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Review

Liquid-crystalline stationary phases for gas chromatography

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Abstract

Physico-chemical properties of new liquid-crystalline stationary phases (LCSPs) for gas chromatography are reviewed. The mechanism of chromatographic separation on liquid-crystalline stationary phases is discussed and examples of analyses of complex mixtures of organic compounds using capillary and packed columns are given.

Keywords: Gas chromatography; Stationary phases; Liquid crystals; Chromatographic columns

Contents

1. Introduction

A search for better stationary phases, including highly selective ones, is an important trend of chromatography development. Among the stationary phases under investigation are liquid-crystalline stationary phases (LCSPs) which have been known for 40 years. In the years, when previous reviews were published, liquid crystals (LCs) were studied as stationary phases mostly for gas chromatography [1–4].

Recently, more and more studies on the use of liquid crystals in liquid chromatography have come out. Their properties have already been described in reviews [5,6]. The liquid-crystalline structure in the conditions prevailing in a column for high-performance liquid chromatography is not so clearly preserved as in a column for gas chromatography. However, in both cases, the separation of components of mixtures occurs on the basis of the different interaction between liquid-crystalline stationary phases and molecules of different geometric shape. In some cases, very small differences in the shapes of molecules of compounds being separated suffice to obtain their good separation. At the same time, the separation of components of mixtures difficult to separate on conventional stationary phases whose separation ability is associated with polarity or non-polarity of interacting molecules of chromatographed substances and stationary phases is obtained.

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Liquid-crystalline stationary phases are not widely used in analytical practice, but their physico-chemical properties are still being studied and examples of obtaining good separations of components of different mixtures are given. Monomeric liquid crystals, used in packed columns, were first used as liquid-crystalline stationary phases in gas chromatography, but for a few years polymeric liquid crystals placed in capillary columns have been more and more popular.

Considering the studies which have been published since our previous review [2], the present survey describes the use of liquid crystals as stationary phases in gas chromatography.

2. Trends in the synthesis of new liquid-crystalline stationary phases

In the first period of investigations on LCSPs monomeric liquid crystals of relatively small molecular weight and of relatively narrow mesophase ranges were dealt with. Despite their good separation properties, the stationary phases were not widely used in laboratory practice. One of the reasons for it was the considerable volatility of LSCPs making their stability unsatisfactory. With the wider use of capillary columns, the high stability of LSCPs was required within the wide range of temperatures where the mesophase should occur. As a result, LSCPs of high stability and wide mesophase ranges have been searched for. Among such LSCPs are, first of all, monomeric liquid crystals of large molecular weight and liquid-crystalline polymers [7]. They can both contain complex compounds with metals [8,9].

Monomeric liquid crystals containing transition metals in organic complexes were described by Hudson and Maitlis [9]. The synthesis of polymeric liquid crystals where complexes zinc(II) and nickel(II) with 4-(dec-9′-en-1′-oxy)dithio-benzoate [8] were bound to the polysiloxane chain. The formula of such a liquid crystal is given in Fig. 1.

Very often polymers with liquid-crystalline properties have a polysiloxane backbone. Among the polymeric liquid crystals are the ones in which molecules possessing alkoxyl groups [7] (Fig. 2) and crown ethers [10,11] (Fig. 3) are bound to the polysiloxane chain.

The liquid-crystalline stationary phase whose molecule contains both crown ether and a cholesterol fragment [12] (Fig. 4) was also obtained.

Liquid crystals with a polyglutamine skeleton are noteworthy among polymers with no polysiloxane skeleton. Decyl- and *n*-hexadecyl groups (Figs. 5 and 6) [13] are connected with this skeleton.

The liquid crystals are chiral cholesterics of the mesophase range equal to 150 °C [13]. Among monomeric liquid crystals, azo- and azoxy-compounds [14–17] and their derivatives [7,17] are still synthesized. Their complexes with metals such as copper (Fig. 7) were also described [15].

Despite the general tendency to obtain monomers of large molecular weights, liquid crystals of relatively small molec-

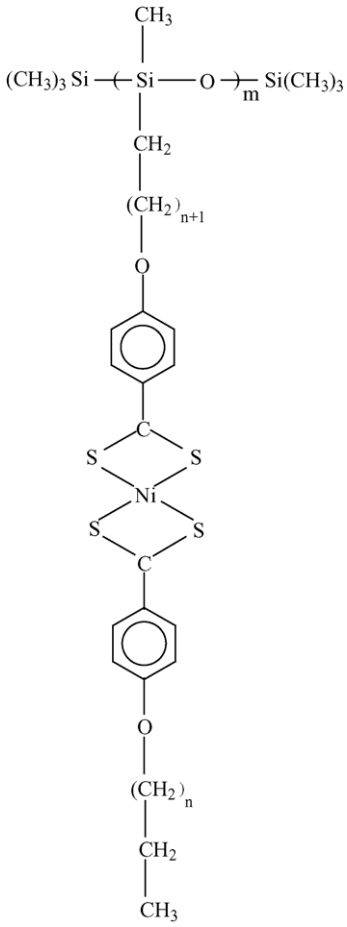


Fig. 1. Nickel(II) complex with 4-(dec-9′-en-1′-oxy) dithio-benzoate bound to the polysiloxane chain [8].

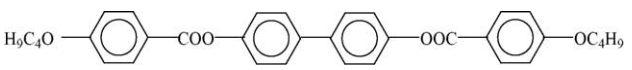


Fig. 2. Monomeric liquid crystal: 4,4′-biphenylene-bis (4-*n*-butyloxybenzoate) [7].

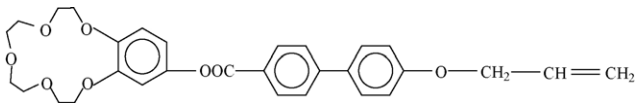


Fig. 3. Monomeric liquid crystal: 4-(allyloxy)-4′-(4′-carboxybenzo-15-crown-5)-biphenyl [10].

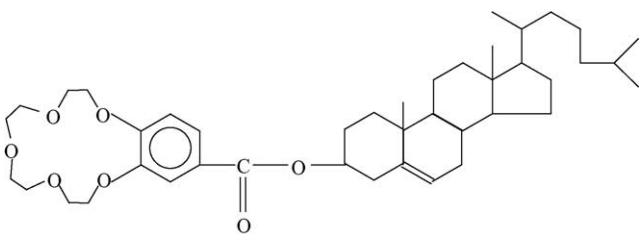


Fig. 4. Monomeric cholesteric liquid crystal: 4′-cholesteroxycarbonyl-benzo-15-crown-5 [12].

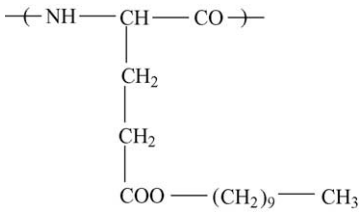


Fig. 5. Polymeric liquid crystal: poly (γ-*n*-decyl-L-glutamate) [13].

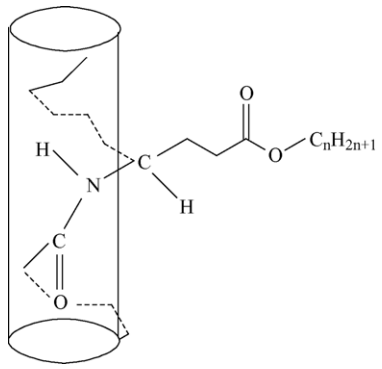


Fig. 6. Polymeric liquid crystal: poly (γ-*n*-hexadecyl-L-glutamate), where $n = 16$ [13].

ular weights and of high melting temperatures, e.g. those shown in Fig. 8 [18], are also synthesized.

Among azoderivatives, compounds of characteristic branched shape are noteworthy (Figs. 9–11) [19].

In the works [14,20–25], the obtaining of liquid-crystalline stationary phases marked LC_1 and LC_2 and their properties useful in the chromatographic separation of composite mixtures of aromatic compounds were described. The structural formulas of the LCSPs are shown in Figs. 12 and 13.

Commercial liquid crystals are available as stationary phases more and more frequently, e.g. bis(methoxybenzylidineanil-chloroaniline) $(MBCA)_2$ [18,26,27] and mesogenic polymeric methyl siloxane (MPMS) [26].

3. Physico-chemical studies of liquid-crystalline stationary phases

The ordering of the liquid crystal structure is known to be of decisive importance in the separation of components of mixtures by distinguishing the shape of their molecules. However, investigations on the effect of other

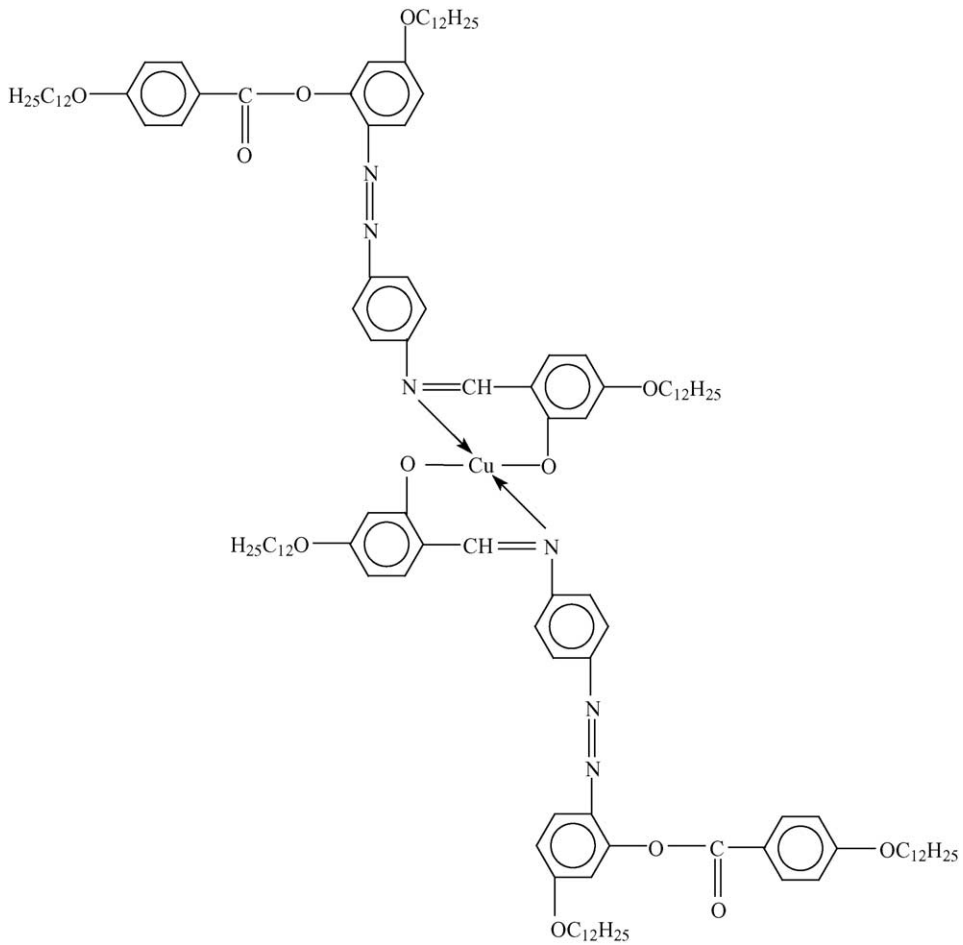
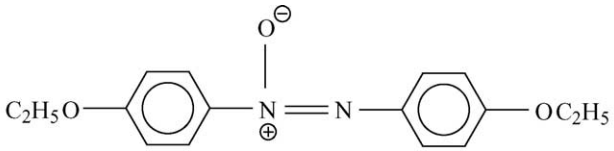
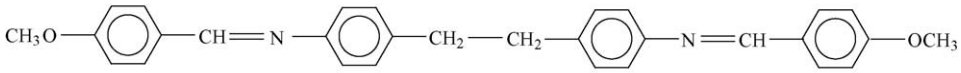


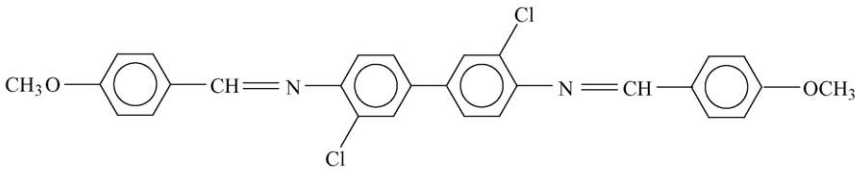
Fig. 7. Liquid-crystalline copper(II) complex: bis [*N*-4-(2′-(4″-dodecyloxybenzoyloxy)-4′-dodecyloxy) azobenzenyl-4-dodecyloxysalicylidene]iminato of copper(II) [15].



