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Self-assembling behaviour of chiral calamitic monoacrylates targeted for polymer stabilisation of polar smectic phases in chiral liquid crystals.

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Abstract

The stabilisation and control of synclinic and anticlinic chiral liquid crystalline phases remain an actual and highlighted task. This work presents the design and mesomorphic properties of new chiral calamitic reactive mesogens, monoacrylates, based on biphenyl benzoate and phenyl biphenyl-4-carboxylate cores with reactive terminal groups placed far from the chiral chain. The compound's structures, compatible with the components of modern ferroelectric and antiferroelectric liquid crystalline mixtures, are confirmed by mass spectrometry (electron ionization) analysis and proton/carbon nuclear magnetic resonance. All the reactive mesogens possess the self-assembling, i.e. liquid crystalline behaviour with high tendency to create smectic phases in a broad temperature range, which was confirmed by a polarizing optical microscopy, differential scanning calorimetry and broad-band dielectric spectroscopy. Doping of advanced multicomponent mixtures possessing the chiral smectic phases by the designed monoacrylates with further cross-linking procedure, can be an effective and functional tool for stabilising ferroelectric and antiferroelectric phases in various states and hence, can allow the symmetrisation of the switching times in the modes employed surface stabilised geometry; this is a very highlighted task for optoelectronics. Moreover, an evident considerable tendency for thermal polymerisation of specific reactive mesogens can reduce the drawbacks of polymer stabilisation.

keywords: self-assembling organic materials; reactive mesogens; monoacrylates; polymer-stabilised liquid crystals; ferroelectric phase; antiferroelectric liquid crystals

Introduction

Among self-assembling organic materials [1,2], chiral calamitic liquid crystalline materials [3] with diverse self-organised superstructures have found a broad potential application in a variety of optical and electro-optical devices such as thermography [4], reflective displays [5], tunable mirrorless lasers [6] and biomedical [7] as well as photonic sensors [8] owing to their remarkable optical properties and high sensitivity to different external stimuli. The self-organising structures formed by these type of smart materials can be effectively controlled, tuned or changed by an applied external stimulus, such as external electric/magnetic field, mechanical stress or irradiation with light of different wavelength [9,10].

Antiferroelectric (AFLC) and ferroelectric liquid crystals (FLCs) are smectic materials formed of chiral calamitic molecules that may exhibit a variety of smectic tilted structures, anticlinic (SmC_A^*) and synclinic (SmC^*) for AFLCs and FLCs respectively. Molecules in both of these phases spontaneously form a helicoid structure. A consequence of chirality in oblique phases is the occurrence of spontaneous polarisation P_s . A spontaneous polarisation enables the control of molecules by means of an external electric field, which makes it possible to control optical properties of the liquid crystal. In the ferroelectric phase, the molecules are arranged in layers, and they are tilted in one direction with respect to the layer normal by an certain angle. In turn, the molecules in the layers are also tilted by the same angle in the antiferroelectric phase, but the layers are arranged alternately. A schematic diagram of the arrangement of molecules in the ferroelectric and antiferroelectric materials is shown in Figure 1 (a) and (b) respectively. The FLCs are bistable, they create two synclinic states that maintain the arrangement without an electric field. It also means that, depending on the applied electric field, all the molecules in the layers reorientate one way or the other. While the AFLCs are used as monostable, but tristate materials. The stable state is the state with no applied voltage ($E = 0$), with anticlinical ordering. Depending on the sign of the applied field, two ferroelectric states are obtained with opposite direction of the vector of spontaneous polarisation.

