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Fifty Years of Chemists' Activity in Studies on Liquid Crystal Materials in Poland

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Abstract. The activities of seven Polish chemical teams in the synthesis of liquid crystals (LCs) are described: Military University of Technology (MUT), University of Siedlce (UwS), Warsaw University of Life Sciences (SGGW), University of Warsaw (UW), University of Wrocław (UWr), Centre of Molecular and Macromolecular Studies (CMMS), and Military Institute of Engineering Technology (WITI). The MUT team was searching for new low-viscosity LCs with low, medium, and high birefringence for application in displays and a wide variety of devices working in the visible, infrared, GHz, and THz ranges of electromagnetic radiation, and for the use of LCs as stationary phases in gas chromatography. Their main research interest was compounds with a terminal NCS group and chiral smectics with an orthoconic antiferroelectric phase, as well as the investigation of non-additive properties of mixtures resulting from the induction of new phases and from the presence of a reentrant nematic phase. The UwS team has synthesized many homologous series of two- and three-ring achiral and chiral thiobenzoates, as well as several of their deuterated analogues. The SGGW team was active in the synthesis of mesogenic esters with a double bond in a terminal chain for use as intermediates in LC comb-like polymers, as well as in the synthesis of esters of (E)-phenoxyacrylic acids and the estroimides, estrothioimides, and estrodithioimides of trimellitic acid. The UW team has synthesized LCs with a 1-aminopropen-3-one moiety in the central part of the molecules, which were then transformed into the LC chelates of transition metals. Other aminoketones were used to prepare LC bent-core metal complexes. Hybrid mesogens comprising gold and silver nanoparticles, as well as banana-shaped LCs, were also prepared. Liquid crystal materials with a chiral structure made of non-chiral molecules were obtained. The UWr team has prepared many long homologous series belonging to the azo and benzylidene families. The CMMS team has prepared LC comb-like polymers belonging to polycarbosilanes and, next, LC molecules with a free radical unit inserted into them, or LCs containing a carborane cluster or its anionic form. The WITI team has manufactured LC oligomers and polymers with azomethine or imine bonds, as well as those containing thiazole and thiophene rings, for use in applications such as solar cells, selective membranes, and solvent-free electrolytes for lithium-ion batteries.

1. Introduction

Seven teams from different Polish universities were active in the synthesis of liquid crystals (LCs) – both low-molecular-weight compounds and polymers – as well as in the investigation of some of their physicochemical properties, mainly the type and structure of mesophases. The studies of their temperatures and enthalpies of phase transitions were simultaneously conducted. They are listed below in the order in which the work started:

1. Military University of Technology (MUT), Warsaw (1975);
2. University of Siedlce (UwS), Siedlce (1976);
3. Warsaw University of Life Sciences (SGGW), Warsaw (1983);
4. University of Warsaw (UW), Warsaw (1985);
5. University of Wrocław (UWr), Wrocław (1990);
6. Centre of Molecular and Macromolecular Studies (CMMS), Łódź (1990);
7. Military Institute of Engineering Technology (WITI), Wrocław (1996).

The MUT team is the largest one, consisting of a dozen scientists. The main tasks of the team were the synthesis of already known and new calamitic (rod-like) LCs with application potential for the formulation of mixtures employed in different electro-optical modes. Searching for the relationship between the chemical structure of mesogenic molecules and their phase sequence, as well as their physical properties, was also an important aim for the team.

The UW group is the second largest in terms of the number of active staff members (5 persons). Its activity was divided between synthesis and structural investigation, especially by X-ray methods. The remaining groups are smaller (1-3 academic scientists). They have synthesized LCs with no commercial potential but significant value for enhancing knowledge about the LC state; the exception is the WITI group, which prepared LC polymers for use in photovoltaic cells and lithium-ion batteries. Below, the main results of the mentioned teams are reviewed.

2. Military University of Technology

2.1. Initial period (1975-1980)

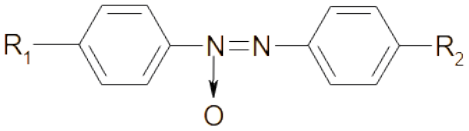
A multidisciplinary team under the direction of Prof. Józef Żmija, was established in 1975 at the Department of Chemistry and Technical Physics (now the Department of Advanced Technologies and Chemistry, MUT) for the development of technology for manufacturing LC displays and flat screens for civilian and military applications. At that time, as the head of the organic chemistry laboratory (comprising nine persons), I was included in this team and tasked with preparing the necessary LC materials. At the beginning, multicomponent nematic mixtures were needed in the temperature range of –20–80°C with different optical and dielectric properties for the twisted nematic effect (TN), the dynamic scattering effect (DS), the cholesteric-nematic transition effect (ChNT), and for temperature sensors (with the property of selective reflection of light). Next, our activity was extended to other optical modes: super twisted nematic (STN), optical birefringence (OCB), vertical alignment (VA), dual frequency addressing (DFA), surface-stabilized ferroelectric (SSFLC) and antiferroelectric (SSAFLC), and V-shaped switching.

George Gray's invention at the University of Hull (GB) was a starting point for our research. He patented and published the results of an investigation on the new classes of LC compounds: 4'-alkyl-4-cyanobiphenyls (nCB), 4'-alkoxy-4-cyanobiphenyls (nOCB), and 4"-alkyl-4-cyanoterphenyls (nCT), in which the aromatic rings are joined directly *via* a single bond [1].

In the synthesis method elaborated by G. Gray, the reaction of exchanging a bromine atom for the cyano group in 4'-alkyl- or 4'-alkoxy-4-bromobiphenyls did not proceed quantitatively, resulting in a purification problem for the product.

To explore more effective methods for nCB, nOCB, and nCT syntheses, we used iodo derivatives instead of bromo derivatives [2–3, Patent PL 113437]. Quantitative efficiency and higher-purity products were obtained; for example, our 5CB had a clearing point of 37°C, while Gray's had 35.5°C. In the same way, chiral analogues were obtained: R and S 4'-(2-methylbutyl)-4-cyanobiphenyl, 4'-(2-methylbutoxy)-4-cyanobiphenyl, and 4'-(1-methylheptyloxy)-4-cyanobiphenyl.

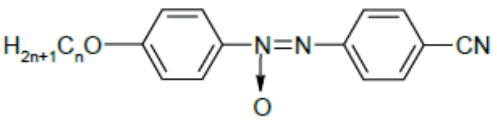
In 1976, the DOLAM factory in Wrocław acquired a license from a Japanese company for the production of LC displays used in electronic calculators. Then, the agreement between DOLAM and MUT was signed for the elaboration of an LC mixture able to replace the original one (it consisted of nitro esters and azoxy compounds). We developed the mixture named W-4 (Patent PL 124264), which was subsequently accepted by the licensor. As a result of the work on the W-4 mixture, we have become interested in azoxy compounds, as shown in formula 1.



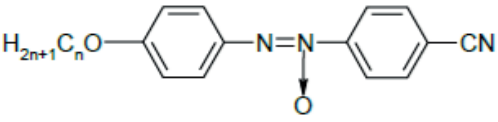
(1)

Several homologous series of azo and azoxy compounds with different terminal groups: $R_1 = H_{2n+1}C_n$, $H_{2n+1}C_nO$, $H_{2n+1}C_nOCOO$ and R_2 = CN, NO_2, C_mH_{2m+1}, OC_mH_{2m+1} were prepared.

Among compounds 1, the asymmetrically substituted dialkyl ones were the most interesting because they have very low melting points. Three homologous series were prepared: $H_{2n+1}C_n$ (n = 1, 2, 3), C_mH_{2m+1} (m = 1 – 10) [4]. The phase transitions for the homologous member with n = 3 and m = 5 are as follows: Cr 0°C N 65.5°C Iso, while for the chiral analogue with $R_1 = C_3H_7$ and $R_2 = CH_2CH^*(CH_3)C_2H_5$ are Cr 12.5°C N* 23°C Iso. Here, I would like to mention work [5] wherein the separation, spectral characterization (NMR, IR, UV and Vis), and dipole moments of pure position isomers (2) and (3) (n = 3, 9) were presented.



(2)



(3)

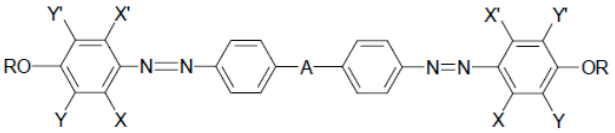
Azoxy compounds have a yellow color, which is their negative feature. Therefore, the LC mixture W-4 was later replaced by colorless LC mixture W-52 composed of cyano and isothiocyanato derivatives of 4-(trans-4'-alkylcyclohexyl)benzenes.

2.2. LC stationary phases for gas chromatography

The color of azo and azoxy compounds is not an obstacle to their application as stationary phases in gas chromatography. LC stationary phases have a feature that allows them to sense the shape of separated molecules. Longer and flatter molecules are kept in the columns for a longer time than shorter and spherical ones, so LCs are excellent for the analysis of mixtures consisting of various substituted benzene and naphthalene isomers,

as well as other multiring aromatic and hydroaromatic compounds. We were the pioneers of these investigations in Poland [6–7]. LC stationary phases were developed in various analytical and physicochemical aspects by Zygfryd Witkiewicz in his habilitation work, and they also held significant importance in his subsequent scientific activity. A great number of multiring liquid crystals with a broad temperature range of the nematic phase were synthesized. The nematic state ensures the best separation of analytes.

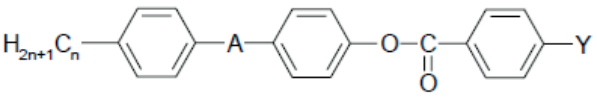
To obtain LC stationary phases with such properties, laterally substituted compounds, and often also with inserted flexible CH_2-CH_2 as bridge A into the rigid core, were prepared as a characteristic example (see azo compound, formula 4):



(4)

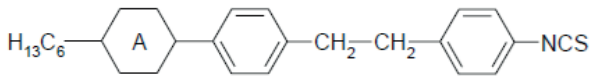
wherein R = H, H_9C_4, H_9C_4CO, $H_{11}C_5$-C_6H_4, H_3C-C_6H_4, Y,Y' = H, CH_3, Cl, CN, X,X' = H, CH_3 [8–10]. Compound 4 with R = C_4H_9, X = CH_3, Y = Y' = X = H has the following phase transitions: Cr 116°C N 229°C Iso. Analogous azoxy compounds were also prepared. It was found that the best separations were obtained in a supercooled nematic phase (a few degrees below the melting point), and much better results were observed when a bi-component or three-component stationary phase was used [11–12]. The stationary phases, such as compounds (4), have a high molecular weight, and the pressure of their own vapors is low at high temperatures, so they were found to be excellent for the analysis of mixtures composed of compounds with significantly different molecular weights, as they allow the temperature to be changed during analysis.