ADP (m.p.=138 °C)



$(MBT)_2$ (m.p.=181 °C)



$(MBCA)_2$ (m.p.=154 °C)

Fig. 8. Monomeric liquid crystals: ADP = azoxy-diphenetole, $(MBT)_2$ = bismethoxy-benzilidinebitoluidine, $(MBCA)_2$ = bis-(methoxy-benzylidineanil-chloroaniline) [18].

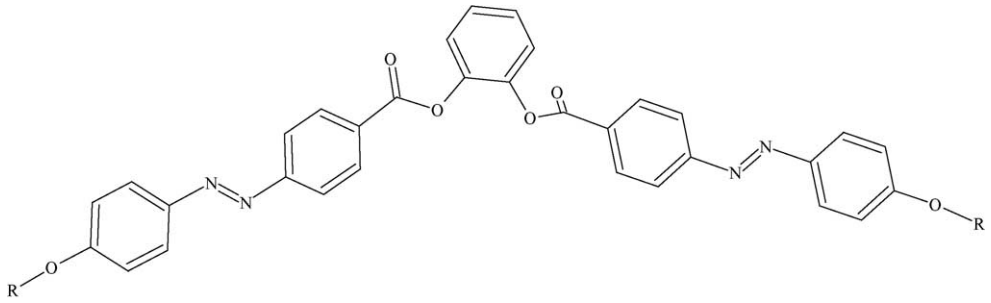


Fig. 9. Liquid-crystalline azo-compound: 1,2-phenylene bis [4-(4-alkyloxyphenylazo)benzoate], where: $R = C_nH_{2n+1}$, $n = 4, 5, \ldots, 10$ [19].

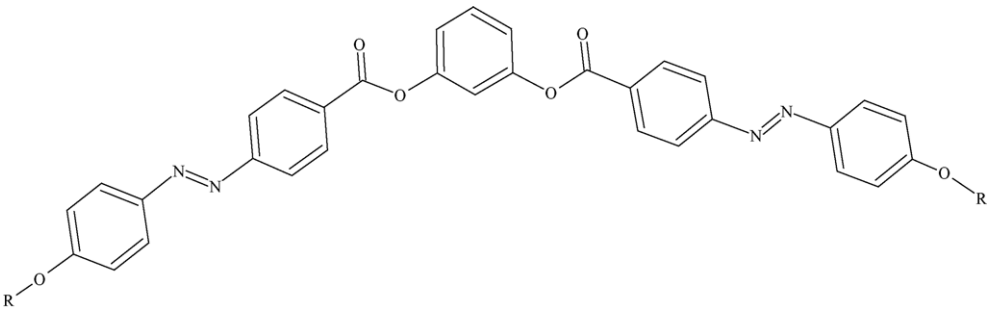


Fig. 10. Liquid-crystalline azo-compound: 1,3-phenylene bis [4-(4-decyloxyphenylazo)benzoate], where: $R = C_{10}H_{21}$ [19].

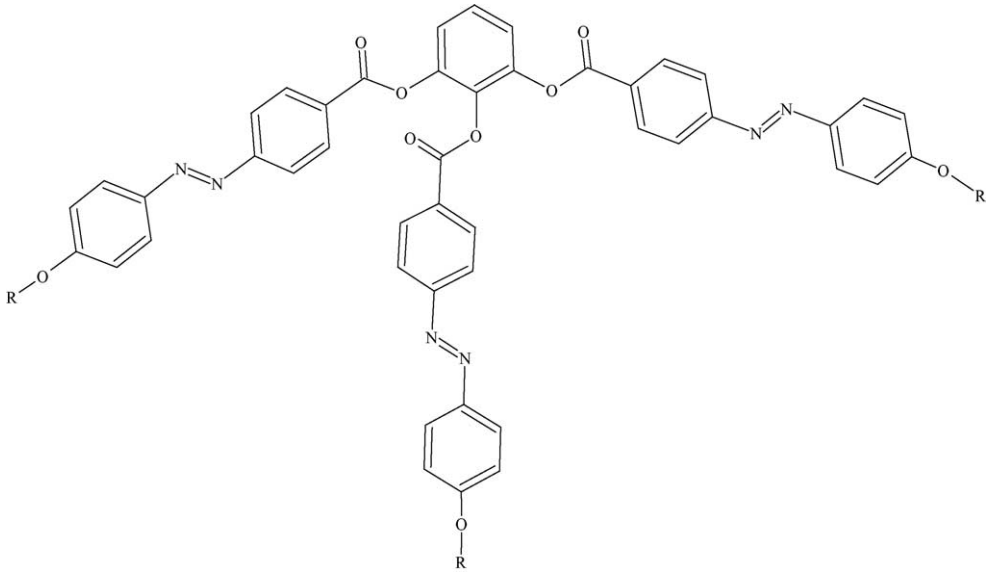


Fig. 11. Liquid-crystalline azo-compound: 1,2,3-phenylene tri [4-(4-decyloxyphenylazo)benzoate], where: $R = C_{10}H_{21}$ [19].

physico-chemical properties of liquid crystals on their behaviour as stationary phases in a chromatographic column are still necessary. The results of such investigations should facilitate a search for liquid crystals of good separation properties and of such physico-chemical properties as to meet the general requirements set for satationary phases best. It is also important to learn more about the relationships between general physico-chemical properies of liquid crystals and their separation ability. Accordingly, the investigation of LCSPs properties by inverse gas chromatography (IGC) is of particular advantage. To rely on the results of such investigations entirely, comparative investigations by IGC and conventional methods of examining liquid crystals, e.g. differential scanning calorimetry (DSC), NMR and FTIR, are also necessary.

The selectivity of liquid crystals in relation to substances of different molecular shape can be determined by the dependence of the selectivity coefficient (α) of test substances on temperature: $\ln \alpha = f(1/T)$. The shape selectivity of 4-octoxyphenyl-4-pentoxylobenzoate was thus examined in relation to polar xylene isomers and non-polar stereoisomers of dimethylcyclohexane and decalin [29,30]. Considering their small polarity, saturated cyclic compounds were found to be better for determining the selectivity of LCSPs connected with the shape of molecules of chromatographed substances than more polar xylene isomers [29]. On the basis of the dependence: $\ln \alpha = -\Delta(\Delta G_{a,b})/(RT)$, it is possible to determine quantitatively differences of partial molar free energies of the substances a and b chromatographed on liquid crystals. Using the equation: $\Delta G = \Delta H - T\Delta S$, from the slope of straight lines $\ln \alpha = f(1/T)$ for each pair of isomers, $\Delta(\Delta H_{a,b}/R)$ was calculated. In the case of chromatographic process on LCSP called 4-octoxyphenyl 4-pentoxybenzoate these values were for *o*- and *p*-xylene = −2.11, for *p*- and *m*-xylene = −2.73, for *cis*- and *trans*-1,2-dimethylcyclohexane = −2.93 and for *cis*- and *trans*-decalin = −3.34, respectively [29].

The retention of isomers of chromatographed substances considerably depends on the type of the mesophase of the liquid-crystalline stationary phase. It results from the fact

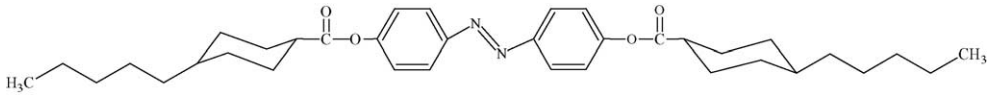


Fig. 12. 4-(4-*trans*-Pentylcyclohexanecarboxyloxy)-2′-methoxy-4′-(4-*trans*-pentylcyclohexanecarboxyloxy)-*trans*-azobenzene [14].

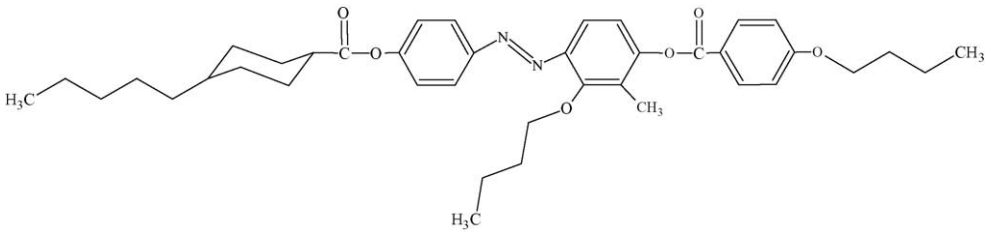


Fig. 13. 4-(4-*trans*-Pentylcyclohexanecarboxyloxy)-2′-butoxy-3′-methyl-(4-butoxybenzoyloxy)-*trans*-azobenzene [14].

Table 1
Activation energies of diffusion of xylene isomers on the liquid-crystalline stationary phase 4,4′-bis(heptyloxy)azoxybenzene [31]

Temperature range (°C)	Phase	Activation energy of diffusion (kJ/mol)		
		o-Xylene	*m*-Xylene	*p*-Xylene
69.0–89.0	Smectic	2.976	2.595	4.299
89.0–116.5	Nematic	6.082	5.626	6.622
>116.5	Isotropic	24.229	21.056	23.421

that the type of mesophase affects the diffusion of isomers of the chromatographed substance to a different degree. Medina [31] studied the influence of the type of mesophase of the liquid-crystalline stationary phase on the diffusion of xylene isomers. 4,4′-bis(Heptyloxy)azoxybenzene (BHOAB) was the stationary phase deposited on glass spheres. The order of elutions of xylene isomers was typical of liquid-crystalline stationary phases—*meta*, *para* and *ortho*. However, the diffusion coefficients in the smectic, nematic and isotropic phases decreased in the order *p*-xylene, *o*-xylene and *m*-xylene. The diffusion coefficient of *p*-xylene regarding *m*- and *o*-xylene was disproportionately larger in the smectic phase than in the other phases. It can be concluded, from the comparison of the values of diffusion coefficients of xylene isomers with their polarity, the length to width ratio and the molar volume that the diffusion coefficient of *para*-isomer larger than *m*- and *o*-isomers is associated with its smaller polarity and the larger molecule length to width ratio than that of the other isomers. Activation energies of diffusion of xylene isomers in individual types of the mesophase BHOAB, calculated on the basis of molecular diffusion coefficients, are shown in Table 1 [31].