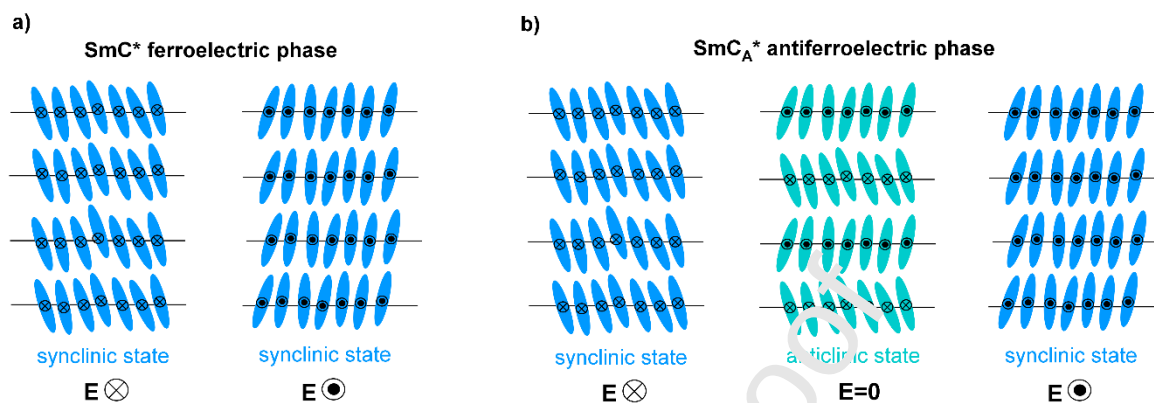


Figure 1. Schematic arrangement of molecules in a) the ferroelectric phase (two stable states for $E = 0$) with marked turns of the spontaneous polarisation vector; b) the antiferroelectric phase (one stable state for $E = 0$, and two synclitic states depending on the applied voltage on the right and left) with marked turns of the spontaneous polarisation vector.

Antiferroelectric smectic liquid crystals could provide an efficient alternative to nematic materials, commonly used in displays and other devices; due to their shorter response times and their specific properties promising for passive addressing [11-13]. AFLCs are extremely interesting for use in large size high-resolution display applications [14]. Unfortunately, the main problem of these materials relies in asymmetrical switching times. Nevertheless, the idea is to design structurally compatible chiral reactive mesogens and add them to the base mixtures. This will allow the polymer-stabilisation of antiferroelectric and ferroelectric systems with a much better symmetry of the switching time [15-17], under the condition that most of the targeted properties remain unchanged.

Reactive mesogens (RMs) are liquid crystalline materials with an additional functionality induced by the presence of the polymerisable terminal chain or lateral groups [18]. For this purpose, acrylate [19-21], methacrylate [22-24], vinyl [25-28] or cinnamoyl groups [29] can be used. The reactive terminal groups can be placed on one side (bifunctional monomers) or both sides (tetrafunctional monomers) of the molecule [30,31]. Acrylate esters belong to very important industrial chemicals which are widely used as precursors in the

fabrication of technically substantial special type polymers due to the presence of a double bond as well as a carbonyl group [32,33]. They are used in the large-scale preparation of useful polymers [33]. The reactive mesogens used to stabilise the liquid crystal phases may themselves be a liquid crystal material, but this is not a prerequisite as long as they have a similar shape and anisotropy of the liquid crystal host material [34]. Polymerisation of RMs leads to creation of cross-linked networks in which the liquid crystalline order is permanently fixed [20,35] (see the example of polymer stabilised antiferroelectric liquid crystals in Figure 2). This process usually occurs under UV light illumination under the presence of specific photoinitiators [36]. The most important advantages of photopolymerisation over the other techniques are reaction speed, energy savings and light control [37,38]. The speed of photopolymerisation is particularly important if one wants to create a polymer network in a given liquid crystal phase of a specific liquid crystal material. Polymerisation of RMs in liquid crystal phases has been widely explored for the stabilisation of particular optical states in blue phases [39-41], nematic/cholesteric phases [42-45], paraelectric smectic phase [27], antiferroelectric phase [46], ferroelectric phase [34] and for the modification of the resulting electro-optical properties [44, 47-48]. The basic idea of creating a polymer network in the presented examples is stabilising a liquid crystal director configuration in which it was created [34]. The use of neat FLCs has some limitations such as homogeneous orientation problems when placed in thin cells and their low resistivity to mechanical shock [49]. The stabilisation of these systems with a polymer network can minimise these technical problems [34, 49-50]. AFLCs without a helicoid structure beyond a synclinic state, when molecules in all layers are tilted in the same direction are characterised by an anticlinic state in which molecules in adjacent layers are tilted in opposite directions [34,51]. The main problem of AFLCs is the asymmetric switching times between these two states. The creation of a polymer network in the anticlinic state causes the relaxation time from synclinic to anticlinic state to be shorter when compared to neat materials [34]. Therefore, it has a significant impact on the electro-optical and physicochemical parameters of these materials. Besides shortening the response time, there is also an improvement in grayscale and greater mechanical resistance [34,49]. However, the presence of a polymer network in (A)FLCS brings also sever disadvantages, such as an increase in operating voltage and a decrease in optical contrast [48]. For this reason, it is very important to develop reactive mesogens with structures compatible with (A)FLCs and smectic phases. It should allow the use of such reactive mesogens in smaller amounts and allow the realisation of polymer-stabilisation of antiferroelectric and

ferroelectric systems, provided that most of the targeted properties of AFLCs or FLCs remain unchanged.

