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Ultra-performance supercritical fluid chromatography: A powerful tool for the enantioseparation of thermotropic fluorinated liquid crystals

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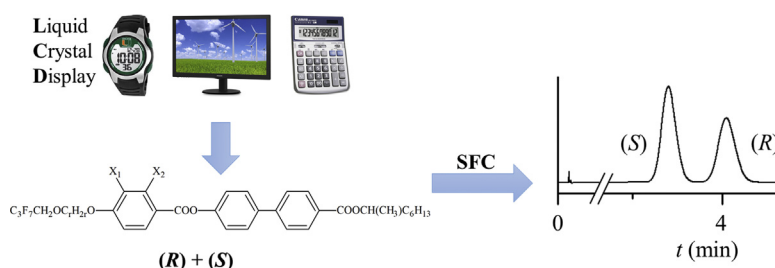
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HIGHLIGHTS

- SFC enantioseparation of liquid crystals is reported for the first time.
- Complementarity of methanol and propane-2-ol as cosolvents was shown.
- The effect of alkoxy spacer length and fluorine atom presence and position on enantioseparation was substantial.

GRAPHICAL ABSTRACT



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ABSTRACT

A fast and simple supercritical fluid chromatography method for the enantioseparation of twenty newly synthesized orthoconic antiferroelectric liquid crystals is reported for the first time. The effects of alkoxy spacer length and fluorine atom presence and position in the phenyl ring on chromatographic behavior were investigated. Baseline enantioseparation of all compounds was achieved using simple mobile phases consisting of carbon dioxide and alcohol as cosolvent on (3,5-dimethylphenylcarbamate) derivative of amylose as chiral stationary phase. The analysis times ranged from 2 to 4 and from 4 to 7 min for most samples when using methanol and propane-2-ol, respectively. The significant effect of cosolvent type on the enantioseparation of these compounds was assessed and partial complementarity of methanol and propane-2-ol was observed.

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Abbreviations: BP, back pressure; CSP, chiral stationary phase; EEO, enantiomer elution order; LCs, liquid crystals; OAFLCs, orthoconic antiferroelectric liquid crystals.

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1. Introduction

Liquid crystals (LCs) are compounds that can create a mesophase – a state of matter with physical properties of both liquid and solid phase – under specific conditions [1]. Although the material is viscous, the molecules are highly organized and can form discrete types of organization, e.g., smectic or nematic mesophases. The LCs used in this study are thermotropic, that is, they do not melt directly from solid state to isotropic liquid (or *vice versa*) when

heated (or cooled) but instead shift to different mesophases, depending on the temperature. The types and number of mesophases that can be formed depend on the structure of liquid crystals. LCs gain new physical and physical-chemical properties when introducing a chiral moiety into the structure of the molecule. Both smectic and nematic mesophases of such materials show additional supramolecular organization – a helix [1]. The helical pitch (the distance between two points of a helix after completing a turn) determines the wavelength of light reflected, while the rest are transmitted. The optical purity of LCs is of the utmost importance as the mesomorphic and opto-electronic properties of chiral LCs (e.g., helical pitch) strongly depend on the enantiomeric ratio of the substance [2–12]. Therefore, there is a big demand for fast and reliable separation methods for the analysis of their optical purity, which is essential for both academic research and manufacturing purposes.

The LCs analyzed in this study were 4-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-(2,2,3,3,4,4,4-heptafluorobutoxy)alkoxybenzoates, which differ either in alkoxy spacer length and/or in the presence/number or position of substituted fluorine atom(s) in the phenyl ring (Fig. 1). These materials belong to the group of orthoconic antiferroelectric liquid crystals (OAFLCs), that is, they form a smectic phase with anticlinal ordering and with a molecular tilt of 45°. OAFLCs have interesting optical and opto-electronic properties, such as fast in-plane switching, wide view angle, high contrast and broad grey scale [13]. Thus, they are suitable for applications in high-definition displays, for example.

Moreover, fluorinated OAFLCs show low viscosity and conductivity and higher thermal stability than non-fluorinated OAFLCs [14]. As shown in Fig. 1, the phenyl ring can be laterally substituted with fluorine at positions X₁, X₂ or both. This results in four different structures for a given length of alkoxy chain, that are marked by following acronyms – rHH for unsubstituted phenyl ring, rFH for substitution at position X₁, rHF for substitution at position X₂ and rFF for substitution at both positions. Thus, the name of each sample consists of a digit depicting the number of carbon atoms in an alkoxy chain and two letters expressing the fluorine substitution.