The described behaviour of *para*-xylene isomer can account for its larger retention on liquid-crystalline stationary phases than that of the *m*-xylene isomer. The retention on conventional stationary phases is reverse, consistent with their boiling points. A clearly great difference in the activation energy of the diffusion of xylene isomers in smectic and nematic mesophases as well as in isotropic liquid results from the ordered structure of a smectic and a nematic mesophases, and from the disorder of the isotropic liquid.

Molar diffusion coefficients of selected PAHs in the side chain liquid-crystalline polymer determined by IGC confirm the influence of the shape of a molecule on its behaviour in nematic and isotropic phases [32]. Non-planar *o*-terphenyl diffuses more easily in the nematic phase of this liquid crystal than planar fluorene. In the isotropic phase molar diffusion coefficients for fluorene and *o*-terphenyl do not differ much. Activation energies of the diffusion of naphthalene with L/B (length-to-width) = 1.24 and that of fluorene with L/B = 1.52 in the isotropic phase do not differ much and are 32 and 30 kJ/mol, respectively, whereas in the ordered nematic phase they are clearly larger and different—for naphthalene 40 kJ/mol and for fluorene 68 kJ/mol [32].

The separation effect of components of mixtures on LC-SPs is associated with the different energy of the interactions of the components of these mixtures with liquid crystals. Therefore, the determination of these interactions in different systems can contribute to a better knowledge of the nature of liquid crystal-chromatographed substance interactions. The values of excess molar thermodynamic functions—enthalpy, entropy and free enthalpy, and of the activity coefficients in the systems: liquid crystal $-C_5-C_9$ alkanes (linear, branched and cyclic) [33] were calculated. The two liquid crystals: *p*-pentylo-triphenyl-*p*′-ethoxyazoxybenzene and *p*-(*n*-hexyloxy)phenyl-*p*′-methoxybenzoate were chosen for the investigations. The activity coefficients of *n*-alkanes dissolved in both liquid crystals decrease in the order: nonane > octane > heptane > hexane > pentane. Excess molar enthalpies of the substances dissolved in liquid crystals are positive, which accounts for the endothermic effect of their mixing. Excess molar enthalpies of the mixing were found to be higher in the mesophase than in the isotropic liquid, which means that the dissolution in the anisotropic liquid needs more energy, i.e. the dissolution of molecules in the ordered structure of the mesophase is made more difficult.

The effect of steric factors on the separation of *m*- and *p*-xylene isomers on liquid crystals: *para*-azoxyanisole (PAA) and 4-methoxy-benzylidene-4-butylaniline (MBBA) was presented in the work [34]. The ratio of dissolution activity factors of *m*-xylene to *p*-xylene is smaller than unity and in practice it does not change in the isotropic phase while it is larger than unity in the nematic phase and depends on the structure of a liquid crystal. The dissolution activity coefficients of *m*-, *o*- and *p*-nitrotoluene in the liquid-crystalline phase PBHpB ($C_7H_{15}–O–C_6H_4–COO–C_6H_4–COO–C_6H_4–O–C_7H_{15}$) calculated on the basis of the lattice model for anisotropic systems given by Flory were consistent with the experimental data obtained from the chromatographic measurements [35].

The diffusion and the dissolution of chromatographed substances in stationary phases are determined by the mass transfer resistance which affects the efficiency of chromatographic columns. The efficiencies of columns with liquid-crystalline stationary phases are generally lower than those of columns with conventional stationary phases. Therefore, it can be advisable to mix liquid-crystalline stationary phases with conventional phases. It was shown by examining the mixtures of 4-propoxy-4′-ethoxyazoxy-benzene (PEAB) with polymethylhydrogen-siloxane (PMHS) in capillary columns [36]. Xylene isomers were chromatographed on these phases. With the suitable mixture ratio, the good separation of LC-SPs and the small mass transfer resistance of the conventional stationary phase result in the optimal separation of the components of the mixture. The mixture of PEAB and PMHS in the ratio of 83:17 showed good separation properties. It is to be noted that the film of the stationary phase mixture upon the wall of a glass capillary column was more homogenous than the film of the liquid-crystalline stationary phase itself.

Little attention is paid to the effect of polarity of LC-SPs on their separation properties. It is justifiable as the

effect of polarity of LCSPs on obtaining the separation of components of mixtures is smaller than the effect of the ordered structure of the stationary phase. The effect of polarity should not be neglected, though, because in some cases it can be positive and may improve the separation of components of mixtures. The investigation of the polarity of three liquid-crystalline stationary phases, azoxydiphenetole (ADP), bis(metoxybenzylidineanil-chloraniline) $(MBCA)_2$ and bis(methoxybenzylidineanil-bi-toluidine) $(MBT)_2$, was made by Betts [18]. Depending on the method used, the first two phases were determined as strongly polar and the third one, respectively, as moderately or weakly polar.

Like in conventional stationary phases, the thickness of the film of a liquid crystal should be great enough not to let the support on which the liquid crystal is deposited affect its interaction with chromatographed substances. With small coverages of the support with liquid crystals (e.g. 7%), the use of gas chromatography makes it possible to examine the effects of the support (e.g. silica gel) on the structure of the mesophase of a liquid phase [37]. To understand these effects and the structure of the mesophase better, investigations made by inverse gas chromatography coupled with IR spectroscopy [37] or differential scanning calorimetry [38] were used.

The retention time of chromatographed substances is known to depend on the temperature of a liquid crystal, practically on its phase state where it is at a given temperature. It contributes to determining the phase transition temperatures of liquid crystals. The phase transition temperatures determined by IGC and DSC are usually in agreement. It was shown, for example, for two liquid crystals containing external and internal nitro groups [38].

The results of determining temperatures of phase transitions for cholesteric [13] and nematic liquid crystals [22] by DSC and IGC were also compared. The phase transition temperatures measured by these methods were different by 5%. To determine the phase transition temperatures on the basis of the dependence of the retention time on the temperature of the cholesteric liquid crystal, isomers of a few alkyl aromatic hydrocarbons were used [13]. The wide range of the cholesteric mesophase from 25 to 180 °C is noteworthy. The wide range of the mesophase is very useful property of liquid-crystalline stationary phases.

The examination of properties of LCSPs, including polymers, by inverse gas chromatography [39–42] makes it possible not only to determine phase transition temperatures of liquid crystals but also to study and compare properties of mesophases in stable and supercooled states [41].

The properties of supercooled smectic phases of the *p*-*n*-alkoxycinnamoyloxy-*p*′-cyanoazobenzene homologues were studied [43]. The mesomorphic stationary phases were classified and their separation properties were characterized using the system of universal retention indicates. The selectivity increase of smectic phases in the supercooled state was described thermodynamically.

Considering the measurements taken by IGC, it is possible to calculate solubility parameters of chromatographed substances and give a thermodynamic description of the interactions of these substances with LCSPs [41,42,44]. The data obtained can be used to obtain better and better stationary phases. Thanks to inverse gas chromatography some interesting information was found about differences in the property of the polymeric polysiloxane LCSP and the mixture of polysiloxane and a liquid crystal from which the liquid-crystalline polymer was obtained [42] as well as monomeric liquid crystals and the polymers obtained from them [40].

4. The separation mechanism on liquid-crystalline stationary phases

The chromatographic separation of compounds of mixtures using most of the conventional stationary phases is associated with the polarity of these phases and with the polarity and polarizability of the chromatographed substances as well as the subsequent intermolecular interactions. The mechanism of the chromatographic separation on LCSPs is mostly connected with the differentiation of the structure of molecules of chromatographed substances. The differentiation of the structure of molecules of chromatographed substances results from the ordering of the liquid crystal structure and depends on the type of mesophase and thermodynamic effects of dissolution of solutes in LCSP [45] related to it. In the case of nematic liquid crystals, the best separations are obtained at the lowest temperatures of their existence, usually slightly above the melting point, but also below it, in the supercooled mesophase. However, the mass transfer resistances in the highly ordered supercooled mesophase are very strong and the efficiencies of chromatographic columns with such mesophases are low. The efficiencies of columns with LCSPs are generally lower than those of the columns with conventional stationary phases and, therefore, the mixture of a liquid crystal with the conventional stationary phase (e.g. the silicon one) can be advantageous [36].

The mixture of a liquid crystal with the conventional stationary phase increases the efficiency of the column by improving the homogeneity of the stationary phase film upon the wall of a capillary column. The mixture of two liquid crystals can also prove advantageous [24,46]. The properties of mixed liquid-crystalline stationary phases were described in detail in the previous review [2]. Apart from non-ideal solutions of such mixed stationary phases, there are systems in which the liquid crystal is dispersed in the conventional stationary phase [47]. In such systems both stationary phases interact with chromatographed substances independently, according to different mechanisms—the liquid crystal by the ordered structure and the conventional stationary phase by polarity. This system can show better properties than the liquid crystal itself as regards the separation taking place according to two different mechanisms. With a certain composition of the mixture being separated, disadvantageous effects of separation cannot be excluded.

Monomeric liquid crystals are successfully used mostly for the separation of low-boiling compounds (VOC), whereas polymeric ones for the separation of high-boiling compounds (e.g. PAHs, PCBs, PCDDs, PCDFs).

Some monomeric LCSPs, of high molecular weights, have been found to contribute to the separation of high-boiling compounds at temperatures corresponding to the solid of a liquid crystal [38]. In such conditions, the good separation is obtained in a shorter time than during the separation in the mesophase range. Small differences in the structure of molecules of liquid crystals related to terminal or lateral position of the same functional group ($-NO_2$) were also found to affect not only the range of their mesophase but also their separation properties.

The properties of LCSP below its melting point (as the supercooled phase) are different depending on whether this phase is heated from the temperature below the melting point or cooled from the temperature higher than the melting point. It was shown by Betts et al. while studying the separation of some aromatic and monoterpenic components of volatile oils within the temperature range of 120–175 °C on *N*,*N*′-bis(*p*-methoxy-benzylidene)-α, α′-bi-*p*-toluidine (BMBT), with the melting temperature of 179 °C [48]. The authors of the paper claim that different mechanisms of the separation of components of mixtures are possible and that they are dependent on the thermic history of LCSP. They examined it by taking the example of the mixtures: terpineol-estragole and anethole-thymol on BMBT depending on the modification of a temperature column and on the way of reaching a definite temperature.

The mesophase of the liquid crystal existing after its melting can be supercooled when the temperature of a column decreases. The stability of the supercooled mesophase depends on the kind of liquid crystal and on the support on which it is deposited. The separation in the supercooled mesophase takes place according to the same mechanism as in the conventional mesophase at stronger mass transfer resistances in the supercooled phase.

The effects of the separation of components of mixtures, including isomers, on LCSPs at temperatures below their melting points, in the solid, similar to the effects of the separation within the temperature mesophase range are difficult to explain. The explanation given by Betts et al. seems very probable [48]. The chromatographed solute moving down in the chromatographic column can produce locally a liquid eutectic mixture with a liquid crystal. If the liquid crystal has been previously heated above the melting point, it can then retain the ordered structure of the mesophase after being cooled below the melting point and solidified. Such ordering does not occur in a liquid crystal which has been not molten earlier. Therefore, the interaction of the liquid crystal melted earlier with the chromatographed substance in the eutectic mixture can be stronger than that of the liquid crystal which has not been molten [48]. It appears that the separation of components of the same mixture can be different and take place according to different mechanisms related to the thermal history of a chromatographic column.