A very good separation of compounds with lower molecular weights, such as alkanes or benzene derivatives, was obtained on the three-ring liquid stationary phases of formula (5) [6] or formula (6) [13], as shown in the chromatogram in Fig. 1.



(5)

n = 2, A = -N=N(O)-, Y = CH_3: Cr 97°C N 263°C Iso



(6)

A = cyclohexane: Cr 58°C N 132°C Iso

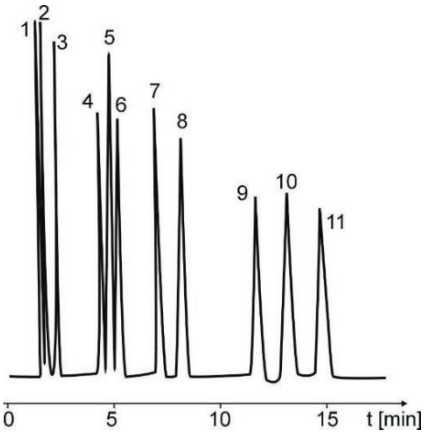
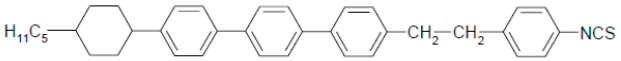


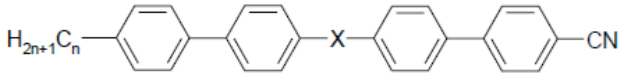
Fig. 1. The separation of alkanes and benzene derivatives on liquid stationary phase (6): 1 – hexane, 2 – heptane, 3 – octane, 4 – *m*-xylene, 5 – *p*-xylene, 6 – *o*-xylene, 7 – *m*-ethyltoluene, 8 – *p* and *o*-ethyltoluene, 9 – *m*-diethylbenzene, 10 – *o*-diethylbenzene, 11 – *p*-diethylbenzene [13]

The polar five-ring isothiocyanates (7) [14] and the four-ring ester (8) [15] also showed good properties as LC stationary phases [15] for the separation of multiring aromatic hydrocarbons [14]:



(7)

Cr 135°C SmA 163°C N 280°C Iso,



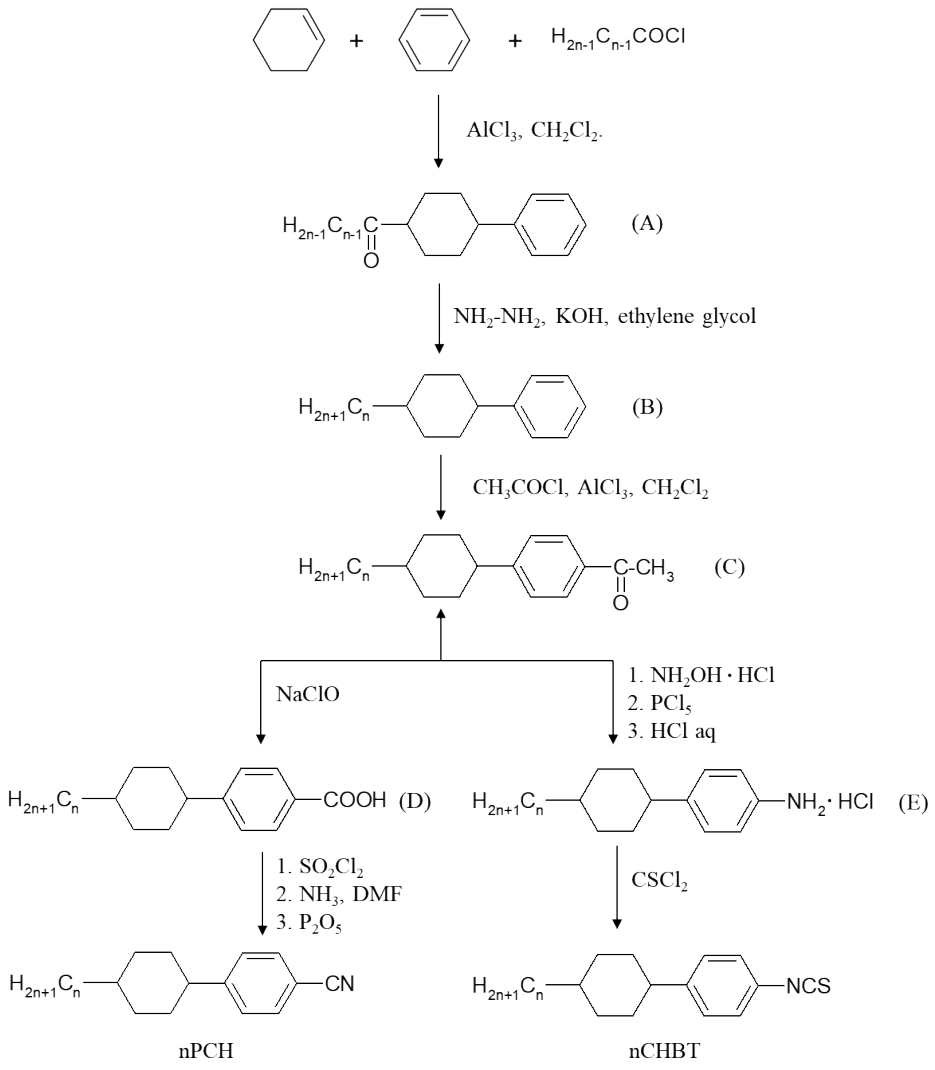
(8)

n = 5, X = COO: Cr 139°C SmA 166.5°C N 360°C Iso.

Jan Błądek proposed an alternative method for using LCs in the detection of organic compounds. He constructed a detector of organic vapors composed of microporous "Nucleopore" foil impregnated with a nematic or cholesteric LC [16–17]. He then proposed the use of this detector to visualize the separated compounds by thin-layer chromatography [18–20].

2.3. LC compounds and mixtures with low viscosity and low or medium birefringence

Taking into account the structure of nCB compounds, we concluded that if the first benzene ring in them were a cyclohexane, then such molecules would also be liquid crystals. At that time, it was not possible to purchase imported necessary substrates in Poland, and R. Eindenschink from Merck was the first who described these compounds [21]. We returned to this synthesis in 1978, when Tomasz Szczuciński joined our team. He proposed a preparation of *trans*-4-alkanoylocyclohexylbenzenes (Scheme 1, compound A) starting from cyclohexene, benzene, and alkanoic acid chlorides (Patent PL 128609).



Scheme 1. Route of syntheses of different derivatives of alkylcyclohexylbenzenes starting from simple and easily available substrates

Compound A was reduced to B, which after acylation to C became an important intermediate for 4-(*trans*-4'-alkylcyclohexyl)benzoic acids D [22], their esters [23], and 4-(*trans*-4'-alkylcyclohexyl)-1-cyanobenzenes (known as nPCH) [22] (one of the most important LCs for commercial applications), as well as to 4-(*trans*-4'-alkylcyclohexyl)-1-isothiocyanatobenzenes, termed by us as nCHBT. Their synthesis and properties were described in [24–30]. They have been protected by patents in Poland (PL 138287 and PL 137996) as well as in the DDR, USSR, USA, Japan, and Western European countries. Licenses were sold to Merck (FRG) and Hoffmann-La Roche (Switzerland). nCHBT compounds are the greatest achievement of our team.

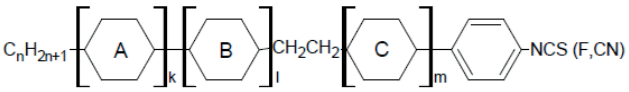
They have physicochemical properties that are very useful as components of LC mixtures, especially for TN and OCB effects. We have used them as the main component of mixtures manufactured in our laboratory. The comparison of the lowest melting members chosen from the nPCH and nCHBT homologous series is given in Table 1.

Table 1. The phase transition temperatures and the comparison of physicochemical properties of 6CHBT and 5PCH at 20°C, based on data provided in [26–27]

Properties	6CHBT	5PCH
Melting point, °C	12.5	31.0
clearing point, °C	43.0	55.0
Dipole moment [D]	3.4	4.7
Dielectric constant, $\varepsilon_{\|\|}$	12.0	17.0
Dielectric anisotropy $\Delta\varepsilon$	8.0	12.2
Refractive index n_e	1.67	1.61
Birefringence Δn	0.15	0.12
Shear viscosity η [mP · s]	13.3	21.5
Rotational viscosity γ [mP · s]	83.0	123.0
Elastic constants [10^{-12} N], k_{11}	8.57	8.98
k_{22}	3.70	4.75
k_{33}	4.51	2.03
Threshold voltage, V_{10}, [V]	1.63	1.55

nCHBT compounds have much lower bulk (shear) and rotational viscosities and a much lower ratio of elastic constants k_{33}/k_{11} than nPCH compounds, but their

birefringence Δn is higher. nCHBT compounds are dimerizing only to a small extent [30], and only the nematic phase is observed in the members of the homologous series up to n = 12. They exhibit very high chemical and photochemical stability, as well as high resistivity 10^{13} ohm/cm [31–33]. LCs with a terminal NCS group have become a dominant object of our research. A dozen homologous series of bi-, tri-, and tetra-ring compounds with a single bond or CH_2-CH_2 bridge between B-C rings, and an NCS terminal group (also F, CN) have been prepared; see formula (9):



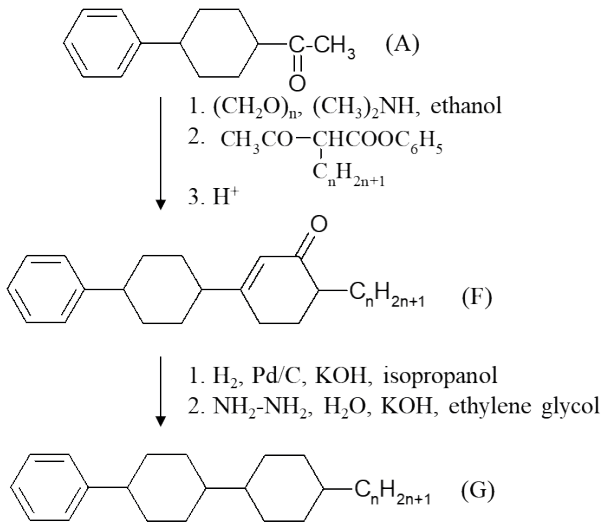
(9)

in which rings A and B are cyclohexane, bicyclo[2,2,2] octane, 1,3-dioxane, 1,3-pyrimidine ones, and indexes k = 1, l and m denote 0 or 1 [34, Patents PL 256832, PL 263243].

