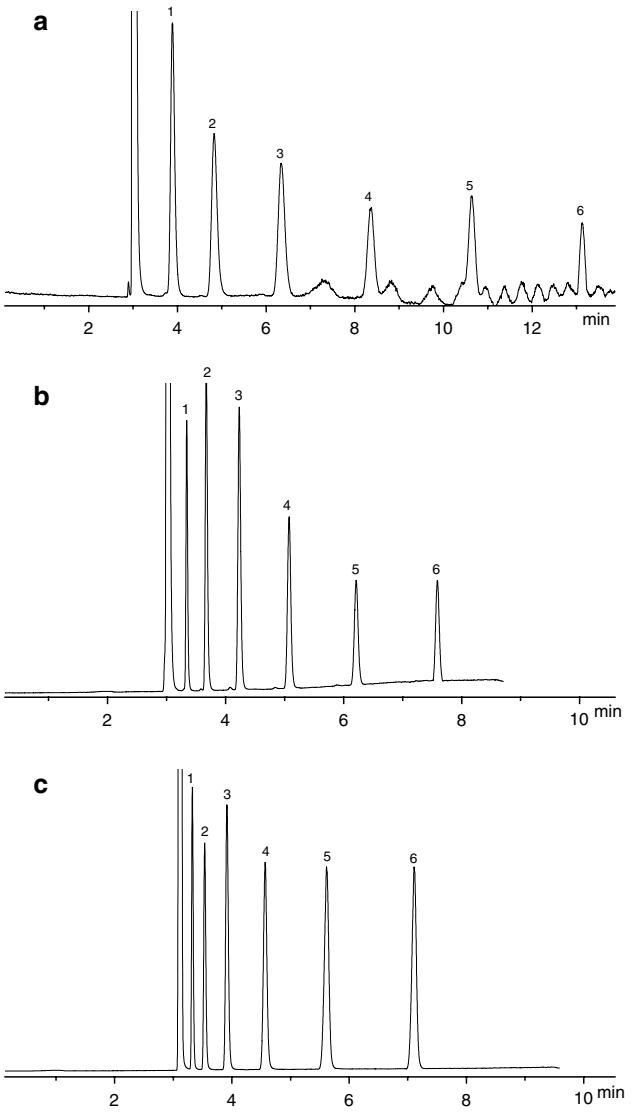

Fig. 6 Separation of 2-ketone compounds on LCC1 (**a**), LCC_3 (**b**) and LCC_4 (**c**). *1* 2-heptanone, *2* 2-octanone, *3* 2-nonanone, *4* 2-decanone, *5* 2-undecanone, *6* 2-dodecanone