Considering the separation properties of LCSPs, the interactions in the chromatographic system, connected with polarity, cannot be completely omitted although they are not large compared with the separation mechanism resulting from the ordered structure of these stationary phases [18,29,48]. It is noticeable in the case of separating *m*- and *p*-xylene isomers. The isomers on the conventional stationary phases, if separated, are eluted in the order *para* and *meta*, whereas on LCSPs they are eluted in the order *meta* and *para* [29,31,49]. The two isomers are very frequently used to assess the separation abilities of LCSPs. However, according to Krupčik et al. the use of saturated cyclic compounds for assessing the selectivity of LCSPs is better than the use of xylenes [29]. It is justified by the fact that the polarity of cyclic compounds is smaller than that of xylenes and the influence of their polarity on the selectivity of the separation can be minimized. It can then be assumed that, like in the case of conventional stationary phases, the polarity of LCSP and the polarity of chromatographed substances are likely to affect the separation of components of mixtures.

With a view to obtaining stationary phases of the wide temperature range of the mesophase, of high stability in columns and of good separation properties, attention is paid to polymeric liquid crystals, including those in the form of complexes with transition metal ions (e.g. copper(II), zinc(II), nickel(II)). The separation of the latter is connected with both their ordered structure and the ability of exchanging organic ligands of a liquid crystal with organic substances, e.g. PAHs [8].

The separation on these LCSPs is then complex and in the case of mixtures whose components can interact with LCSPs according to both mechanisms the separations obtained can be very good.

It is also possible to achieve good separation of drugs, environmental pollutants and components of biological liquids of electrondonor properties on such liquid-crystalline complexes.

Sojak et al. [50] examined regularities and irregularities in the values of retention of chromatographed substances, affecting the selectivity of separation, with regard to the relationship: retention of a chromatographed substance–structure of a liquid crystal. They measured retentions of 49 branched alkynes C_5–C_{13} on squalane and a liquid crystal: 4-*n*-pentylacetophenone-*O*-(4-*n*-pentyloxybenzoyl) oxime (PBO). The selectivity of a liquid crystal for isomers of *n*-alkynes increased with a shift of the triple bond from the centre to the end of the carbon chain. With a decrease in the length-to-width ratio of molecules of alkynes and with an increase in the screening of the triple bond, their retention indices on PBO decrease in comparison with squalane (SQ); ΔI^{PBO-SQ}. Table 2 gives a list of ΔI^{PBO-SQ} values for several alkynes [50].

The different separation of the same mixtures in different types of the mesophase of liquid crystals (smectic, nematic,

Table 2
Differences in retention indices of selected alkynes on squalane and liquid-crystalline stationary phase (4-*n*-pentylacetophenone-*O*-(4-*n*-pentyloxybenzoyl)oxime (PBO)) [50]

Alkyne	ΔI^{PBO-SQ}
3-Heptyne	65.1
2-Methyl-3-heptyne	47.7
6,6-Dimethyl-3-heptyne	43.0
2,6,6-Trimethyl-3-heptyne	15.9
2,2,6,6-Tetramethyl-3-heptyne	4.3
2,2,5,6,6-Pentamethyl-3-heptyne	−5.6
2,2,5,5,6,6-Hexamethyl-3-heptyne	−17.7

Table 3
Values of $H_2^{e,\infty}$ and $S_2^{e,\infty}$ of selected solutes obtained with liquid crystal: *N*,*N*′-diphenyl-[4-(2,3,4-tri(2-methoxyethoxy)ethoxy) benzylidene)imine]piperidine [25]

Compounds	Nematic liquid crystal		Isotropic liquid	
	$H_2^{e,\infty}$ (kJ/mol)	$S_2^{e,\infty}$ (kJ/mol)	$H_2^{e,\infty}$ (kJ/mol)	$S_2^{e,\infty}$ (kJ/mol)
n-Hexane	3.7	21.9	0.2	13.3
n-Heptane	5	24.4	0.45	13.6
n-Octane	7.1	29.3	1.3	15.9
n-Nonane	8.1	30.8	1.5	15.8
n-Decane	9.2	33.0	1.8	16.0
n-Undecane	10.4	33.0	2.9	17.0
n-Dodecane	11.4	37.3	3.9	18.5
o-Xylene	3.8	22.6	0.7	15.5
m-Xylene	4.1	22.9	0.3	13.1
p-Xylene	3.9	2.5	0.9	15.3

$H_2^{e,\infty}$, molar partial excess enthalpy in infinite dilution; $S_2^{e,\infty}$, molar partial excess entropy in infinite dilution.

isotropic) can be related to different diffusion coefficients of the same substances in individual types of mesophase [31]. Different interactions of chromatographed substances with different states of the liquid crystal: *N*,*N*′-diphenyl-[4-(2,3,4-tri(2-methoxyethoxy)ethoxy) benzylidene)imine]piperidine was illustrated by partial molar excess enthalpy and entropy in the case of the nematic and the isotropic liquid [25] (Table 3). Their values are much higher in the mesophase than in the isotropic liquid. It results from the different interaction of molecules of solutes with the ordered and disordered structures of a liquid crystal.

5. Examples of separations of components of mixtures on liquid-crystalline stationary phases

Most investigations on LCSPs are carried out with using capillary columns (Table 4), which allows for combining the high separation of LCSPs with advantages of capillary columns.

A commercial capillary column of fused silica is filled with polymeric liquid crystal MPMS [28,51]. However, packed columns guaranteeing the good separation of components of different mixtures are not excluded [26,52,53].

Although there is a tendency to obtain new liquid crystals, mostly as polymers, it is evident that they have clearly better separation properties than monomeric liquid crystals. It cannot even be expected because the structure of polymeric liquid crystals where molecules of liquid crystals are usually bound to the polysiloxane chain. Distances of molecules of liquid crystals in such polymers may not be optimal enough for the liquid-crystalline structure to be organised to a maximum.

Kraus et al. found that polycyclic hydrocarbons, difficult to separate, were separated better on monomeric nematic liquid crystals than on a polymeric liquid crystal and on conventional stationary phases—non-polar OV-1 and polar DB-17 [7]. The main advantage of polymeric LCSPs is usually their wide, range of the mesophase and high stability of the column used [54].

The separation effects on LCSPs are not always better than on conventional stationary phases. It was observed in composite mixtures of congeners of polychlorinated naphthalenes and polychlorinated biphenyls, separated on conventional stationary phases, on polysiloxane cyanobiphenyl phases and on the smectic phase [55,56]. Although the final effect of the separation of the composite mixture on LCSPs, connected with the differentiation of the shape of molecules, can be unsatisfactory, the separation of individual pairs or small groups of isomers according to this mechanism is usually much better on liquid crystals than on conventional stationary phases. On LCSPs isomers whose molecules are more planar, or whose length to width ratio is larger, are eluted from a column later than molecules less planar or of the smaller length to width ratio, even if their molecular weights and boiling points favour the reverse order of elution [56]. It can cause the overlapping of peaks of some components of composite mixtures and can then result in the worse separation of these components in comparison with the separation obtained on the conventional stationary phase.

An analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans presents a very difficult problem. The side-chain liquid-crystalline polysiloxane polymer of the smectic and nematic mesophases and of the transition temperature to the isotropic liquid 270 °C guarantees the separation of some isomers of PCDDs and PCDFs better than commercial conventional phases: HP-5MS and RTX-5MS [54], for example: 2,3,7,8-TeCDF, 2,3,7,8-TeCDD and 1,2,3,4-TeCDD; 1,2,3,4,7,8-HxCDD versus 1,2,3,6,7,8-HxCDD. It is shown in Fig. 14 containing chromatograms of the standard solution of PCDDs and PCDFs (1613CS4).

In order to separate congeners of PCDD/PCDF Riehle et al. used the smectic liquid-crystalline phase before [57]. The phase guaranteed a very good separation of 2,3,7,8-TCDF from all other tetrachlorodibenzofurans.

The advantages of mixed stationary phases containing, among other components, a liquid crystal were already mentioned. Janini and Filfil, who mixed the liquid crystal with the conventional phase Dexsil 300 in the ratio of 23:77, gave an example of such a stationary phase [47]. They

Table 4
Examples of characteristics of capillary columns filled with liquid crystal stationary phases

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm); Method of column filling	Stationary phase film thickness (nm)	Separated compounds [RRT][c]; temperature of separation	Reference
BPBBB	C 182–184 N 355–358 I	Gl, 5 × 0.32	200	Polynuclear aromatic hydrocarbons: phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene (180 °C (5 min) next 15 °C/min to 310 °C)	[7]
Polysiloxane-CBOBPCABB	C 150–160 N 320 I	Gl, 10 × 0.32	170		
		Gl, 16 × 0.25	100		
		Gl, 30 × 0.32; static	250		
DODTBA-Ni	C 122.6 S_H 162.9 S_C 230 I	FS, 12 × 0.25; static	250	Polynuclear aromatic hydrocarbons: naphthalene [1.00], 2-methylnaphthalene [1.49], 1-methylnaphthalene [1.61], biphenyl [2.01], diphenylmethane [2.33], acenaphthylene [2.85], acenaphthene [3.11], dibenzofuran [3.49], fluorene [4.25], phenanthrene [6.85], anthracene [6.99], fluoranthene [13.15], pyrene [15.41] (150 °C (5 min) next 3 °C/min to 190 °C)	[8]
DODTBA-Zn	C 123.1 S_C 143.8 N 162.9 I				
Polymer-DODTBA-Ni	C 116.1 S_H 154.1 S_C 240 I				
Polymer-DODTBA-Zn	C 84.1 S_C 123.1 N 140.8 I				
OC-1	C 116 N 161 I	FS, 10 × 0.25	290	*m*-Xylene [1.00], *p*-xylene [1.06] (80 °C)	[10]
PSC-3	C 68 S 101 N 172 I			*o*-Chlorotoluene [1.00], *m*-chlorotoluene [1.07], *p*-chlorotoluene [1.15] *o*-Bromotoluene [1.00], *m*-bromotoluene [1.08], *p*-bromotoluene [1.16] (100 °C) *o*-Cresol [1.00], *m*-cresol [1.37], *p*-cresol [1.36] (150 °C) 2,6-Dimethylphenol [1.00], 2,5-dimethylphenol [2.18], 2,4-dimethylphenol [2.23], 2,3-dimethyl-phenol [2.96], 3,5-dimethylphenol [3.29], 3,4-dimethylphenol [4.33] (100 °C)	
PSC-3		FS, 10 × 0.25; static		Di- and trisubstituted benzene isomers: xylenes, chlorotoluenes, bromotoluenes, dichlorobenzenes, dibromobenzenes, nitrochlorobenzenes, nitrotoluenes, nitrobromobenzenes, cresoles, xylenoles, dinitrotoluenes (80, 100, 120, 150, 180 °C)	[11]
PDB-14-C4					
PSC-3 + PM β-CD					
PDB-14-C4 + PM β-CD					

Table 4 (*Continued*)