Phase transition temperatures for a few characteristic compounds (9) are listed below:
A = cyclohexane, n = 5, l = 0, m = 0: Cr 38.5°C N 47.0°C Iso;
A = bicyclo[2,2,2]octane, n = 5, l = 0, m = 0: Cr 64.0°C N 101.0°C Iso;
A = C = cyclohexane, B = benzene, n = 4, l = 1, m = 1: Cr 87.5°C N 260°C Iso.

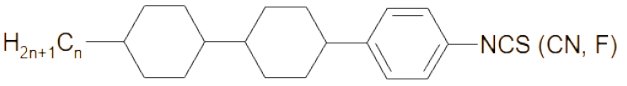
The last family of LC compounds was protected by Polish and foreign patents, and the license was sold to Dainippon Inc.

Compound A (n = 2), shown in Scheme 1, turned out to be a very important intermediate for the syntheses of different classes of LCs. In collaboration with Valery Bezborodov from the University of Minsk (Belarus), we have developed a method for the synthesis of bicyclohexyl derivatives [35–36], as shown in Scheme 2.



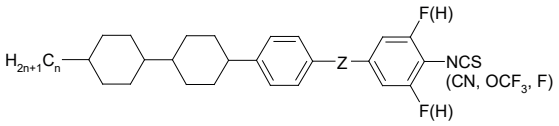
Scheme 2. The elaborated method of synthesis of compounds with *trans,trans*-bicyclohexane moiety using Mannich salts

Further functionalization of the compound G resulted in compounds with formulae (10) or (11). They are characterized by a low melting point and a very broad range of the nematic phase [37–40]. Compounds (11) are very useful components for DFA mixtures [39].



(10)

see example n = 6, NCS: Cr 47.7°C N 223°C Iso;



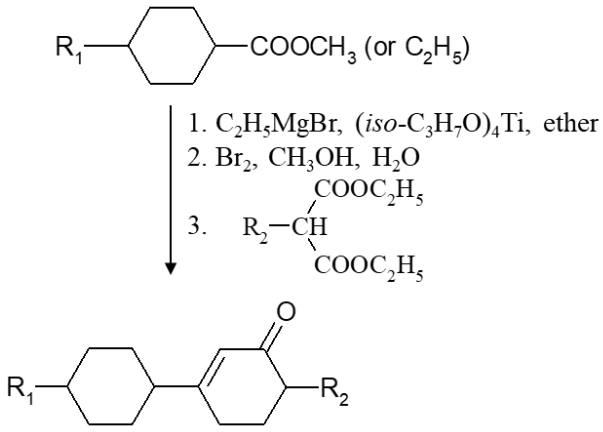
(11)

see examples: n = 3, F, F, NCS, Z = single bond: Cr 80.2°C N 350°C Iso;

n = 3, F, F, F, Z = single bond: Cr 103.1°C N 260°C Iso;
n = 3, F, H, OCF_3, Z = single bond: Cr 114.6°C N 280°C Iso.

Cyclohexenones F, Scheme 2, enable the preparation of liquid crystals containing laterally substituted cyclohexane or benzene rings [40–44].

A second method for creating molecules with cyclohexane-cyclohexene or bicyclohexane rings was also developed in collaboration with Gienadij Sasnouski from the University of Minsk, as shown in Scheme 3.



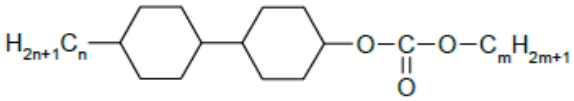
Scheme 3. Recommended synthesis route of cyclohexenones wherein R_1 is an alkyl or cycloalkyl group with the use of Kulinkovich reaction [45]

In this method, alkylcyclohexanoic acid ester was treated with ethyl magnesium bromide in the presence of isopropyl titanate and then with malonic acid diester, and 3,6-disubstituted cyclohexenone was obtained, which was a substrate for bicyclohexane LCs [46–48].

In the early 1990s, we started to cooperate with Tomasz Wolinski's team from the Technical University of Warsaw, who was investigating photonic liquid crystal fibers (PLCF). For their research, we developed LC mixtures having, in some temperature range, an ordinary refractive index lower than 1.46 (a value characteristic

for quartz glass), $n_o < n_q$. Such LCs placed in the outer part (in holes) of PLCF enabled the observation of light propagation according to the mechanism of total internal reflection (TIR) – all wavelengths of light are transmitted freely through quartz fiber – while for LCs with $n_o > n_q$, according to the mechanism of the photonic band gap (PBG), only the selected wavelenghts of light are transmitted through optical fiber [49–50].

To achieve this purpose, a new family of LCs was prepared [51], as shown in formula (12).

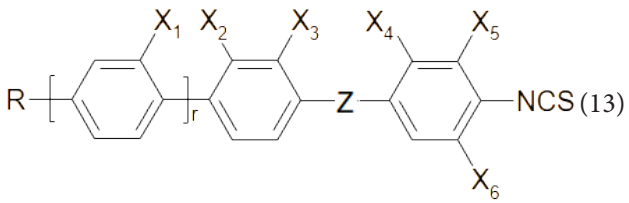


(12)

For compound (12) with n = 5 and m = 2, the value n_o = 1.4482, measured at a temperature of 84.1°C, is the lowest among known LCs. Mixture W-1550 was formulated with positive dielectric anisotropy from compounds (12) and *trans,trans*-4'-propyl-4-cyanobicyclohexane exhibiting $n_o < n_q$ at temperatures higher than 34°C [51]. Subsequently, several mixtures were prepared, in which the temperatures of the transition from $n_o > 1.46$ to $n_o < 1.46$ are between –13°C and 48°C [52].

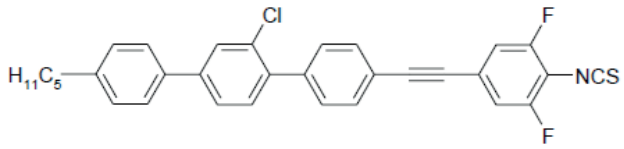
2.4. LCs with low viscosities and high birefringence (Δn)

We have synthesized LC compounds with high birefringence in order to formulate mixtures with n = 0.3–0.7, needed for displays with short switching times, for devices working at GHz and THz radiation, and for metamaterials. We supplied them to many domestic and foreign laboratories, e.g. to Janusz Parka (MUT), Shin-Tson Wu (University of Central Florida), and Martin Koch (University of Marburg). Molecules with large Δn might have a long conjugated system of π bonds; they typically contain a few aromatic (benzene) rings joined directly or *via* a triple bond, and an NCS terminal group. Such a structure involves an increase in melting points and the presence of smectic phases. To counteract these disadvantages, laterally substituted compounds by F, Cl atoms and a CH_3 group belonging to tolanes, phenyltolanes, biphenyltolanes, terphenyltolanes, biphenyls, terphenyls, quaterphenyls, and quintaphenyls with general formula (13):



(13)

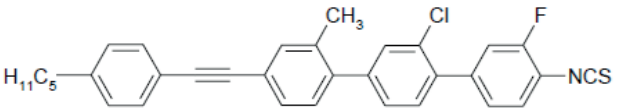
wherein R = alkyl or thioalkyl, r = 0, 1, 2, $X_1 – X_6$ = H, F, Cl, or CH_3, Z = single or triple bond (C≡C), were synthesized [53–66]. Compound (13a) is an example of a nematic compound belonging to setup (13).



(13a)

Cr 95.9°C N 280°C Iso.

Many other compounds similar to (13) but with a triple bond in the other position of the molecule, see formula (14), or with two triple bonds were prepared [57, 64].



(14)

Cr 83.5°C N 211.9°C Iso.

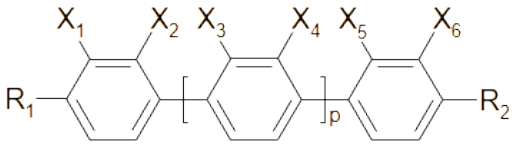
High birefringent compounds were described in detail in our review paper [66]. High birefringence mixtures formulated from isothiocyanate compounds (13) have significantly better properties than those prepared from similar cyano compounds; see examples listed in Table 2.

Table 2. Comparison of properties of mixture D [65] and W-1825 [67–70] composed of isothiocyanates with the often used mixture E-7 composed of cyanides

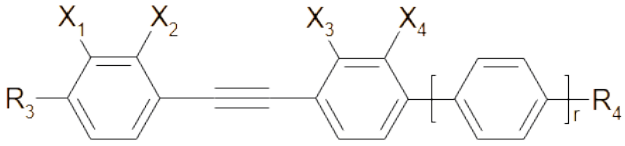
property	D	W-1825	E-7
T_m (°C)	< –20	–12	–10
T_{N-I} (°C)	97.2	136.0	60
Δn (20°C)	0.32	0.42	0.29
Δε (20°C)	21.6	17.0	14.1
η (mPa · s, 20°C)	17.0	31.0	40.0

Isothiocyanate mixtures not only have lower viscosity and higher birefringence, but their dielectric anisotropy may sometimes also be greater. They are especially useful for GHz and THz applications due to their low absorption and dielectric losses [68–69]. Mixture W-1825 was identified as the most suitable for these purposes [71]. Mixtures comprising simultaneously isothiocyanates and cyanides exhibit very low dichroism of absorption coefficients (Δα~0) [72].

Four-ring quaterphenyl and biphenyl tolane isothiocyanates, mentioned above, which exhibit positive dielectric anisotropy, were also used as the first component of DFA mixtures [39, 73]. The second component of these mixtures, with negative dielectric anisotropy, was composed of biphenyls, terphenyls, tolanes, and phenyl tolanes laterally substituted by fluorine atoms; see formulae (15) and (16):



(15)



(16)

wherein p = 0, 1, 2, 3, r = 0, 1, 2, R_1 and R_2 mean an alkyl, alkynyl, alkoxyl, alkyl carbonate group [39, 74–80].

Such bi-component LC mixtures change their dielectric properties versus the frequency of an electric field in the manner presented in Figure 2.

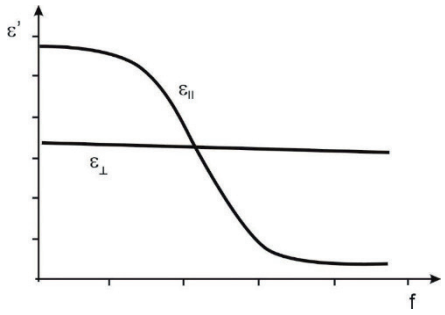


Fig. 2. The dependence of dielectric constants upon the frequency of an electric field

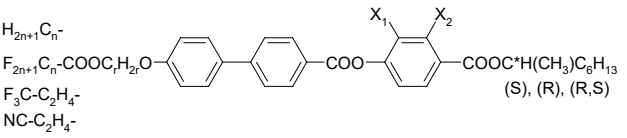
For lower frequencies Δε > 0, while for higher frequencies Δε < 0, and not only on-time (t_{on}) but also off-time (t_{off}) are dependent on the electric field, and the symmetrization of response times is achieved. Compounds (15) and (16) were useful not only for the formulation of DFA mixtures [39, 73], but also for VA [66], ferroelectric [80], and induced smectic A mixtures [81–83].