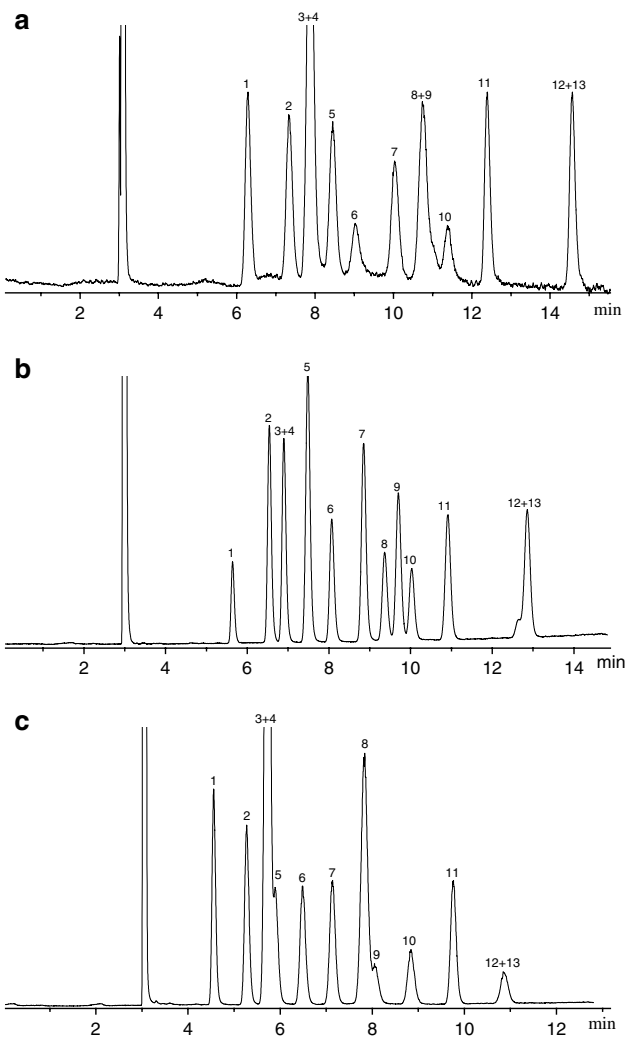

Fig. 7 Separation of phenol derivatives on LCC_1 (**a**), LCC_3 (**b**) and LCC_4 (**c**). *1* phenol, *2* *o*-cresol, *3* *m*-cresol, *4* *p*-cresol, *5* 2,6-dimethylphenol, *6* 2-ethylphenol, *7* 2,5-dimethylphenol, *8* 2,3-dimethylphenol, *9* 2,4,6-trimethylphenol, *10* 3,5-dimethylphenol, *11* 3,4-dimethylphenol, *12* 2,3,5-trimethylphenol, *13* 2,4,5-trimethylphenol

(Carbowax 20M), they were well separated with LCC_1, LCC_3 and LCC_4 stationary phases.

Figure 7 shows the chromatograms related to the phenol derivatives with the three columns. It appeared that best separations were perceived with LCC_3 stationary phase. *m*-cresol and *p*-cresol were not distinguished with the three stationary phases. The positional isomers of 2,6/2,5/2,3/3,5 and 3/4-dimethylphenols were eluted in this order on the nematic state with the three stationary phases. 2,6-Dimethylphenol (203 °C) was first eluted: the hydroxyl functional group is sterically hindered for the intermolecular interactions due to the presence of methyl groups in its neighborhood (2–6 positions). The same outcome was noticed with the trimethylphenols (2,4,6 phenol was eluted before the pair of 2,3,5/2,4,5 phenols). The positional isomers of 2,3,5/2,4,5 phenols were coeluted with each liquid crystalline stationary phase.

Halogenophenols which are classified as highly toxic organic compounds are well known to cause serious health risk for the living organism [32]. A series of this family was tested with the three columns (Table 3). 2,6-Dichlorophenol/2,4-dichlorophenol were coeluted with LCC_1 (isotropic) and partially resolved on LCC_4 (isotropic); whereas on LCC_3, they were well discriminated on the nematic state: the parallel ordering of the nematic state retained the more elongated solute and this enabled their separation. The isomer pairs of *m*-chlorophenol/*p*-chlorophenol and *m*-bromophenol/*p*-bromophenol were not separated with the three columns. LCC_4 revealed better baseline