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm); Method of column filling	Stationary phase film thickness (nm)	Separated compounds [RRT][c]; temperature of separation	Reference
POLY 10	C 21 Ch 176 I	Gl, 30 × 0.25; dynamic		Alkanes, alkylobenzenes, *cis–trans* isomers, polyaromatic hydrocarbons: *n*-octane, 2,2-dimethylhexane, 2,4-dimethyl-hexane, 2-methylheptane, *n*-nonane, 3-methyl-octane, 2-methyloctane, *n*-tridecane, *n*-octadecane, *n*-eicosane, *m*-xylene, *p*-xylene, *o*-xylene, isopropylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, *trans*-decaline, *cis*-decaline, *trans*-2-hexene-1-ol, *cis*-2-hexene-1-ol, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene (170 °C)	[13]
POLY 16	C 51 Ch 181 I				
LC_1	C 93.8 N 274.5 I	Gl, 35 × 0.25; dynamic		Alkanes, aromatics, *cis* and *trans* isomers, polyaromatics, halogen compounds, volatile aromatic compounds:	[14]
LC_2	C 110.3 N 245.4 I				
LC_2				*n*-Nonane[1.00], 2,3,5-trimethylhexane [0.17], 2,2,4-trimethylhexane [0.33] (60 °C)	
LC_2				Toluene [1.00], *m*-xylene [2.11], *p*-xylene [2.22] (60 °C (12 min) next 4 °C/min to 250 °C)	
LC_1				*trans*-Decalin [1.00], *cis*-decalin [0.89] (110 °C next 4 °C/min to 280 °C)	
LC_2				Naphthalene [1.00], 2-methylnaphthalene [1.41], 1-methylnaphthalene [1.47], acenaphthene [3.14], fluorene [3.28], *trans*-stilbene [3.43], anthracene [3.57], phenanthrene [3.75] (110 °C next 4 °C/min to 250 °C)	
LC_1				*m*-Dichlorobenzene [1.00], *o*-dichlorobenzene [1.22], 1,3-dichloropropanol-2 [2.38], 1-bromo-3-chloropropanol-2 [2.84], 1,3-dibromopropanol-2 [3.16] (100 °C (10 min) next 4 °C/min to 280 °C)	
LC_1				*α*-Pinene [0.32], *β*-pinene [0.42], eucalyptol [0.53], limonene [0.53], camphor [0.68], linalool [1.00], linalyl acetate [1.05], nerol [1.18], eugenol [1.21], geranyl acetate [1.34], *α*-cedrene [1.45], *cis*-isoeugenol [1.47], geraniol [1.50], *β*-cedrene [1.55], *trans*-isoeugenol [2.00], estragole [2.34], thymol [2.39], carvacrol [2.53], anethole [2.63] (120 °C (10 min) next 4 °C/min to 280 °C)	

Table 4 (*Continued*)

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm); Method of column filling	Stationary phase film thickness (nm)	Separated compounds [RRT][c]; temperature of separation	Reference
LH	C 88 N 155 I	Gl, 25 × 0.25; dynamic		Alkanes, aromatics and PAHs, halogen compounds, volatile aromatic compounds: 5-methyldodecane [1.00], 4-methyldodecane [1.03], 2-methyldodecane [1.05], 3-methyl-dodecane [1.08] (90 °C)	[15]
CuL_2	C 89 N 180 I			Acenaphthylene [1.00], acenaphthene [1.03], fluorene [1.74], phenanthrene [2.45], anthracene [2.52], pyrene [6.32] (120 °C next 4 °C/min to 280 °C)	
				m-Dichlorobenzene [1.00], *o*-dichlorobenzene [1.09] (100 °C)	
				Estragol [1.00], anethol [1.68], thymol [2.73], carvacrol [2.82]; (85 °C next 4 °C/min to 135 °C)	
				Linalool [1.00], linalyl acetate [1.83], nerol [2.25], geraniol [2.83], β-cedrene [3.33], γ-cedrene [3.33], eugenol [4.33], *cis*-eugenol [5.83], *trans*-eugenol [6.08] (88 °C next 4 °C/min to 150 °C)	
CL_1	C 88.5 N 237.5 I	BS, 25 × 0.25		Alkanes, xylenes, aromatics, polyaromatic hydrocarbons, chlorobenzenes, methyl esters C_{13}–C_{18} carboxylic acid, natural compounds (60, 100, 150, 180, 210, 100 °C next 4 °C/min to 210 °C)	[20]
CL_2	C 100.3 N 214.5 I	BS, 25 × 0.25			
CL_3	C 107.5 N 181.6 I	BS, 20 × 0.20			
POE-LC_1	C 56.2 N 120.5 I (DSC)	BS, 30 × 0.25; dynamic		Volatile aroma compounds: α-pinene [0.15], β-pinene [0.30], eucalyptol [0.71], limonene [0.61], *d*-camphor [0.93], linalool [1.00], linalyl acetate [1.20], citronellal [1.41], terpineol [2.20], menthol [2.32], borneol [2.51], nerol [2.83], citronellol [2.86], geraniol [3.25], estragole [3.47], thymol [3.60], carvacol [3.72], *cis*-isoeugenol [5.05], anethole [5.76], *trans*-isoeugenol [5.84] (60 °C next 4 °C/min to 120 °C)	[22]
POE-LC_2				Alkanes and aromatics (40, 50, 60, 70, 80, and 100 °C)	
	C 155.2 N 179.2 I (DSC)			Polyaromatic hydrocarbons: naphthalene [1.00], 2-methylnaphthalene [1.59], 1-methylnaphthalene [1.80], acenaphthene [4.00], acenaphthylene [4.31], fluorene [4.70], anthracene [5.22], phenanthrene [5.72] (130 °C next 4 °C/min to 160 °C)	
	C 155 N 180 I (GC)				
				Phenols and derivatives (130, 140, 170 °C)	
				Cis and trans isomers: *cis*-decalin [1.00], *trans*-decalin [1.05] (120 °C)	
				cis-stilbene [1.00], *trans*-stilbene [1.09] (160 °C)	

Table 4 (*Continued*)

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm); Method of column filling	Stationary phase film thickness (nm)	Separated compounds [RRT][c]; temperature of separation	Reference
MPMS (commercial liquid crystal polysiloxane phase)	C 130 S 160 I	FS, 25 × 0.25		Volatile aroma compounds: α-terpinene [0.25], cineole [0.26], limonene [0.28], *p*-cymene [0.31], γ-terpinene [0.32], (+)-linalool [0.47], citronellal [0.65], camphor [0.88], 4-terpineol [1.05], citronellol [1.09], α-terpineol [1.29], geraniol [1.47], estragole [1.50], citral [2.03], cuminal [2.64], safrole [2.68], thymol [3.62] (130 °C)	[28]
OPPB	C 53 N 85 I	Gl, 30 × 0.30	120	*trans*-1,2-Dimethylcyclohexane [1.0], *cis*-1,2-dimethylcyclohexane [1.1], *m*-xylene [1.4], *p*-xylene [1.5], *o*-xylene [1.5], *trans*-decalin [3.1], *cis*-decalin [4.0] (54 °C next 5 °C/min to 83 °C)	[29]
OBAP	C 65 N87 I	Gl, 30 × 0.31; static	310	Xylenes: *m*-xylene [1.00], *p*-xylene [1.21] (65 °C)	[30]
POBAP	C 67 S_B 82 S.A. 156 I		630		
ABOP	C 63 N 85 I				
PABOP	G 28 S 89 N 111 I				
SC LCP ($P_{10,4,4}$)	G 17 N 98 I	FS, 17 × 0.20		Polyaromatic hydrocarbons: naphthalene, fluorene, *o*-terphenyl, pyrene	[32]
PEAB	C 101 N 147 I	Gl 20 × 0.3	300	Nonane, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, undecane (100 °C)	[36]
PEAB:PMHS = 83:17					
NMHBMA	C 94.5 N 141.5 I C 116 N 191.5 I	Gl, 25 × 0.25; dynamic		Xylenes: *m*-xylene [1.00], *p*-xylene [1.04], *o*-xylene [1.19] (70 °C) Volatile aroma compounds: estragol [1.00], anethole [1.70], γ-cedrene [1.80], β-cedrene [1.99], thymol [2.05], eugenol [2.50] (120 °C next 4 °C/min to 160 °C)	[38]
DMHBNA				Alkanes: 8-methylheptadecane [1.00], 4-methylheptadecane [1.07], 3-methylheptadecane [1.08], 2-methyl-heptadecane [1.10] (140 °C) Polyaromatic hydrocarbons: naphthalene [1.00], 2-methylnaphthalene [1.46], 1-methylnaphthalene [1.54] (110 °C) Acenaphthylene [1.00], acenaphthene,[1.05], phe-nanthrene [1.21],anthracene [1.29],fluorene [1.47] (140 °C next 8 °C/min to 189 °C)	
HBBNBP	C 100 S 200 N 300 I	Gl, 50 × 0.25; dynamic, static		Isomers of xylenes and cresoles: *m*-xylene, *p*-xylene, *o*-xylene, *m*-cresol, *p*-cresol, *o*-cresol (130, 150, and 160 °C)	[49]
MPAHBN	C 131–133 N 204.5–205 I				
PBO	C 63 N 94 I	Gl, 106 × 0.25;		C_5–C_8 alkynes (40–60 °C) C_9–C_{13} alkynes (80–90 °C)	[50]

Table 4 (*Continued*)

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm); Method of column filling	Stationary phase film thickness (nm)	Separated compounds [RRT][c]; temperature of separation	Reference
MPMS	C 130 S 160 I	FS, 25 × 0.25		Sweet fennel oil Mace oil 100 °C next 4.5 °C/min	[51]
MS3DBDE1 (monomer)	C 151.29 N 230.32 I	FS, 30 × 0.25; dynamic	250	US EPA standard solution 1613CS4 containing selected PCDDs an PCDFs (see Fig. 14) (150 °C next 10 °C/min to 210 °C (10 min), next 2 °C/min to 240 °C))	[54]
PS3DBDE1 (polimer)	I 219.5 N 108.35 C C 122.34–142.46 S 215.87 N 270.27 I I 262.80 N 204.82 S 128.84–108.54 C				
SB-smectic		FS, 25 × 0.32	150	Polychlorinated chloronaphthalenes (mono, di, tri, tetra, penta, hexa, hepta, octa) (90 °C next 10 °C/min to 150 °C (2 min), next 2 °C/min to 180 °C (8 min), next 1.5 °C/min to 230 °C (25 min))	[55]
SB-smectic		FS, 25 × 0.20	150	Polychlorinated biphenyls (80 °C (5 min) next 15 °C/min to 150 °C (2 min), next 1 °C/min to 220 °C)	[56]