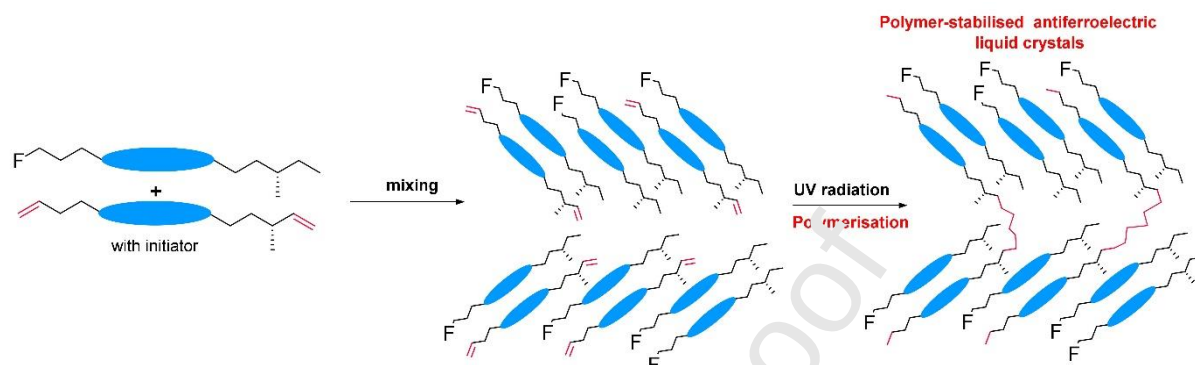


Figure 2. A simplified scheme for the formation of a polymer-stabilised antiferroelectric liquid crystal structure with a hypothetical simplified arrangement of molecules.

The design synthesis and characterisation of two homologues series of new chiral monoacrylates based on biphenyl benzoate and phenyl biphenyl-4-carboxylate molecular cores (see Figure 3) aimed for stabilisation of anticlinic or synclinic structures are presented in this work. These cores, bridge bonds, flexible spencer's or chiral centre, are commonly used in stable ferroelectric and antiferroelectric systems [52-54]. This structural compatibility should ensure good miscibility of reactive mesogens with the (A)FLC materials. Similar low molar mass materials with molecular core based on biphenyl benzoate [55] and phenyl biphenyl-4-carboxylate [27, 56-57] are quite common. However, the reactive mesogens with similar molecular core are also described in literature; nevertheless, most designed reactive mesogens possess only one ester linkage in the structure; moreover, mostly the single compounds (not the homologues series) with specific molecular structure are described [58-63]. In the literature, there are examples of stabilisation by a polymer network of antiferroelectric materials with reactive mesogens with a nematic phase [64,65], which were initially intended to stabilise the nematic and cholesteric phases [34] or reactive mesogens based on bent-core [66]. To the best of our knowledge there are no studies on stabilising AFLC materials with reactive mesogens having ferroelectric and/or antiferroelectric phases.

This work presents the systematic design of the new reactive mesogens that are structurally compatible with the components of ferroelectric and antiferroelectric liquid crystals mixtures [52-54, 64, 66-69]. This should help stabilise these phases and minimise the

negative influence of these monoacrylates on destabilisation of synclinic and anticlinic smectic phases and their target properties responding to the demands of various electro-optical modes [67-76]. The effect of the addition of some synthesised here monoacrylates on the properties of the newly developed high-tilted AFLC mixtures with different phase sequence, before and after polymer stabilisation is described in [77].