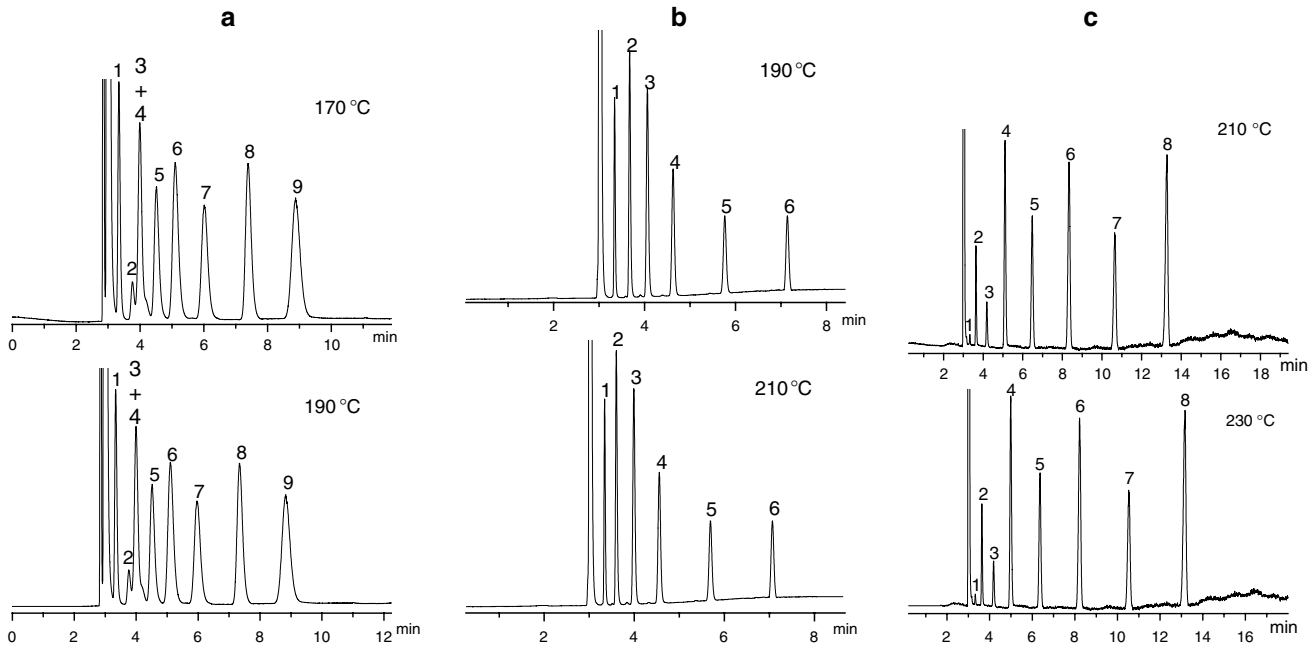

Fig. 8 Chromatographic performance of LCC_1 (**a**), LCC_3 (**b**) and LCC_4 (**c**) after conditioning step. **a** *1* toluene, *2* ethylbenzene *3* *m*-xylene*4* *p*-xylene, *5* *o*-xylene, *6* *n*-propylbenzene, *7* 1,3,5-trimethyl benzene, *8* 1,2,4-trimethylbenzene, *9* *n*-butylbenzene. **b** *1* 2-heptanone, *2* 2-octanone, *3* 2-nonanone, *4* 2-decanone, *5* 2-undecanone, *6* 2-dodecanone. **c** *1* *n*-nonane, *2* *n*-decane, *3* *n*-undecane, *4* *n*-dodecane, *5* *n*-tridecane, *6* *n*-tetradecane, *7* *n*-pentadecane, *8* *n*-hexadecane. GC conditions: LCC_1 (**a**) 90 °C (5 min) $R = 5$ °C min^{-1}, LCC_3 (**b**) 100 °C $R = 7$ °C min^{-1} and LCC_4 (**c**) 100 °C $R = 10$ °C min^{-1}

stability, thus other solutes with higher boiling points were allowed to be injected. 2,6-Dibromophenol, 3,5-dichlorophenol and 3,4-dichlorophenol were eluted and resolved in this order.

Thermal Stability of the Three LCSPs into the Capillary Column

For this part, thermal stability of the liquid crystal columns was evaluated according to the recommended approach of Lizhen et al. [33]. Each column was conditioned twice at 170 and 190 °C (LCC_1), 190 and 210 °C (LCC_3) and 210 and 230 °C (LCC_4), respectively, for at least 4 h. Subsequently, a test mixture of homologous series was injected to evaluate the separation ability and the baseline behavior of each LCSP. The obtained chromatograms (Fig. 8a–c) exhibited the separations after every conditioning step. From Fig. 8a, it can be seen that the separation ability was well preserved either after the first or the second conditioning step (170 and 190 °C). With LCC3 (Fig. 8b), similar results were obtained, the retention times of the corresponding peaks (2-*n*-ketones) remained almost unaltered; however, a small lift of the baseline was noticed at the end of the run. With LCC_4, even though separation and resolution properties were well exhibited with the homologous series of *n*-alkanes after conditioning it up to 230 °C, the lift of the baseline was relatively well pronounced, which may be due to this last elevated conditioning temperature and GC conditions. Here again, it can be emphasized how the longest lateral alkyl chain helped to improving the thermal strength of the liquid crystal by enhancing the temperature of its chromatographic condition runs. In overall, it can be stated that the three LCSPs presented very interesting thermal stability as their separating behavior and resolution ability remained well sustained after being conditioned at higher temperatures for several hours.

Conclusion

The results obtained with the three liquid crystals demonstrated the significant influence of the lateral substituent on the thermal and analytical properties of the mesogenic material. The LCC_4 liquid crystal with the longest lateral group owns the narrowest nematic range whereas relatively wider nematic ranges were exhibited in LCC_1 and LCC_3. The three liquid crystalline stationary phases exhibited interesting chromatographic abilities towards various substances, especially with the *cis* and *trans* isomers, *n*-alkanes and *n*-ketones; however, relatively lower selectivity was shown from LCC_4 with regard to essential oil constituents and phenols conversely to LCC_1 and LCC_3. The lengthening of the lateral chain by increasing the methylene groups seemed to decrease the polarity of this liquid crystalline

stationary phase. On the other hand, this lengthening made LCC_4 compound thermally more stable with respect to LCC_1 and LCC_3.

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