Mixture A9 [39] is a characteristic mixture with Δε < 0 elaborated by us:

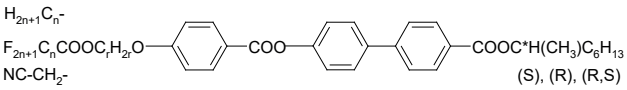
T_m < –20°C, T_{N-I} = 72.7°C, Δn (20°C) = 0.29, Δε (20°C) = –5.44, η (mPa · s, 20°C) = 29.6.

2.5. Ferro- and antiferroelectric liquid crystals

We started syntheses of compounds with ferroelectric properties in the mid-1980s for our own and other physics teams. Multicomponent mixtures comprising chiral and achiral esters have been elaborated first. Mixture W-22 is a characteristic example [84–86]. Then, the mixtures composed of achiral pyrimidines or achiral terphenyls having a smectic C phase (SmC) and various chiral dopants were formulated [80, 87]. Research on antiferroelectric compounds and mixtures began in the early 1990s and soon became one of the main directions of our activity. The homologous series of biphenylates and benzoates, see formulae (17) and (18), were synthesized [88–92]:



(17)



(18)

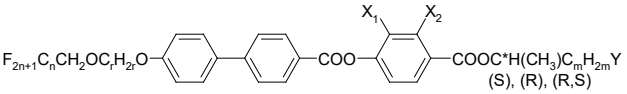
wherein n = 1 – 8, r = 2 – 9, X_1 and X_2 are H or F atoms. They were prepared from chiral (R) or (S) or achiral (racemic R,S) octanol-2, and they contained in the second terminal chain $F_{2n+1}C_nCOO$ or $H_{2n+1}C_nCOO$ or $F_3CC_2H_4COO$ or $NCCH_2COO$ unit. Fluorinated compounds (17) and (18) have low melting points and an antiferroelectric phase (SmC^*_a) in a broad temperature range; see the examples below:

(17) (S): F_7C_3COO, r = 6, X_1, X_2 = H: Cr 29.4°C SmC^*_a 114.4°C SmC* 122.5°C SmA 129.3°C Iso;

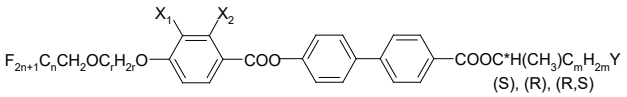
(18) (S): F_7C_3COO, r = 6: Cr 27.6°C SmC^*_a 91.1°C SmC* 118.1°C SmA 118.5°C Iso.

It was found that these new esters, with the presence of perfluorinated $F_{2n+1}C_nCOO$ unit in the achiral terminal chain, exhibited a high tilt of molecules in the smectic layers, near or equal to 45 degrees. They were termed orthoconic antiferroelectric liquid crystals (OALCs). These materials are a uniaxial optical medium in surface-stabilized cells and planar geometry (SSOALC) [93–95] and behave as an isotropic medium. Defects on the cell surfaces are not seen, and displays with an excellent dark state and high contrast may be manufactured. Classical low-tilted antiferroelectrics are biaxial, and poor contrast is seen in displays. The US patent claiming the use of OALCs for displays was obtained from our and S. T. Lagerwall's (Göteborg University) patent [US 69119950].

Then similar families of esters of general formulae (19) and (20) were prepared:



(19)



(20)

wherein n = 3 or 4, r = 2 – 8, m = 1 – 9, X_1, X_2 = H or F independently, Y = H or cyclohexyl [96–100].

Here, the easily hydrolyzable unit $F_{2n+1}C_nCOO$ was exchanged for a more stable $F_{2n+1}C_nCH_2O$ unit. Compounds (19) and (20) not only have higher chemical stability, but the anticlinic order is present both in optically active (R) or (S) isomers and in their racemic mixtures (R,S) without optical activity. This feature enables the

formulation of OAFLC mixtures cheaply and with a longer helical pitch p [101]. It was found that the length of the oligomethylene spacer r determines the value of helix pitch p and its temperature dependence, as well as the phase sequence. The pitch p increases with temperature for compounds with r < 5, while for compounds with r > 5, it decreases with temperature, and for r = 5, two branches of p upon temperature are observed, and the helix becomes unwound in between [97, 102]. Moreover, compounds with r = 3 exhibit a direct transition from SmC^*_a to Iso, and mixtures with such a transition show very small shrinkage of smectic layers upon temperature change [103–104]. Mixture W-1000 is a characteristic example of a mixture with a long helix pitch p [105]. Crosslinking antiferroelectric mixtures by polymeric network involves the symmetrization of switching times t_{on} and t_{off} [106]. Antiferroelectric liquid crystals investigated up to the year 2010 were described in detail in Ref. [107].

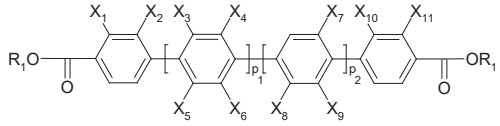
2.6. Optically active compounds and blue phases

Optically active compounds (chiral compounds) were the object of our interest throughout the entire period of our activity. We needed them as dopants for TN and STN mixtures, for mixtures exhibiting selective reflection of light used in thermometric and thermographic applications, for fiber optic sensors, and as components of ferroelectric and blue phase mixtures or dual frequency mixtures for the protection of eyes against laser attack. For most of the mentioned applications, chiral compounds with a large helical twisting power (HTP) were required.

$$\mathrm{HTP}\left[\mu m^{-1}\right]=\frac{1}{\mathrm{pcr}}$$

where p – helix pitch measured by a selective reflection method, c – mole ratio of optical compound in liquid crystal solvent, r – enantiomeric excess.

Many dozens of R and S enantiomers were prepared, and much work was dedicated to the compounds expressed by the general formula (21) [108]:



(21)

substituted by two or four fluorine atoms or by two methyl groups in the positions X_1–X_{11}, R_1 is a chiral alkyl coming from different chiral alcohols, $p_1 = p_2 = 0$ or $p_1 = 0$ and $p_2 = 1$ or $p_1 = 1$ and $p_2 = 0$. Compounds (21) show HTP in the range of 10–50 μm^{-1}, depending on the position and number of substituents X_1–X_{11}. The syntheses of chiral 1-methylalkanol and 1-methyl-ω-cyclohexyl alkanols were elaborated from chiral esters of lactic acid [100].

Blue phase mixtures existing in a broad temperature range, composed of fluorinated derivatives of biphenyls, terphenyls and quaterphenyls, and chiral compounds (21), crosslinked with a composition of mono-, bi-, and triacrylates, were elaborated. They show positive dielectric anisotropy or negative dielectric anisotropy and may also change the sign of dielectric anisotropy from positive to negative (DFA mixtures) [109–110]. Their total switching times $t_{on} + t_{off} < 300$ μs.

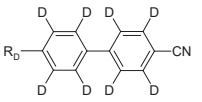
2.7. Nematic mixtures transparent in infrared

Nematic mixtures with increased transparency in the near-infrared (NIR) and mid-infrared (MIR) have been developed [111–115]. The mixture of the first group was formulated from fully deuterated compounds in terminal alkyl chains as well as in a rigid benzene core.

A new effective preparative method for obtaining deuterated alkyl chains was proposed starting from 1,3-diynes [115]. The compounds with positive (22 and 23) as well as negative (24 and 25) dielectric anisotropy were prepared.

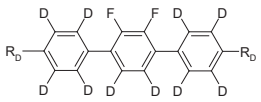
Δε > 0 Δε < 0

Δε > 0

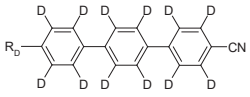


(22)

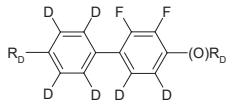
Δε < 0



(24)

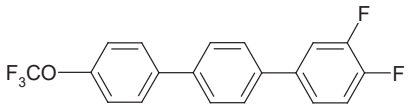


(23)



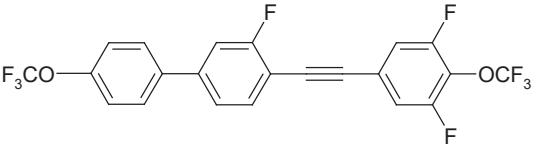
(25)

The mixtures of the second group were manufactured from compounds in which C-H bonds in the tails were replaced by C-F bonds; however, only compounds with very short terminal chains exhibited nematic behavior [116]. Their examples are given below for positive (formulae 26 and 27) and negative (formula 28) dielectric anisotropy.



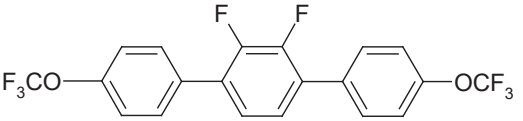
(26)

Cr 81.0°C N 84.7°C Iso



(27)

Cr 70.9°C N 83.7°C Iso



(28)

Cr 83.0°C N 86.0°C Iso

Such three-ring compounds mixed with bi-ring analogues enable the formulation of nematic mixtures with a melting point below 0°C.

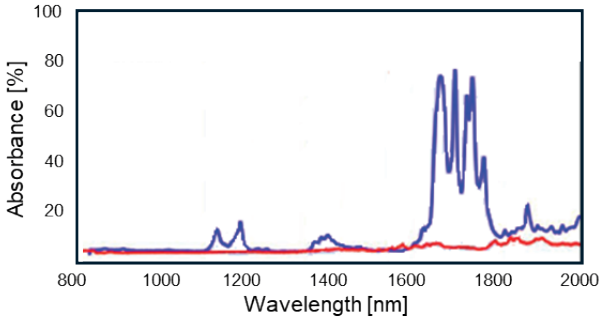


Fig. 3. The comparison of the NIR spectra of a mixture composed of fully deuterated compounds (red) with an analogous one comprising only normal compounds with C-H bonds (blue)

2.8. Non-additive properties of liquid crystal compounds in mixtures. Induction of new phases. Reentrant nematic phase

During the formulation of mixtures, we sometimes observe that their properties differ from what would be expected based on the properties of the individual components, and new phases may form. We have devoted considerable effort to understanding such atypical behaviors, and the results obtained are reviewed in Ref. [117]. Here, they are presented in short form. Five types of non-additive behaviors appearing in liquid crystal mixtures tested by us are discussed below.