In this study, five series of LCs with alkoxy chain length ranging from 3 to 7 carbon atoms were of interest. All substitution patterns (HH, FH, HF, FF) were enantio-separated in each series on (3,5-dimethylphenylcarbamate) derivative of amylose chiral stationary phase. The optical activity of the studied compounds derives from an asymmetric carbon in the (methyl)heptyl moiety. The chiral part of the molecule is much smaller than the achiral bulky part, and the (methyl)heptyl chain is not a rigid structure. Therefore, the enantio-separation of such compounds is challenging.

High-performance liquid chromatography (HPLC) has been the technique most widely used for enantio-separation in many fields [15–18]. Several chiral stationary phases (CSP) are available for optimization of the chiral separation of structurally various compounds [19,20]. A few normal-phase (NP) HPLC methods for the enantio-separation of several types of OAFLCs have been described [21–23]. In all cases, polysaccharide-based CSPs were used. Six LCs

tested in this study have been previously enantio-separated in NP HPLC [21]. The baseline separation of only three of them was achieved, but the analysis time was long, inclusively lasting up to 40 min, and the consumption of organic solvents was inevitably high. Therefore, faster and more reliable and robust separation methods are needed. A suitable alternative could be supercritical fluid chromatography (SFC). Enantio-separation by SFC offers some advantages over HPLC for both analytical and preparative scale separations [24–26]. Additionally, SFC has short analysis times and is an environmentally friendly separation process [27,28]. On one hand, SFC analysis is fast because the super/subcritical fluid has two orders of magnitude lower viscosity than corresponding liquids [29]. On the other hand, SFC can be considered a “green” method due to low organic solvent consumption and to the ease of solvent removal [27,30].

Polysaccharide-based CSPs stand out among the several commercially available CSPs because they are successfully used in different separation techniques, including SFC [31–35]. Thanks to the apolar nature of supercritical carbon dioxide, the separation mechanism of SFC resembles that of normal phase environment. Thus, separation by NP HPLC can be usually transferred to by SFC, thereby shortening the analysis and upgrading both resolution and selectivity [16]. The non-polar character of carbon dioxide also favors the solubility of hydrophobic compounds in the mobile phase. For these compounds, SFC can replace reversed-phase liquid chromatography [36].

To our best knowledge no study dealing with LCs separation by SFC was conducted until now. The aim of this work was to develop fast and robust SFC methods for optical purity control of OAFLCs. The effects of both the presence and/or position of fluorine atom(s) on their structure and the effects of alkoxy chain length on OAFLCs retention and enantio-separation on (3,5-dimethylphenylcarbamate) derivative of amylose as chiral stationary phase were assessed. The effect of mobile phase composition, i.e., cosolvent type and carbon dioxide: cosolvent volume ratio were also examined. Based on the properties of mobile phase components related to the properties of individual liquid crystals, this study proposes optimized conditions for the enantio-separation of liquid crystals by SFC.

2. Materials and methods

2.1. Chemicals and reagents

Methanol (Chromasolv, gradient grade, ≥ 99.9%), propane-2-ol (Chromasolv, for HPLC, ≥ 99.8%) and propane-1-ol (Chromasolv, for HPLC, ≥ 99.8%) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Ethanol (LiChrosolv, gradient grade, ≥ 99.9%) was purchased from Merck (Burlington, MA, USA) and acetonitrile (Fischer Chemical, gradient grade) was purchased from Fisher Scientific (Pardubice, CZ). Pressurized liquid CO₂ 4.5 grade (99.995%) was purchased from Messer (Prague, Czech Republic). Both racemic mixtures and *S* enantiomers of 3HH, 3HF, 3FH, 3FF, 4HH, 4HF, 4FH, 4FF, 5HH, 5HF, 5FH, 5FF, 6HH, 6HF, 6FH, 6FF, 7HH, 7HF, 7FH and 7FF were synthesized at the Military University of Technology (Warsaw,

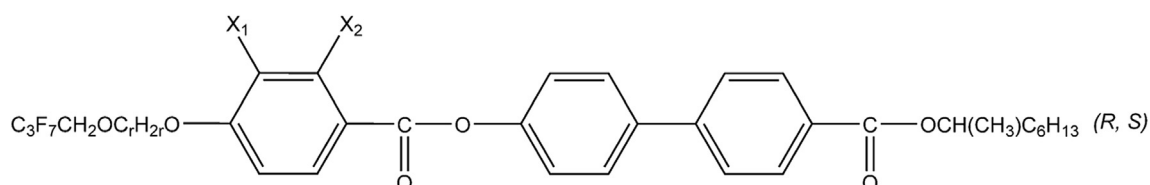


Fig. 1. General formula of studied liquid crystals (4-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-(2,2,3,3,4,4,4-heptafluorobutoxy)alkoxybenzoate).

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