BPBBB: 4,4′-biphenylene-bis(4-*n*-buthyloxybenzoate); CBOBPCABB: 4-cyano-benzyl-2-(4-*n*-octyloxybiphenylcarboxy)-5-(4-alloxybenzoyloxy)-benzoate; DODTBA: 4-(dec-9′-en-1′-oxy)dithiobenzoate; OC-1: 4-(allyloxy)-4′-(4′-carboxybenzobiphenyl); PSC-3: poly(methylsiloxane) containing 4-(allyloxy)-4′-(4′-carboxybenzo-15-crown-5)biphenyl side chain; PDB-14-C4: side-chain crown ether polysiloxane; PM β-CD: permethylated *β*-cyclodextrin; POLY 10: poly(γ-*n*-decyl-L-glutamate); POLY 16: poly(γ-*n*-hexadecyl-L-glutamate); LC_1: 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-methoxy-4′-(4-*trans*-pentylcyclohexanecarboxyloxy)-*trans*-azobenzene; LC_2: 4-(4-*trans*-pentylcyclohexanecarboxyloxy)-2′-butoxy-3′-methyl-(4-butoxybenzoyloxy)-*trans*-azobenzene; LH: *N*-4-(2′-(4″-dodecyloxybenzoyloxy)-4′-dodecyloxy) azobenzenyl-4-dodecyloxysalicylidene imine; CuL_2: bis[*N*-4-(2′-(4″-dodecyloxybenzoyloxy)-4′-dodecyloxy) azobenzenyl-4-dodecyloxysalicylidene]iminato of copper(II); CL_1: 2-hexyloxy-3-methyl-4-(4-ethoxybenzoyloxy)-4′-(4-*trans*-*n*-pentylcyclohexanecarbonyloxy)-azobenzene; CL_2: 4-cyano-2′,3′-dimethyl-4′-(4-heptylbenzoyloxy)-azobenzene; CL_3: 4-(4′-(4″-dodecyloxyphenyl)azobenzoyloxy)-salicylidene imine *N*-propyl; POE-LC_1: *N*,*N*′-diphenyl-[4-{2,3,4-tri[2-(2-methoxyethoxy)ethoxy]-benzylidene}imine]piperidine substituted with poly(ethylene oxide)chain; POE–LC_2: 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4′-{4-[2-(2-butoxyethoxy)ethoxy]styryl}azobenzene substituted with poly(ethylene oxide) chain; MPMS: mesogenic polymeric methyl siloxane; OBAP: 4-octyloxy (4-allyloxyphenylbenzoate); POBAP: polymer obtained by reaction OBAP with polymethylhydrogensiloxane; ABOP: 4-alloxy(4-octyloxyphenylbenzoate); PABOP: polymer obtained by reaction ABOP with polymethylhydrogensiloxane; SC LCP ($P_{10,\ 4,\ 4}$): side chain liquid-crystalline polymer, the mesogenic group is of the three phenyl ring benzoate type with terminal alkoxy chains (C_4) and lateral alkyl ester spacer arm (C_{10}); OPPB: 4-octoxyphenyl 4-pentoxybenzoate; PEAB: 4-propoxy-4′-ethoxyazoxybenzene; PMHS: polymethylhydrogensiloxane; NMHBMA: 2-nitro-3-methyl 4-(4-heptylbenzoyloxy) 4′-methylazobenzene; DMHBNA: 2,3-dimethyl 4-(4heptylbenzoyloxy) 4′-nitroazobenzene; HBBNBP: *p*-{(4-hexylobenzoiloxy)-(4″-4‴-benzoilonitrobenzoiloxy)}phenylene; MPAHBN: 1-(methoxyphenyl-4′-azo)-4-(4′-hexylobenzoiloxy)naphthalene; PBO: 4-*n*-pentylacetophenone-*O*-(4-*n*-pentyloxybenzoyl)oxime; PS3DBDE1: side chain liquid-crystalline polysiloxane polymer; SB-smectic: biphenylcarboxylate ester methylpolysiloxane (Dionex, Lee Scientific Division).

[a] C: crystalline; N: nematic; I: isotropic liquid; Ch: cholesteric; S: smectic; G: glassy.

[b] FS: fused silica; Gl: glass; M: metal; BS: borosilicate.

[c] RRT: relative retention time.

used the phase in a packed column for separating four pentacyclic aromatic hydrocarbons—benzo(k)fluoranthene, benzo(e)pyrene, perylene and benzo(a)pyrene.

The separation of PAHs on LCSPs is not only of scientific significance but can be used in analytical practice as well. On LCSP called *N*,*N*′-di(*p*-butoxy-benzylidene)-α,α′-di-*p*-toluidine (BBBT) homogenously mixed with the phase SE-30, carbochemical products (carbazole and anthracene oil) containing polycyclic aromatic hydrocarbons were separated [58]. The good separation of PAHs, including phenanthrene and anthracene, was obtained using a packed glass column 1.9 m long. The column was filled with a mixture of 3% BBBT phase and 2% SE-30 phase on Chromosorb G AW.

On monomeric LCSP: 4,4′-biphenylene-bis(4-*n*-butyloxy-benzoate) placed in a capillary column 12 PAHs present in both the standard mixture (Fig. 15a) and the mixture derived from coal tar were successfully separated (Fig. 15b) [7].

Composite mixtures of vegetable origin (e.g. volatile oils) are difficult to separate. Therefore, highly selective

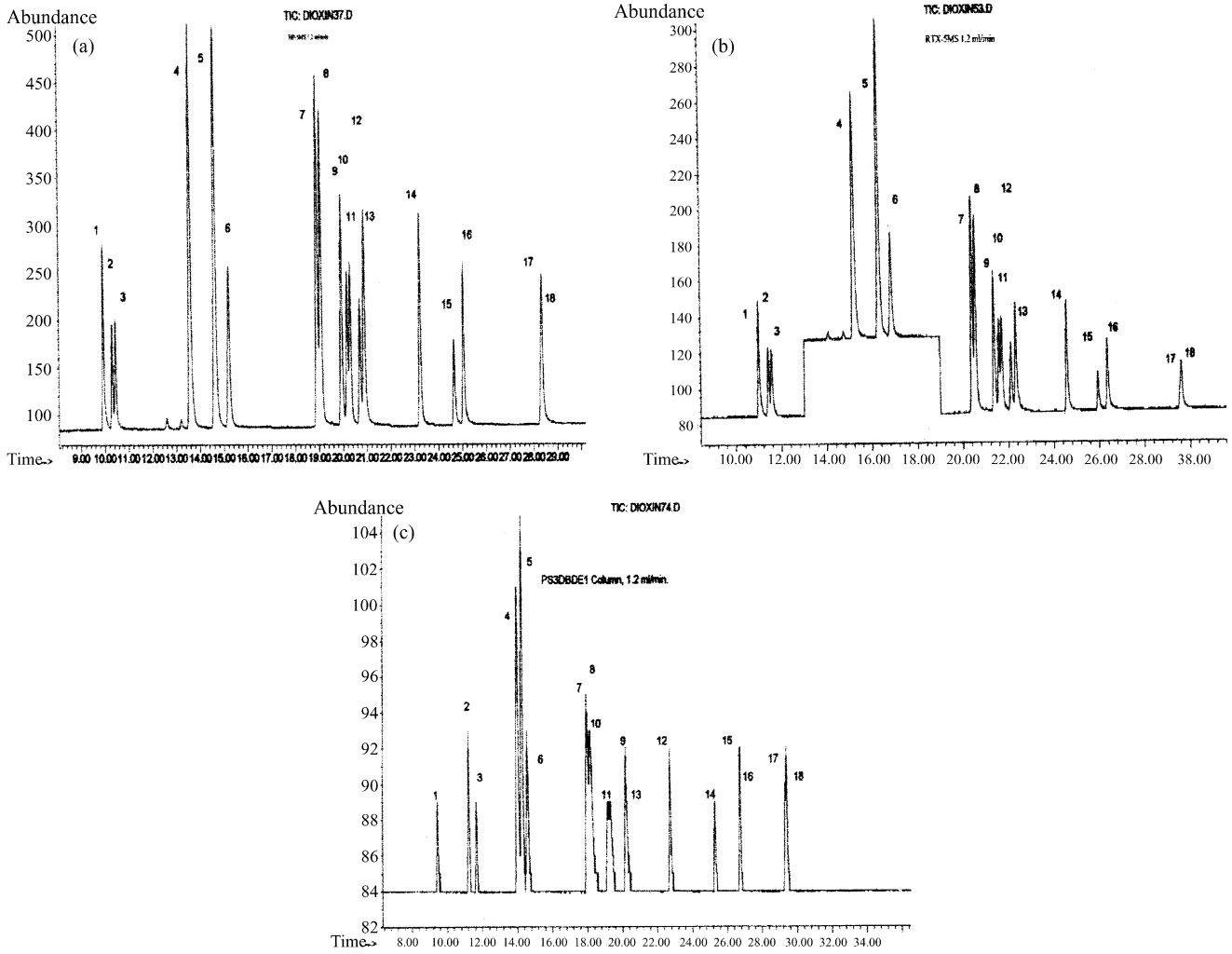


Fig. 14. Chromatograms of the standard solution of PCDDs and PCDFs on two commercial stationary phases: HP-5MS (a) and RTX-5MS (b) and on side-chain liquid-crystalline polysiloxane polymer (c). Peak identification: (1) $^{13}C_{12}$-2,3,7,8-TeCDF; (2) $^{13}C_{12}$-2,3,7,8-TeCDD; (3) $^{13}C_{12}$-1,2,3,4-TeCDD; (4) 1,2,3,7,8-PeCDF; (5) 2,3,4,7,8-PeCDF; (6) 1,2,3,7,8-PeCDD; (7) 1,2,3,4,7,8-HxCDF; (8) 1,2,3,6,7,8-HxCDF; (9) 2,3,4,6,7,8-HxCDF; (10) 1,2,3,4,7,8-HxCDD; (11) 1,2,3,6,7,8-HxCDD; (12) 1,2,3,7,8,9-HxCDD; (13) 1,2,3,7,8,9-HxCDF; (14) 1,2,3,4,6,7,8-HpCDF; (15) 1,2,3,4,6,7,8-HpCDD; (16) 1,2,3,4,7,8,9-HpCDF; (17) OCDD; and (18) OCDF. Reprinted from [54], Copyright (2001), with permission from Elsevier.

stationary phases, including liquid-crystalline nematic and cholesteric ones, are used for their separation with good results [22,26,27,51–53,59,60]. Some liquid crystals, used for the separation of components of volatile oils, could be used supercooled [26]. Although the good separation of components of some mixtures is possible in the solid state of LCSP in its supercooled mesophase and also in the range of the isotropic liquid, the best chromatographic effects are generally obtained within the temperature range of the stable mesophase. It was shown, among others, when 94 compounds were chromatographed on two nematic liquid crystals (LC_1 and LC_2) containing poly(ethylene oxide) chains in molecules [22].

Fig. 16 shows the chromatographic separations of volatile aromatic compounds on liquid crystals LC_1 and LC_2 [22], whereas Fig. 17 shows the dependence $\ln V_g = f(1/T)$ for selected *n*-alkanes and decalin isomers on the liquid crystal: 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4′-[4-[2-(2-butoxy-ethoxy)ethoxy]styryl}azobenzene. The increase of plates number in the nematic phase is noticeable [22].

A lot of attention is traditionally paid to the separation of di-substituted benzene isomers. These isomers can be successfully separated on a great number of liquid crystals, both nematic and smectic [38,49,61]. Methylnaphthalenes (MN) and dimethylnaphthalenes (DMN) are more difficult to separate, but some pairs of these isomers difficult to separate were successfully separated, namely 1,2- and 2,6-DMN, 2,6- and 2,3-DMN as well as 1-MN and 2-MN [62].