2.8.1. Induced monolayer smectic A phase (SmA_1)

It was found that if polar nematic compounds such as nCB, nOCB, or nCHBT were mixed with less polar 4'4-dialkyl or 4'-alkyl-4-alkoxyazoxybenzenes [118], the SmA phase appeared in the central part of the diagram, with a maximum of temperature and density in SmA_1-N and N-Iso transitions for the almost equimolar concentration; see Fig. 4a.

A similar type of the SmA_1 phase induction was observed in mixtures comprising laterally substituted by a few fluorine atoms 4'4-dialkyl, 4'-alkyl-4-alkoxybiphenyls, 4'4-dialkyl, 4'-alkyl-4-alkoxytolanes having $\Delta\varepsilon < 0$ as one component, and a multiring compound with $\Delta\varepsilon > 0$ comprising OCF_3 group in one terminal chain [81–83]. Strong enhancement of the temperature range of the SmA_1 phase was also observed in the mixture composed of 4'-alkyl-3-fluoro-4-alkoxybiphenyls and 4"-alkyl-3-fluoro-4-alkoxyterphenyl as the first component, and 4'-alkyl-3,4,5-trifluorobiphenyls and 4"-alkyl-3,4,5-trifluoroterphenyls. Such SmA_1 mixtures doped with ionic compounds show very high chemical and photochemical stability and have been proposed for use as smart windows or displays with memory [119, Patent PL 240079].

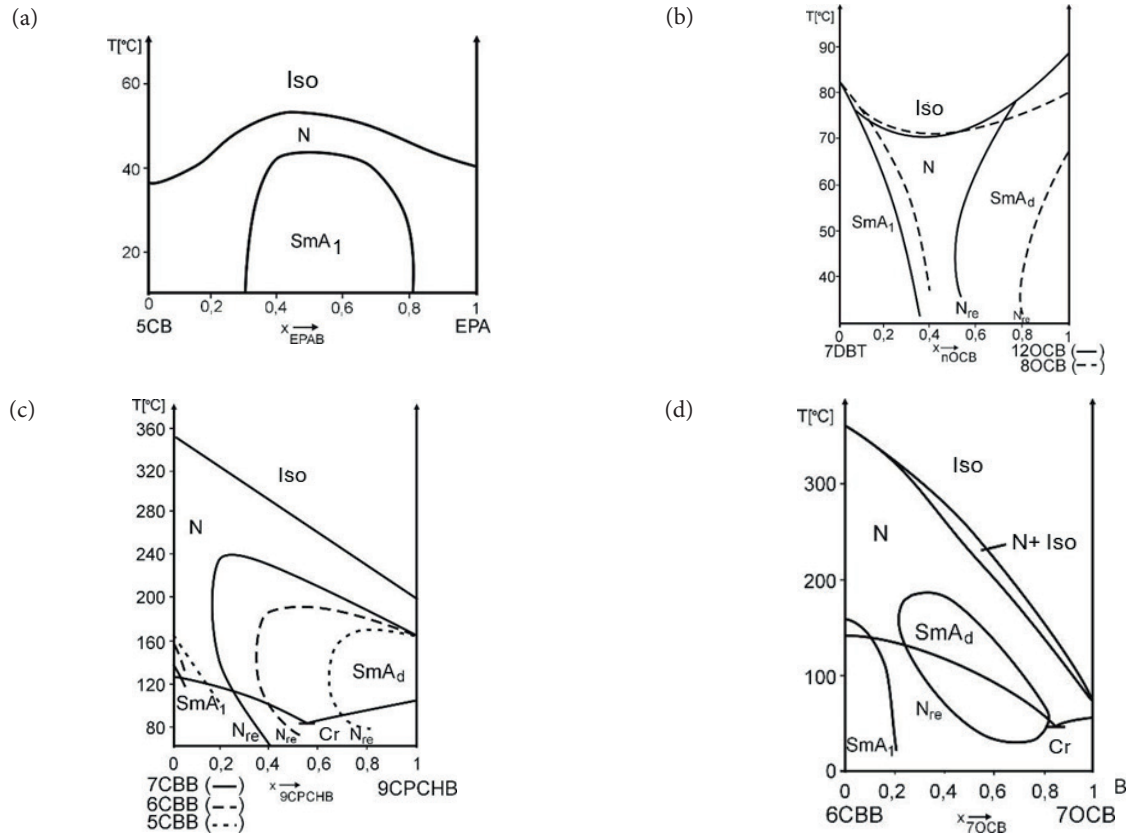


Fig. 4. The examples of non-additive properties of liquid crystal compounds in bi-component mixtures: (a) – induced monolayer SmA_1 phase, (b) – induced nematic phase, (c) – enhanced SmA_d phase, (d) – induced SmA_d phase; EPAB – 4'-ethyl-4-pentylazoxybenzene, 7DBT – 5-heptyl-2-(4'-isothiocyanatophenyl)-1,3-dioxane, 9CPCHB – 4-cyanophenyl-4-(*trans*-4'-nonylcyclohexyl)benzoate

2.8.2. Induced or enhanced nematic phase

A strong destabilization of smectic phases was observed in the mixture composed of partially bilayer smectic A (SmA_d) compounds with SmA_d-Iso or SmA_d-N-Iso phase sequences with terminal groups CN, NO_2, or COH as one component, and SmA_1 compounds with SmA_1-Iso or SmA_1-N-Iso sequences (containing in the terminal position an NCS, Cl, J, F, or $COCH_3$ group) as the other component [120–123], Fig. 4b.

The smectic phases are separated by a nematic gap. The nematic phase in the gap exhibits properties similar to those of the normal nematic phase.

2.8.3. Enhancement of smectic A_d phase and presence of reentrant nematic phase

Strong enhancement of SmA_d phase and the presence of a reentrant nematic phase were observed in the bi-component mixture composed of 4'-cyanobiphenyl-4-yl alkylbiphenyl-4-carboxylate (nCBB, for n = 4, 5, 6, 7, with SmA_1-N-Iso phase sequence, and for n = 8, 9 with N_{re}-SmA_d-N-Iso phase sequence). Similar behavior was observed in the mixture of nCBB compounds (n = 4, 5, 6, 7) with the smectic members chosen from homologous series of 4-cyanophenyl or 4-nitrophenyl 4-(4'-*trans*-alkylcyclohexyl)benzoates, or analogous phenyl 4-(4'-*trans*-alkylcyclohexyl)benzoates with terminal groups NCS, Cl, F, $COCH_3$, but only for members n > 7, Fig. 4c [124–127].

2.8.4. Induced partially bilayer smectic A (SmA_d) phase

The induction of SmA_d phase in the form of an "island" surrounded by a nematic "sea" was observed in the mixtures of compounds nCBB, with the phase sequence SmA_1-N-Iso (n = 4, 5, 6, 7), with nematic members of nCB, nOCB compounds, or similar bi-ring 4-cyanophenyl benzoates [128–134], Fig. 4d.

It was found that the presence of a cyclohexane ring in the bi-ring cyano molecules increases the induction of SmA_d phase, but the presence of an aromatic polar ring (pyridine or pyrimidine) decreases the induction of SmA_d phase [132].

2.8.5. Induction of antiferroelectric phase

The induction of the antiferroelectric phase was observed in bi- and multicomponent mixtures, wherein one component was chosen from chiral SmC* compounds with a partially fluorinated terminal chain, and the other component was chosen from chiral SmC* compounds with a terminal chain containing only hydrogenated carbon atoms [135–137]. A pair of such compounds, giving the induction of an antiferroelectric phase, is presented in Fig. 5.

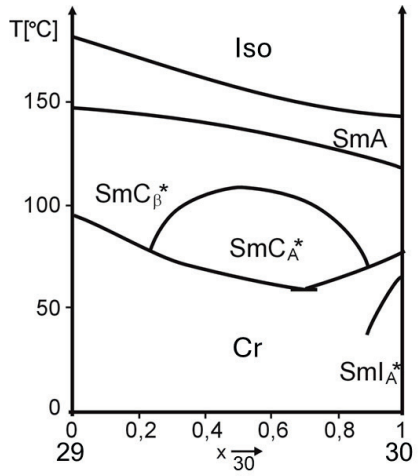
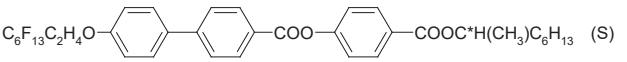
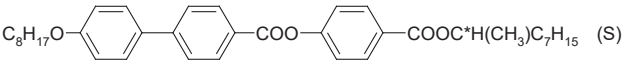


Fig. 5. The induction of antiferroelectric phase (SmC^*_a) in a mixture consisting of compounds with ferroelectric phase (SmC*) [137]



(29)



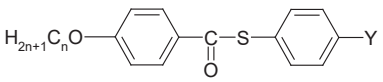
(30)

The influence of different structural units and optical activity on the ability to induce the chiral SmC^*_a phase (antiferroelectric) is discussed in Ref. [137].

3. University of Siedlce

In 1975, Professors Janina and Jerzy Janik from the Jagiellonian University inspired a young married couple, Janusz and Mirosława Chruściel, employed at the newly established university in Siedlce, to synthesize substances necessary for research using neutron scattering and dielectric spectroscopy methods.

4-Pentylphenyl 4-heptyloxythiobenzoate (formula (31), n = 7, Y = C_5H_{11}) was the first compound that they prepared. It exhibited SmC and SmA phases [138].

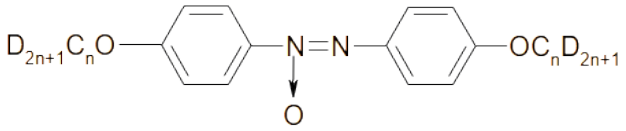


(31)

Then, the further members of the homologous series (31) ((31a) and two others, (31b) and (31c)) have been synthesized:

(31a) – n = 4 – 12, Y = C_5H_{11} [139]
(31b) – n = 4 – 12, Y = Cl [139]
(31c) – n = 4 – 12, Y = NO_2 [140]

The synthesis of selectively deuterated azoxy compounds in the terminal chains, as shown in formula (32), was performed in parallel by M.D. Ossowska-Chruściel [141, Patent PL 121096].



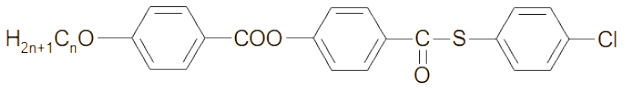
(32)

Then, her coworker K. Lipiński prepared two thiobenzoates, (31a) (n = 7 and n = 8), with deuterated alkoxy and alkyl chains (D = 30 and D = 34, respectively) [142].