Liquid crystals, with a relatively wide range of the mesophase (e.g. 116–191.5 K), belonging to a group of nitroazocompounds, make the separation of different compounds possible in a short time [38]. Among them are benzene alkylderivatives, position isomers of alkanes, *cis*- and *trans*-

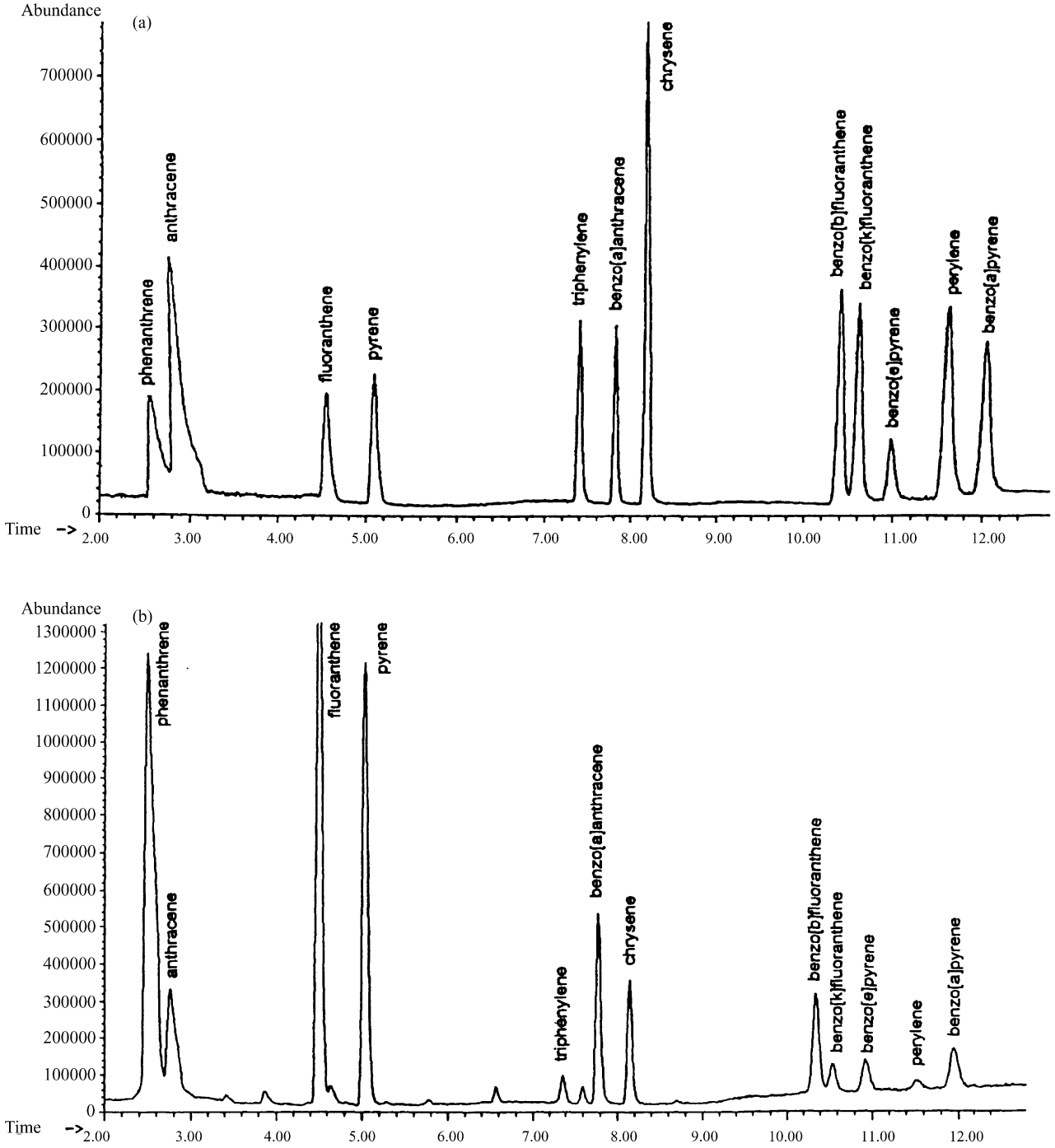


Fig. 15. Chromatograms of the separation of PAHs contained in standard mixture: (a) and PAHs from coal tar; (b) on monomeric liquid crystal column. Reprinted from [7], Copyright (1997), with permission from PAS Poland.

isomers and numerous components of volatile oils. The separations obtained were much better than those obtained using the conventional phases—SE 30 and Carbowax 20 M.

Relatively little attention is still paid to cholesteric liquid-crystalline stationary phases. They used to be examined with monomers of narrow ranges of mesophases. However, polymeric cholesterics of the wide mesophase range were obtained, e.g. from 25 to 180 °C or from 54 to 190 °C [13]. These stationary phases are useful for the separation of isomers of alkanes from C_8 to C_{20}, polyaromatic and aromatic hydrocarbons, volatile aromatic compounds as well as *cis*- and *trans*-isomers of some chemical compounds. Enantiomers still could not be separated on these phases.

Cholesteric liquid crystal crown ether was successfully used as a stationary phase for the chromatographic separation of positional isomers and enantiomers [12].

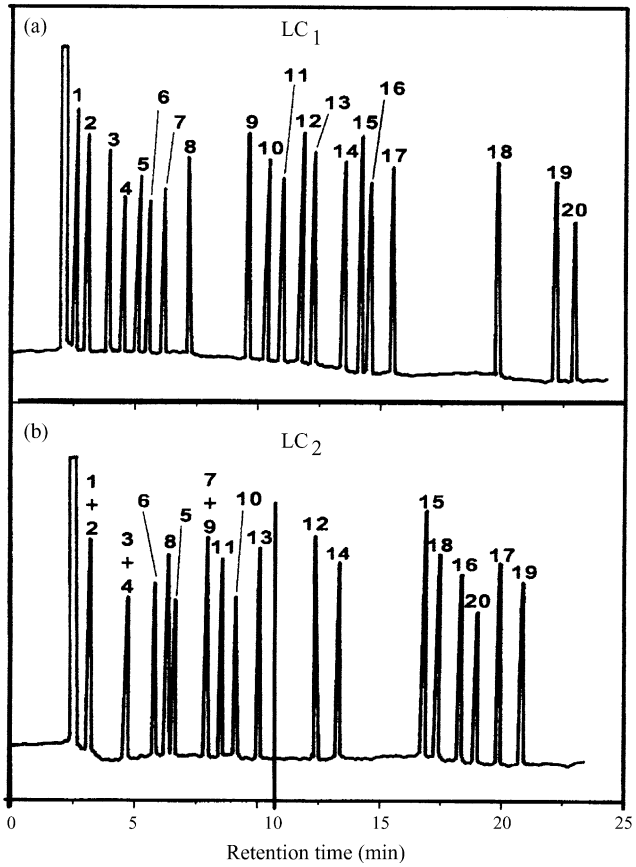


Fig. 16. Chromatographic separation of volatile aromatic compounds on LC_1: *N*,*N*′-diphenyl-[4-(2,3,4-tri(2-methoxyethoxy)ethoxy)benzylidene) imine]piperidine in the nematic state (a) and on LC_2: 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4′-[4-[2-(2-butoxyethoxy) ethoxy]styryl}azobenzene (b). The vertical line appearing in (b) corresponds to LC_2 solid-nematic transition. Peak identification: (1) α-pinene; (2) β-pinene; (3) eucalyptol; (4) limonene; (5) *d*-camphor; (6) linalool; (7) linalyl acetate; (8) citronellal; (9) terpineol; (10) menthol; (11) borneol; (12) nerol; (13) citronellol; (14) geraniol; (15) estragole; (16) thymol; (17) carvacrol; (18) *cis*-isoeugenol; (19) anethole; and (20) *trans*-isoeugenol. Reprinted from [22], Copyright (1999), with permission from Elsevier.

Side-chain liquid-crystalline polysiloxane containing crown ethers were used [11] as a matrix for β-cyclodextrins for the chromatographic separation of both di- and tri-substituted benzene isomers as well as enantiomers.

The separation ability of *cis*- and *trans*-isomers is shown by quite a lot of LCSPs such as 2-[4′-(4-*trans*-pentylcyklohexyl)biphenyl]-2-(4-isothiocyanatophenyl)ethane on which *cis*- and *trans*-isomers of alkylcyclohexylbenzenes are separated [63]. The good separation of isomers of alkenes (including *cis* and *trans*), alkadienes and diastereoisomers was obtained on pyrimidine LCSPs [64]. The obtained separations were better than those on conventional stationary phases and some other liquid-crystalline phases. The pyrimidine stationary phase of the wide range of the mesophase (65–170 °C), subject to supercooling up to 28 °C, guarantees the good separation of *cis*- and *trans*-isomers of *n*-heptadecenes and

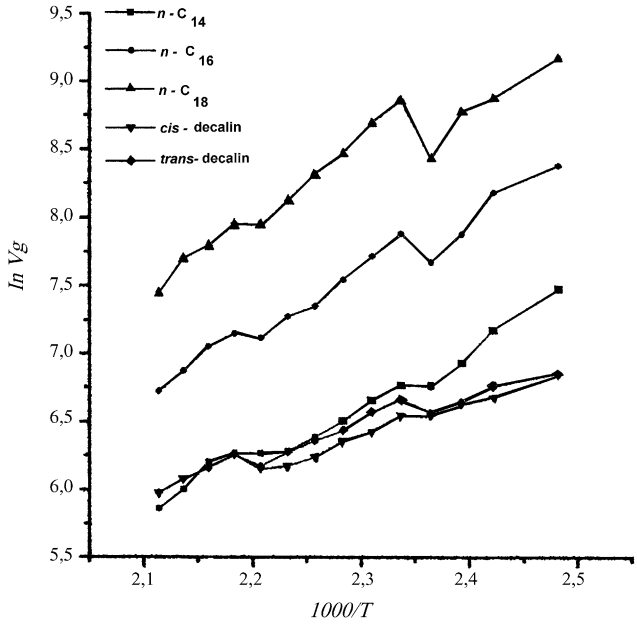


Fig. 17. Dependence $\ln V_g = f(1/T)$ for crystalline phase, mesophase and isotropic phase of liquid crystal: 2-hydroxy-3-methyl-4-{4-[2-(2-butoxyethoxy)ethoxy]} 4′-[4-[2-(2-butoxyethoxy)ethoxy]styryl}azobenzene [22].

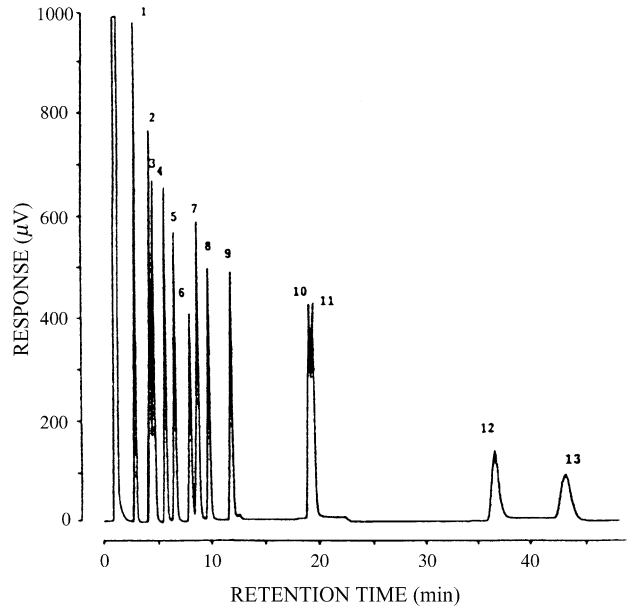


Fig. 18. Separation of PAHs with the optimized programmed temperature. Stationary phase: P-DODTBA-Ni, column:12 m × 0.25 mm i.d.; sample concentration: 480 μg ml^{-1}; injector volume: 1 μl; injector temperature: 260 °C; oven temperature: 150 °C (5 min) to 190 °C at 3 °C min^{-1}; total flow-rate of carrier gas (N_2): 25 ml min^{-1}; split ratio: 1:25; make-up gas flow-rate: 50 ml min^{-1}. Peak identification: (1) naphthalene (t_R = 2.80 min); (2) 2-methylnaphthalene (t_R = 4.17 min); (3) 1-methylnaphthalene (t_R = 4.51 min); (4) biphenyl (t_R = 5.62 min); (5) diphenylmethane (t_R = 6.52 min); (6) acenaphthylene (t_R = 7.99 min); (7) acenaphthene (t_R = 8.71 min); (8) dibenzofuran (t_R = 9.77 min); (9) fluorene (t_R = 11.91 min); (10) phenanthrene (t_R = 19.18 min); (11) anthracene (t_R = 19.58 min); (12) fluoranthene (t_R = 36.83 min); (13) pyrene (t_R = 43.15 min). Reprinted from [8], Copyright (1997), with permission from Elsevier.

Table 5
Examples of characteristics of packed columns filled with liquid crystal stationary phases

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm)	Phase amount on support (% w/w)	Separated compounds [RRT][c]; temperature of separation	Reference
DDTBA-Ni	C 140.2 S_H 167.5 S_C 235 I	Gl, 2.1 × 3.2	5	Dialkyl sulphides, PAHs (100, 135, and 165 °C)	[8]
DDTBA-Zn	C 131.4 S_C 160.9 N 173.2 I				
$(MBT)_2$		Gl, 1.5 × 2	3.0	α-Pinene [0.36], eucalyptol [0.53], limonene [0.62], fenchone [0.87], linalool [1.00], 4-terpineol [1.35], α-terpineol [1.53], estragole [1.58], geraniol [1.77], safrole [2.11], cuminal [2.26], thymol [2.35], anethole [2.77] (230 °C)	[9]
CH-B-15-C-5	Ch 125 → C	SS, 2 × 3	10	C_5–C_{12} *n*-alkanes, C_1–C_8 alcohols, ethyl esters of C_1–C_8 carboxylic acid, xylenes, dichlorobenzenes, nitro-chlorobenzenes, trimethylobenzenes, optical isomers of ethyl lactate and isoamyl alcohol (25 °C next 10 °C/min to 182 °C (30 min) next 2 °C/min to 165 °C (30 min) next 2 °C/min to 125 °C)	[12]
	Ch 165 ← → I C 182 → I				
CBOCA	C 123 S 143 N 185 I	5.0 × 2	2.5	*m*-Xylene [1.22], *p*-xylene [1.25], *o*-xylene [1.42] (90 °C) *m*-Ethyltoluene [1.52], *p*-ethyltoluene [1.89] (90 °C)	[16]
I	C 165 S 184 N 303 I	Gl 3.0 × 3	10.0	*trans* and *cis* isomers of aliphatic acetates with 10–13 carbon atoms (insect sex pheromones) (200–100 °C)	[17]
II	C 122 S 143 N 300 I		7.5		
III	C 134 N 285 I		7.5		
IV	C 120 N 195 I		7.5		
ADP	C 138 N 168 I	Gl, 1.5 × 4	3.0	α-Pinene [0.06], α-terpinene [0.11], limonene [0.12], p-cymene [0.12], α-phellandrene [0.13], γ-terpinene [0.14], terpinolene [0.15], cineole [0.19], linalool [1.00] (125 °C)	[26]
$(MBCA)_2$	C 154 N 344 I	Gl, 1.5 × 4	3.0	α-Pinene [0.09], phellandrene [0.19], α-terpinene [0.20], limonene [0.21], p-cymene [0.24], γ-terpinene [0.25], cineole [0.32], linalool [1.00] (120 °C)	[26]
$(MBT)_2$	C 181 320 I	Gl, 1.5 × 2	3.0	α-Pinene [0.23], α-terpinene [0.38], phellandrene [0.39], limonene [0.40], *p*-cymene [0.43], γ-terpinene [0.44], cineole [0.44], terpinolene [0.44], linalool [1.00] (150 °C)	[26]
BHOAB	C 69.0 S 89.0 N 116.5 I	Gl 1.7 × 0.2	13.5	*m*-Xylene, *p*-xylene, *o*-xylene (70–140 °C)	[31]
HPMB	C 55 N 78 I	SS 1.8 × 6	20	Normal, branched and cyclic alkanes C_5–C_9 (60–150 °C)	[33]
PPEAB	C 60 N 136 I				
PBHpB	N 212.9 I			*o*-Nitrotoluene [1.00], *m*-nitrotoluene [1.36], *p*-nitrotoluene [1.71] (162.1 °C)	[35]
CBPB	C 108 N 267 I	Gl, 1.0 × 3.5		Hydrocarbons: *n*-hexane, *n*-heptane, *n*-octane, benzene, toluene, ethylbenzene (80–130 °C)	[37]
BPB	C 148 I				

Table 5 *(Continued)*

Liquid crystal stationary phase	Temperatures of phase[a] transition (°C)	Column[b] (m × mm)	Phase amount on support (% w/w)	Separated compounds [RRT][c]; temperature of separation	Reference
HCB	C 58 N 74 I	M, 1.5 × 0.635	8–16	*n*-Pentane to *n*-nonane, five isomers of heptanes, benzene, toluene, ethylbenzene, xylene isomers	[40]
OCB	C 55 S_A 66 N 78 I				[41]
PDCBB	G 3.9 S_A 79 I				[42]
MBHPT	C 53 S_C.113 $N^{\#}$ 147 I S_C. 67 I				
PMMBTPS					
BMBT	m.p. = 179 °C	Gl, 1.5 × 4	3	Volatile oil constituents	[48]
$(MBT)_2$	m.p. = 181 °C	Gl, 1.5 × 2			
Cholesteryl acetate	C 112 Ch 116 I	Gl, 1.5 × 2	10	Volatile oil constituents (115 °C)	[52]

DDTBA: 4-(dec-1′-oxy)dithiobenzoate; $(MBT)_2$: bismethoxybenzylidinebitoluidine; CH-B-15-C-5: 4′-cholesteroxycarbonyl-benzo-15-crown-5; CBOCA: 4-[(4-chlorobenzyl)oxy]-4′-cyanoazobenzene; I: C_4H_9COO-*p*-C_6H_4-N=N-*p*-C_6H_4-CH_2CH_2-*p*-C_6H_4-N=N-*p*-C_6H_4-$COOC_4H_9$; II: C_7H_{15}-*p*-C_6H_4-*p*-C_6H_4-COO-*p*-C_6H_4-*p*-C_6H_4-CN; III: C_2H_5O-*p*-C_6H_4-CH=CHCOO-*p*-C_6H_4-N=N-*p*-C_6H_4-C_4H_9; IV: $C_7H_{15}O$-*p*-C_6H_4-COO-*p*-C_6H_4-OOC-*p*-C_6H_4-OC_7H_{15}; ADP: azoxy-diphenetole; $(MBCA)_2$: bis-(methoxy-benzylidineanil-chloroaniline); BHOAB: 4,4′-bis(heptyloxy)azoxybenzene; HPMB: *p*-(*n*-hexyloxy)phenyl-*p*′-methoxybenzoate; PPEAB: *p*-pentyloxyphenyl-*p*′-ethoxyazoxybenzene; PBHpB: $H_{15}C_7O$-C_6H_4COO-C_6H_4COO-$C_6H_4COC_7H_{17}$; CBPB: 4′-cyano-4-biphenyl 4-(4-pentyloxy)benzoate; BPB: 4-biphenyl 4-(4-pentyloxy)benzoate; HCB: 4-(*n*-hexyloxy)-4′-cyanobiphenyl; OCB: 4-(*n*-octyloxy)-4′-cyanobiphenyl; PDCBBS: poly(dimethyl-co-methyl(4-cyanobiphenoxy)butylsiloxane; MBHPT: (2-methylbutyl)(4-hexyloxyphenyl)terephthalate; PMMBTPS: poly(methylbutylterephthaloylphenoxypentyl)siloxane); BMBT: *N*,*N*′-bis(*p*-methoxy-benzylidine)-α,α′-bi-*p*-toluidine.

[a] C: crystalline; N: nematic; I: isotropic liquid; Ch: cholesteric; S: smectic; G: glassy.

[b] FS: fused silica; Gl: glass; M: metal; SS: stainless steel.

[c] RRT: relative retention time.

n-octadecenes [65]. The chromatographic process was carried out in a 90 m × 0.25 mm i.d. fused silica capillary column with the thickness of the stationary phase film 0.005 μm.

The separation properties of mesogenic complexes of nickel(II) and zinc(II) with the ligand 4-(dec-9′-en-1′-oxy)dithiobenzoate bound to the polysiloxane skeleton are noteworthy [8]. The nickel(II) complex shows particularly good properties. Thirteen PAHs from naphthalene to pyrene were separated on it in a capillary column 12 m long within the temperature range of 150–190 °C. It turned out that the smectic phase of complex liquid crystals is as useful for the separation of PAHs as commonly used nematic phases (Fig. 18).

Comparing the separation properties of the nematic liquid crystal: *N*-4-(2′-(4″-dodecyloxybenzoyloxy)-4′-dodecyloxy)azobenzenyl-4-dodecyloxy-salicylideneimine (LH) with its copper(II) complex: bis [*N*-4-(2′-(4″-dodecyl-oxybenzoyloxy)-4′-dodecyloxy)azobenzenyl-4-dodecyloxy-salicylidene] iminato of copper (II) (CuL_2), it has been found that CuL_2 makes it possible to obtain better separations of some compounds than LH [15]. These LCSPs were used in packed columns on Chromosorb W AW DMCS 80–100 mesh with the amount of 10% and in capillary columns 25 m long. In the latter, the good separation of isomers of aliphatic hydrocarbons and their halide derivatives, aromatic and polyaromatic hydrocarbons, and components of volatile oils was obtained [15].

The application of side-chain liquid-crystalline polymers as LCSPs for gas chromatography separations was described in a part of the paper [66].

Examples of separations of components of various mixtures in capillary and packed columns, respectively, are given in Tables 4 and 5.

6. Conclusions

An analysis of the information given in the present survey indicates that LCSPs are still being studied but not so intensely as in the 1980s. It arises from the fact that there is an increasing interest in liquid crystals as stationary phases in liquid chromatography. Some research workers who used to study liquid crystals as stationary phases in gas chromatography are now involved in examining LCSPs for liquid chromatography [5,6,67,68]. Nevertheless, further progress in investigations on LCSPs for gas chromatography has been made. New problems have been tackled, new LCSPs, including polymeric ones, of wide mesophase ranges and containing of metal ions in molecules have been obtained. The knowledge of the separation mechanism on LCSPs has been deepened and new examples of separations were given. However, it is noteworthy that the commercialization of research achievements is still of little importance and the trade offer related to LCSPs is modest.

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