The syntheses of chiral two-ring and chiral and achiral three-ring thioesters have become a characteristic feature of Chruściel's further activity.

They synthesized the following groups of thioesters:

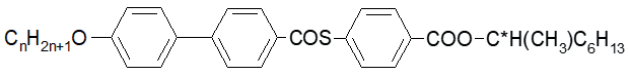
– the optically active analogues (31a) and (31b), in which the $H_{2n+1}C_nO$ terminal group was exchanged for the chiral (S)-1-methylheptyloxy group [143–145];
– those of formula (33) [144]:



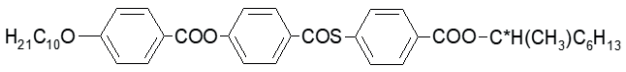
(33)

and its chiral analogue with (S)-1-methylheptyloxy terminal group instead of $H_{2n+1}C_nO$;

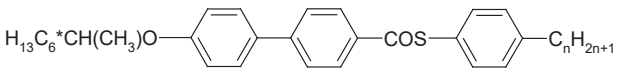
– those of formulae: (34), (35), (36):



(34)



(35)

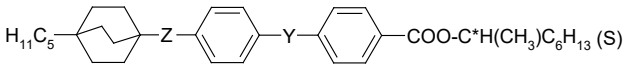


(36)

wherein n = 4 – 10.

The compounds (34)–(36) form ferroelectric (SmC*) and antiferroelectric (SmC*$_a$) phases [145–148].

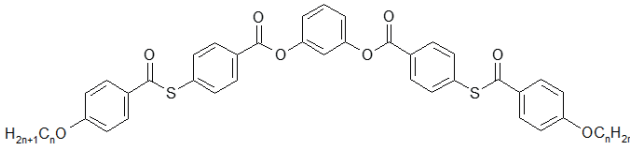
– those of formula (37) – the derivative of bicyclo[2.2.2]octane:



(37)

wherein Z = COO or COS and Y = COO or COS [149];

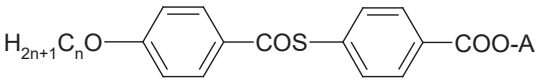
– those of formula (38) with bent-core (banana shape) molecules [150–154]:



(38)

and the substituted compounds (38) by a Cl atom or a CH_3 group in the central benzene ring at positions 2, 4, or 5. B_2 phase was observed here [152];

– those of formula (39) with chiral group A derived from cholesterol, menthol, thymol, carvacrol, or lithocholic acid ester (n = 7 – 10, 12) [155].

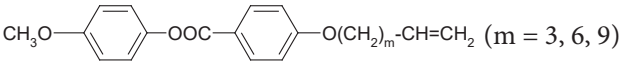


(39)

4. Warsaw University of Life Sciences

The investigation of LCs has been conducted by Ewa Białecka-Florjańczyk and Andrzej Orzeszko at the Department of General Chemistry of Warsaw University of Life Sciences (SGGW). E. Białecka-Florjańczyk has synthesized the following families of LCs:

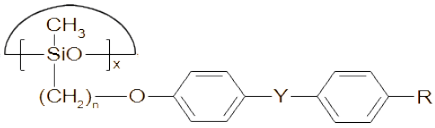
– different mesogenic alkenes with a double bond in the terminal position of molecules; see formula (40) as a characteristic example:



(40)

These monomers were used by W. Stańczyk for the preparation of comb-like liquid crystal polymers and oligomers [156–158]:

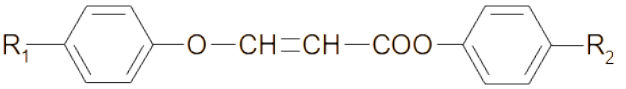
– cyclic oligosilanes with chiral group R [159–160]; see formula (41):



(41)

wherein x = 4, 5, 6, n = 5, 8, 11, Y = single bond, or COO or CH=CHCOO bridge and
R = $CH{=}CHCOOCH_2C^*H(CH_3)CH_2CH_3$, $CH{=}CHCOOC_6H_4COOC^*H(CH_3)CH_2CH_3$, $COOCH_2C^*H(CH_3)CH_2CH_3$, $OOCC^*H(Cl)CH_2CH(CH_3)_2$, $OOCC^*H(Cl)C^*H(CH_3)CH_2CH_3$;

– phenyl esters of (E)-phenoxyacrylic acids; see formula (42) [161]

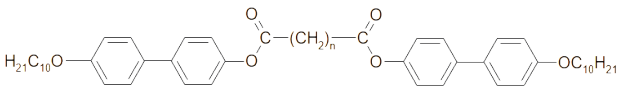


(42)

wherein $R_1 = H_{21}C_{10}O$, $H_9C_4OC_6H_4$, $H_{21}C_{10}OC_6H_4$, NC-, and $R_2 = C_6H_4CN$, $C_6H_4OC_4H_9$, $C_6H_4OC_{10}H_{21}$.

The compounds (42) with terminal groups CN or NO_2 form a partially bilayer smectic A phase (SmA_d); see the example: Cr 85.4°C SmA_d 89.6°C Iso for $R_1 = H_{21}C_{10}OC_6H_4$ and R_2 = CN;

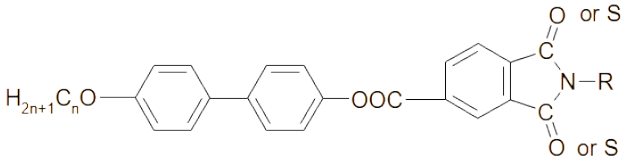
– bis-mesogenic diester molecules separated by a flexible polymethylene spacer, formula (43), n = 3 – 12 [162].



(43)

The influence of flexible spacers n on the ability to form LC phases was tested. Clearing points strongly decrease with the increase of spacer length n.

A. Orzeszko synthesized many estroimides, estrothioimides and estrodithioimides [163–166]. The compounds prepared from trimellitic acid were the most interesting mesogens; for example, see the compounds given by formula (44). The dithioimides have the lowest melting point.

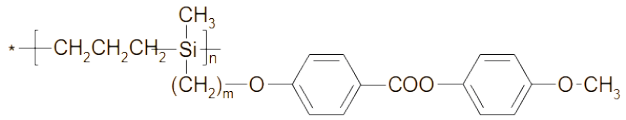


(44)

n = 10, dithioimide: Cr 82ºC N 171ºC Iso.

5. Centre of Molecular and Macromolecular Studies in Łódź

The investigation of liquid crystal polymers was conducted by W. Stańczyk's team in the years 1990–2015. The series of polycarbosilanes: poly(1-methyl-1-silaethylene), poly(1-methyl-1-silapropylene), poly(1-methyl-1-silabutylene), poly(1-silabutylene), and polyethylene substituted with a silyl group have been prepared. These polymers had an active Si-H bond, which enabled them to join with the double bond of mesogenic molecules (40), obtained by E. Białecka-Florjańczyk, and comb-like polymers were formed [156–158, 167]; see formula (45) as an example.



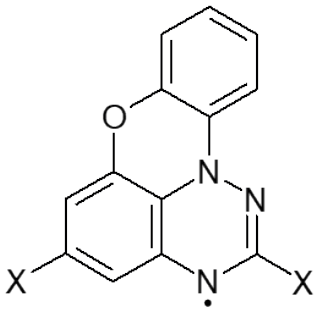
(45)

It has the following phase transition temperatures for m = 8: Cr 5ºC Sm 82.6ºC Iso. The molecular weight of this polymer was 40000.

Piotr Kaszyński joined the CMMS in 2015, after his thirty-year work at U.S. universities, continuing his previous research on LCs with a free radical moiety or a boronic cluster in the rigid core of LC molecules.

The prepared paramagnetic disc-like LCs containing dibenzo(c,e)thiazinyl radical or benzo[1,2,4]thiadiazinyl radical at Nashville University had poor chemical stability, which was not sufficient for practical applications [168, 169].

Progress was achieved when stable verdazyl or Blatter radicals were inserted into LC molecules [170–175]. The new planar Blatter radical with a 19 π delocalized conjugated electron system was developed and used to obtain bent-core LCs; see formula (46):



(46)

wherein X = $H_{25}C_{12}OC_6H_4COOC_6H_4$ or $H_{2n+1}C_nOC_6H_4CO$-$OC_6H_4COOC_6H_4$ (n = 12 or 16) or $F_{25}C_{12}C_6H_{12}OC_6H_4CO$-$OC_6H_4$. The last compound has the following phase sequence: Cr 152°C SmC 162°C SmA 243°C Iso.

Compared to the classical Blatter's radical, the rotation of the upper benzene ring was hindered by the connection of the two benzene rings by means of an oxy bridge (-O-). The planarization of the molecule results in higher stability of mesophases and enables the formation of better-ordered paramagnetic banana and columnar LCs. It indicated the way to further syntheses of such materials. Then, multicomponent banana-shaped LC mixtures exhibiting photoconducting and paramagnetic properties, as well as a polar antiferroelectric phase, were prepared [175].

P. Kaszyński had put much effort into the elaboration of syntheses of new classes of rod-like LCs with 1,10-dicarborane or 1,12-dicarborane rings inserted into their rigid cores: $C_2B_8H_{10}$ (Fig. 6a), $C_2B_{10}H_{12}$ (Fig. 6b), [176–178], or a carborane anion: [closo-1-CB_9H_{10}]$^-$ (Fig. 6c),

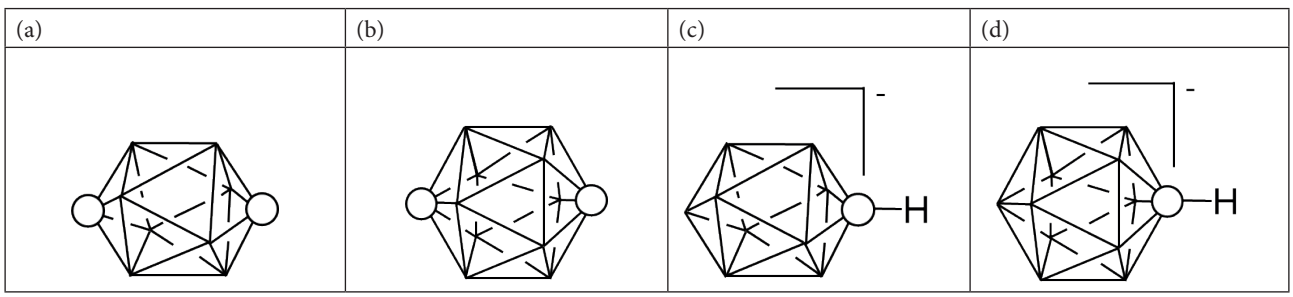
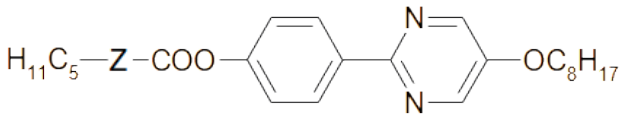


Fig. 6. Structures of non-ionic dicarboranes: a – $C_2B_8H_{10}$ and b – $C_2B_{10}H_{12}$, and their mono-anionic form c – [closo-1-CB_9H_{10}]$^-$ and d – [closo-1-$CB_{11}H_{12}$]$^-$

[closo-1-$CB_{11}H_{12}$]$^-$ (Fig. 6d) [179–182], or a carborane dianion [closo-$B_{10}H_{10}$]$^{-2}$ [183].

The successful functionalization of σ aromatic carborane clusters shown in Fig. 6a, b, c, d enabled him to synthesize more than two hundred new liquid crystal compounds with low polarity or high polarity (anionic or zwitterionic). Owing to the large volume of the borane unit, its presence in molecules results in a decrease in the stability of all liquid crystal phases, but the nematic one is less decreased than the other, more ordered phases.

The phase transitions for four compounds expressed by formula (47) are listed below to illustrate this feature.

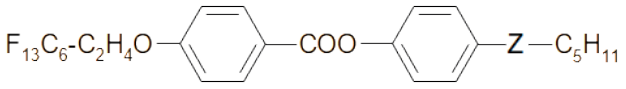


(47)

Symbol Z means the carborane cluster, the same as in Fig. 6a or b (compounds 47a and 47b), or the bicyclo[2.2.2]octane ring (47e) or benzene ring (47f).
(47a) – Cr 104ºC N 175ºC Iso;
(47b) – Cr 79ºC N 152ºC Iso;
(47e) – Cr 100.5ºC (SmG 95.5ºC) N 222ºC Iso;
(47f) – Cr 67ºC (SmA 63ºC) N 171ºC Iso.

The stability of the nematic phase follows the order: 47e > 47a > 47f > 47b.

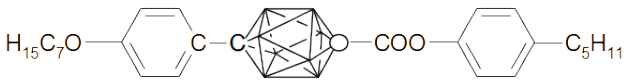
The same relation was observed in the compounds with a fluorinated terminal chain; see formula (48).



(48)

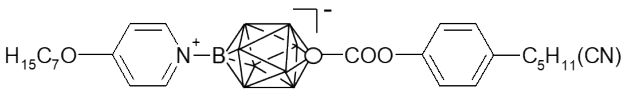
Compounds (48) with Z = benzene ring (48f) or bicyclo[2.2.2]octane ring (48e) exhibit only smectic phases, while the compound with Z = carborane ring (48a) also exhibits the nematic phase:
(48a) – Cr 128ºC (SmC 120ºC) SmA 189ºC N 193ºC Iso;
(48e) – Cr 141ºC SmX 188ºC SmA 280ºC Iso;
(48f) – Cr 113ºC (SmF 97ºC SmI 111ºC) SmC 178ºC SmA 248ºC Iso.

Below, the properties of two isosteric compounds are compared: the nonpolar compound (49) with the zwitterionic compound (50). Ionic compounds have larger dipole moments and dielectric anisotropies.



(49)

Cr 45ºC N 105ºC Iso;



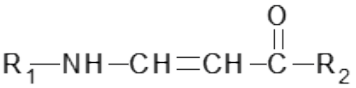
(50)

Cr 121ºC (N 114ºC) Iso, Δε = 42, and for the compound with -CN group instead of C_5H_{11} Δε=113.

The use of polar borane compounds as components of nematic mixtures was proposed because it led to an effective increase in the dielectric anisotropy of mixtures [184, 185].

6. University of Warsaw

In the second part of the 1980s, Wiesław Pyżyk, a physicochemist from the Department of Chemistry, University of Warsaw, organized a team for the investigation of LC materials, to which he invited two organic chemists: Adam Krówczyński and Józef Mieczkowski. A. Krówczyński started to synthesize the homologous series of new families of LCs with 1-aminopropen-3-on moiety in the central part of molecules; see formula (51).

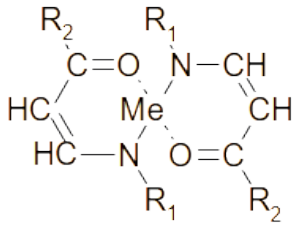


(51)

where $R_1 = H_{2n+1}C_n$-C_6H_4 or $H_{2n+1}C_nO$-C_6H_4,
$R_2 = C_6H_4$-C_nH_{2n+1}, C_6H_4-NO_2 or C_6H_4-CN [186, 187].

There are intermolecular hydrogen bonds in these compounds. A rarely observed phase sequence, SmB_{cr}-SmB_{hex}, was found in nonpolar compounds (51) [187, 188]. The presence of SmA_d phase and phase sequence N_{re}-SmA_d-N was observed for compounds (51) with polar NO_2 and CN groups in the terminal position [188].

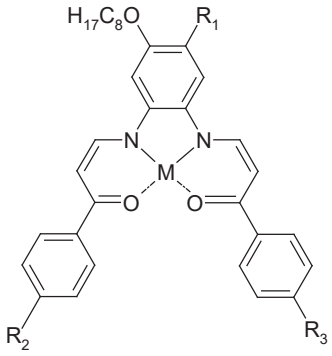
Compounds (51) have the ability to form chelate complexes with transition metals; see formula (52).



(52)

A. Krówczyński prepared a few homologous series of the cupric complexes [189]. They have paramagnetic properties and are low-melting monotropic nematogens (the nematic phase is observed only during cooling at temperatures below the melting point) for R_1 = alkyl and R_2 = alkylphenyl or alkoxyphenyl. The change of the alkyl group into a *trans*-cyclohexyl one leads to enantiotropic nematogens (the nematic phase is observed above the melting point). Compounds (52), wherein both R_1 and R_2 are alkylphenyl or alkoxyphenyl, exhibit high melting points as well as high clearing points. They usually decompose at temperatures above the clearing point.

Then he synthesized the metallic complexes of other aminoketones starting from the derivatives of ortho-diaminobenzene, whose molecules are strongly bent; their shape resembles a triangle; see formula (53):

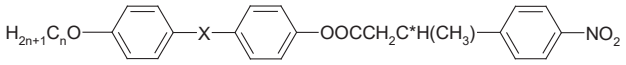


(53)

wherein R_1 = C_8F_{17}, C_9H_{19}; R_2 = OC_8H_{17}, C_8F_{17}, C_9H_{19}; R_3 = OC_8H_{17}, C_8F_{17}, C_9H_{19}; M = Ni(II), Cu(II) [190].

The presence of an unusual phase sequence was observed: Cr-SmA-Iso-Col_h-Iso during heating for the nickel complex. The transition from the lamellar SmA phase to the columnar phase with hexagonal order does not occur directly, but rather via the isotropic phase without long-range order. Next, more compounds with bent-core were synthesized, which were able to form lamellar and columnar phases. It was evidenced that they can be built from the fragment of smectic B_1 layers [190].

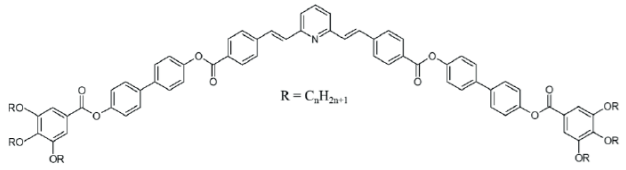
In parallel, J. Mieczkowski synthesized a homologous series of LC given by formula 54 with (R) or (S) chiral and achiral racemic (R,S) semiflexible bridge $CH^*(CH_3)CH_2COO$ [191, 192]:



(54)

wherein X is an azo (N=N) or azoxy (N=N→O) group.

The phase sequence SmA_1-N_{re}-SmA_d-N-Iso was observed for longer members (n > 11), but the reentrant nematic phase (N_{re}) appeared in racemates (R,S) for smaller n than for pure enantiomers [191, 192]. Lately, he has prepared banana-shaped compounds (55). Here, the columnar phases consisted of a few molecules forming a disc or cone [193].

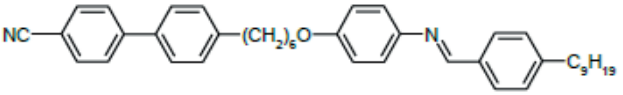


(55)

In the last period, he has been synthesizing hybrid mesogens comprising gold or silver nanoparticles whose surfaces were functionalized by thiophene or stilbene mesogenic molecules [194, 195]. These materials exhibit lamellar layer smectic structures as well as columnar smectic structures.

W. Pyżuk died in 1995, and Ewa Górecka took the leadership of the team. After 2005, her laboratory was equipped with three complementary X-ray apparatuses, which enabled the beginning of analyses of more sophisticated LC structures and fruitful cooperation with other groups in Poland as well as abroad.

The investigation of the dimeric mesogenic compounds of formula (56):



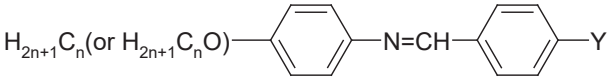
(56)

prepared in C.T. Imrie's laboratory may be an example of such cooperation. Although compounds (56) are achiral, they form a helical space structure due to a long-distance correlation of dipole moments, and this was confirmed by the presence of the selective reflection of light [196–198].

7.1. University of Wrocław

The syntheses of LCs were started by Zbigniew Galewski in the late 1980s at the Chair of Physical Chemistry (Department of Chemistry, University of Wrocław) directed by Lucjan Sobczyk. The first work was published in 1994 [199]. Until now, he has synthesized many homologous series with long alkyl or alkoxy chains containing up to 12 carbon atoms belonging to families:

1. two-ring benzylidene anilines (Schiff's bases) of formula (57).



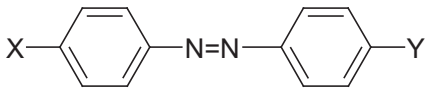
(57)

wherein:

a) Y = Cl, Br, F or NO_2 [199];
b) Y = OC_mH_{2m+1}, m = 6 [200], m = 7 [201], m = 9 [202], m = 10 [203], m = 12 [204].

Benzylidene anilines (57) do not have practical meaning at the present time, because they are not stable in contact with air humidity (they easily hydrolyze). However, they exhibit a rich mesomorphism and rare sequences of liquid crystal phases, which have been observed for longer alkyl and alkoxy terminal chains. They were investigated using various methods, including polarizing optical microscopy, differential scanning calorimetry, and transmission optical analysis, as conducted by Z. Galewski and his students. The last technique was developed and improved by him [205].

2. two-ring azo compounds of formula (58):

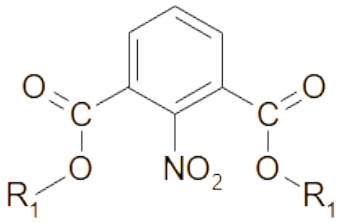


(58)

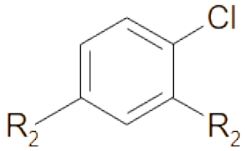
a) X = $H_{2n+1}C_nO$, Y = Cl [206],
b) X = $H_{2n+1}C_nO$, Y = OC_mH_{2m+1}, m = 1, 2, 3, 4 [207], 5, 6, 7 [208],
c) X = $H_{2n+1}C_nO$, Y = $OOCC_mH_{2m+1}$ [209-211],
d) X = $H_{2n+1}C_nCOO$, Y = $COOC_mH_{2m+1}$, m = 1, 2 [212],

e) X = $H_{2n+1}C_n$, Y = $OOCCH_2CH(Cl)CH_3$ (S) [213],
f) X = $H_{2n+1}C_n$ O, Y = $SOCC_mH_{2m+1}$ [214],
g) X = F, Cl, Br, J, Y = $OOCC{=}CC_6H_4NO_2$ [215].

3. five-ring bent-core azo compounds with a central unit formed from 2-nitroisophthalic acid ester, formula (59) [216], wherein branches R_1 are C_6H_4-N=N-C_6H_4-C_nH_{2n+1} or formed from 4-chloro-1,3-dihydroxybenzene, formula (60), wherein branches R_2 are OOC-C_6H_4-N=N-C_6H_4-OC_nH_{2n+1} [217].

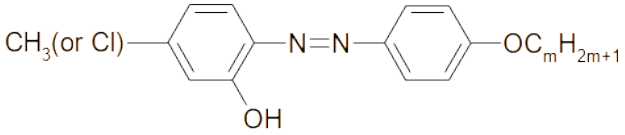


(59)



(60)

The azo compounds have a red color, so their applications are limited to special cases. They transform themselves under lighting from the linear trans- to the bent cis-isomer. This feature is used after inserting azo compounds into a polymer matrix for the transformation of photon energy into mechanical energy or to the reorientation of LC molecules in devices that use this effect, for example in dynamic optical switchers [218]. Maria Rospenk, the other member of L. Sobczyk's team, has investigated the structure of azo compounds with a hydroxy (OH) group in position 2 against the central N=N bond, see formula (61), by X-ray and IR methods [219–221].



(61)

Intramolecular hydrogen bonds make these molecules more rigid, which leads to an enhancement of the mesophase range.

8 Military Institute of Engineering Technology

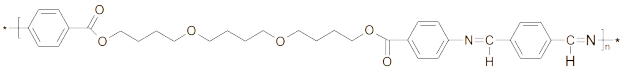
The investigation of LCs at the Military Institute of Engineering Technology has been conducted by Adam Januszko, Agnieszka Iwan, and Krzysztof Bogdanowicz. A. Januszko has been working there the longest, directly after graduating from MUT (1996). He had begun researching LC mixtures in his diploma work, and subsequently, his further activities were mainly related to their application in various devices. His activity in syntheses, physicochemical and mesomorphic property studies was limited to the period of his stay at Vanderbilt University (Nashville, USA) in P. Kaszyński's team (2003–2008) [177, 184, 222–226]. The properties of rod-like molecules containing one or two borane clusters with 8 or 10 boron atoms in the rings of 1,10-dicarbodecaborane or 1,12-dicarbododecaborane were compared by him with analogous structures with a cyclohexane, benzene or bicyclo[2.2.2] octane ring. Examples of such compounds are given in paragraph 5. He also attempted to modify carboranes to increase their effectiveness in detecting neutron radiation and, lately, also in detecting X and γ radiation [Patent PL 224639].

A. Iwan was very active in the synthesis of liquid crystal oligomers and polymers and in the use of them as photoactive layers in solar cells or as luminescent materials [227–229].

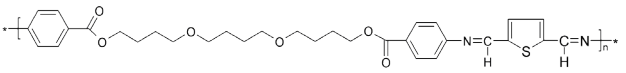
The inspiration for this investigation was a year-long stay in a postdoctoral position at CNRS-Grenoble (2006). There, she synthesized liquid crystal dendrimers with cyclotriphosphazene or with thiophosphonyl group as the center of molecules and imine or azine bonds in branches [230].

After returning to Poland, she has prepared and investigated successfully:

– aliphatic and aromatic, linear and branched polymers containing imine [231–233] or azomethine bonds [234–240]; see formulae (62) and (63) as typical examples;

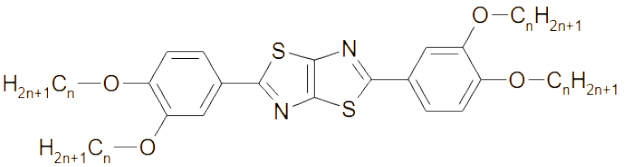


(62)



(63)

– thiazolo[5,4-d]thiazole (TT), see formula (64), and benzo[1,2-d:4,5-d']bis-thiazole (BBT) derivatives [241, 242]. They show n-type conductivity.



(64)

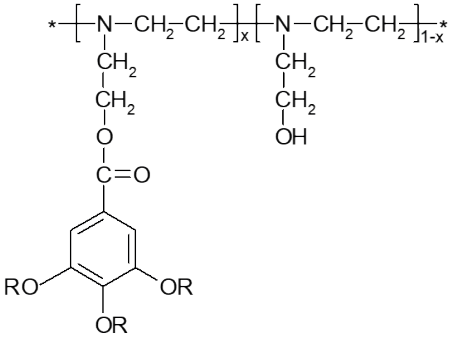
n = 8, 10, 12, 14, 16;

– poly (hexylthiophene-2,5-diyl)-(P3HT). It shows p-type conductivity.

A new donor-acceptor solar cell was developed, consisting of active layers composed of polymers with p- and n-conductivity, with the following composition: P3HT:PCBM:TT (BBT). PCBM is a derivative of fullerene – [6,6]-phenyl-C_{61}-butyric acid methyl ester exhibiting n-type conductivity.

K. Bogdanowicz was included in the investigation of solar cells in 2017 [243–245]. He then enhanced his activity in the applications of LC polymers as selective membranes and solvent-free electrolytes [246–248] for reversible batteries in lithium-ion technology [246]. He has synthesized:

– new LC polymers having the ability to form a columnar phase, wherein the space of ionic conductivity has dimensions correlated with the lithium cation;
– LC poly [(2-aziridin-1-yl)ethanol]; see formula (65):



(65)

wherein R = $CH_2C_6H_4OC_{12}H_{25}$, x = 0.40 or 0.72.

It was modified with dendrimer -3,4,5-tris[4-(dodecan-1-yloxy)benzyloxy]benzoic acid, and the membrane with conductivity 10^{-5} S/cm was obtained [248].

– LC polyepichlorohydrin and a copolymer of epichlorohydrin and ethylene oxide with side mesogenic groups give a membrane with conductivity 10^{-3} S/cm [249].

Summary

Polish chemists have made a significant contribution to the science of liquid crystals, both in terms of materials with low molecular weights and polymers. Novel methods for synthesizing liquid crystals with cyclohexane, bicyclohexane, or carborane rings have been developed and introduced. About ten thousand new LC compounds were prepared. Many of them showed new LC phases. New families of LCs with an NCS terminal group, having low viscosity and medium or large birefringence, useful for the formulation of nematic mixtures for different optical modes (especially in the GHz and THz regions), were synthesized.

LC compounds and mixtures:

– with high transparency in the infrared region,
– with the low value of ordinary refractive index for optical fibers,
– with paramagnetic properties containing free radical or chelate transition metal complexes,
– orthoconic antiferroelectrics ensuring a large contrast in devices,
– polymers for solar cells or lithium batteries

were elaborated.

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Pięćdziesiąt lat aktywności polskich chemików w badaniach materiałów ciekłokrystalicznych

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Streszczenie. W pracy została opisana aktywność w syntezie i badaniach ciekłych kryształów (CK) siedmiu polskich chemicznych zespołów badawczych: Wojskowej Akademii Technicznej (WAT), Uniwersytetu w Siedlcach (UwS), Szkoły Głównej Gospodarstwa Wiejskiego (SGGW), Centrum Badań Molekularnych i Makromolekularnych (CBMM), Uniwersytetu Warszawskiego (UW), Uniwersytetu Wrocławskiego (UWr), Wojskowego Instytutu Techniki Inżynieryjnej (WITI). Zespół WAT otrzymał nowe CK o małej lepkości oraz małej, średniej i dużej dwójłomności, przydatne do zastosowań we wskaźnikach i przyrządach pracujących w zakresie promieniowania elektromagnetycznego widzialnego, podczerwonego, GHz i THz. CK z grupą terminalną NCS i chiralne związki z ortokoniczną fazą antyferroelektryczną były przedmiotem ich głównego zainteresowania, tak jak badanie nieaddytywnych właściwości mieszanin prowadzące do indukcji nowych faz ciekłokrystalicznych. Zespół UwS wytworzył wiele serii homologicznych dwu- i trójpierścieniowych tiobenzoesanów o cechach ferroelektryków i kilka ich deuterowanych analogów. Zespół SGGW wytworzył: mezogeniczne estry mające w łańcuchu terminalnym wiązanie podwójne (wykorzystane przez CBMM do syntezy ciekłokrystalicznych polimerów grzebieniowych), estry kwasu (E) akrylowego, estroimidy i estrotioimidy kwasu trimelitowego. CBMM wytworzył polimery grzebieniowe z rodziny karbosilanów, a następnie CK zawierające centra rodnikowe i CK zawierające klastry karboboranowe lub ich anionowe formy. Zespół UW otrzymał CK z pochodnych 1-aminopropen-3-onu, które były następnie przekształcane w kompleksy chelatowe metali przejściowych. Inne aminoketony były stosowane do syntezy ciekłokrystalicznych metalokompleksów o zgiętych rdzeniach cząsteczek. Wytworzono również mezogeny hybrydowe zawierające nanocząstki złota lub srebra i CK o kształcie bananopodobnym. Zespół UWr wytworzył

wiele serii homologicznych CK należących do rodzin benzylidenoanilin i azozwiązków. Zespół WITI otrzymał CK oligomery i polimery zawierające wiązania iminowe lub azometinowe i pierścienie tiazolowe lub tiofenowe do wykorzystania w ogniwach słonecznych lub jako membrany i stałe elektrolity w bateriach litowo-jonowych.
Słowa kluczowe: ciekłe kryształy, synteza ciekłych kryształów, historia badań ciekłych kryształów w Polsce