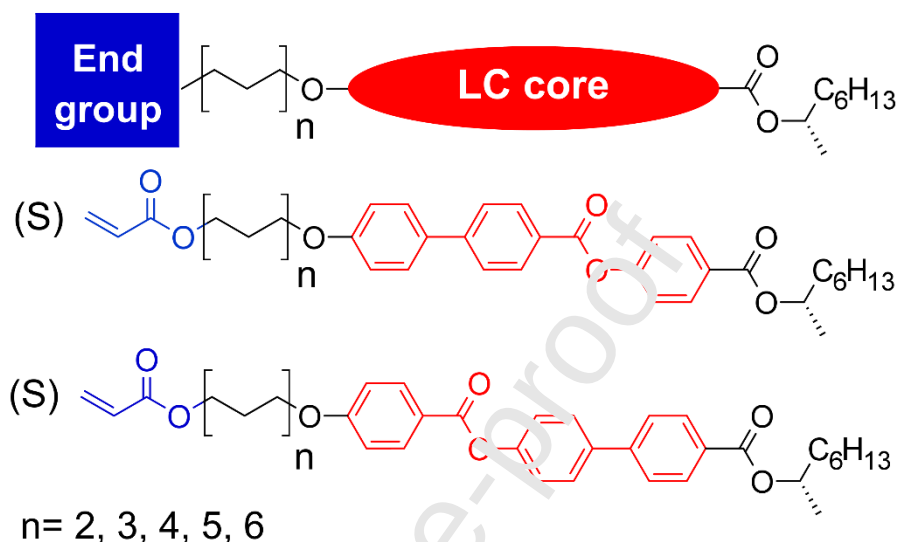


Figure 3. General molecular structures of synthesised chiral monoacrylates.

Experimental

The chemical purity of synthesised compounds was determined by thin layer chromatography, Shimadzu GCMS-QP2010S series gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a quadrupole mass analyser (MS), high-performance liquid chromatography HPLC PDA-MS (APCI-ESI dual source) Shimadzu LCMS 2010 EV (Shimadzu, Kyoto, Japan) equipped with a polychromatic UV-VIS detector (Shimadzu, Kyoto, Japan). The optical purity was determined by HPLC analysis using Lux® 5 μ m Cellulose-1 column (Phenomenx, Torrance, USA) (hexane-i-PrOH 90:10, 1 mL/min). Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra in CDCl_3 was collected using a Bruker, model Avance III spectrometer (Bruker, Billerica, MA, USA).

The planar cells (Military University of Technology, Warsaw, Poland) in bookshelf geometry (where the long axes of molecules are oriented parallel to the substrates) made from glasses with transparent electrodes of indium-tin-oxide (ITO) ($5 \times 5 \text{ mm}^2$) 5 μm thick were used for texture observations and electro-optical measurement of the spontaneous polarisation.

The planar cells (Military University of Technology, Warsaw, Poland) in bookshelf geometry with gold electrodes 5 μm thick were used for broad-band dielectric spectroscopy. The sample cells were filled with the studied LC materials in the isotropic phase by the capillary action.

The sequence of phase transitions and temperature of phase transitions were determined by polarizing optical microscopy (POM) using "Olympus" BX51 polarizing microscope (Shinjuku, Tokyo, Japan) equipped with a Linkam heating/cooling stage THMS-600 (Linkam Scientific Instruments Ltd., Tadworth, United Kingdom). The differential scanning calorimetry DSC 204 F1 Phoenix instrument (Netzsch, Selb, Germany) was used to estimate enthalpy of phase transitions and as a precise technique for determining temperature of phase transitions. In both cases the scanning rate was 2 K min^{-1} on both the heating and cooling cycles.

The frequency dispersion of complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) has been measured within the temperature range of the SmA* and SmC* phases on cooling, using a Schlumberger 1260 Impedance/Gain-Phase Analyzer (Solartron Group Ltd Hampshire, United Kingdom) in the frequency range of 1 Hz $\div$ 1 MHz keeping the temperature stable during the frequency sweep within ± 0.1 K. The measurements have been performed under zero d.c. bias voltage.

The values of spontaneous polarisation, P_s , were determined using the switching current profile detected with Tektronix oscilloscope (Tektronix, Beaverton, OR, USA); a specific software for automation of the spontaneous polarisation measurements was used. An electric field of triangular modulation at frequency of 50 Hz with amplitude of 10 V/ μm was applied during the P_s measurements.

Materials

(S)-2-octanol, acryloyl chloride, methanesulfonyl chloride, benzyl chloride, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Solvents were purchased from Avantor Performance Materials Poland S.A (Gliwice, Poland). and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and stored under nitrogen and toluene was distilled from P_2O_5 .

Synthesis

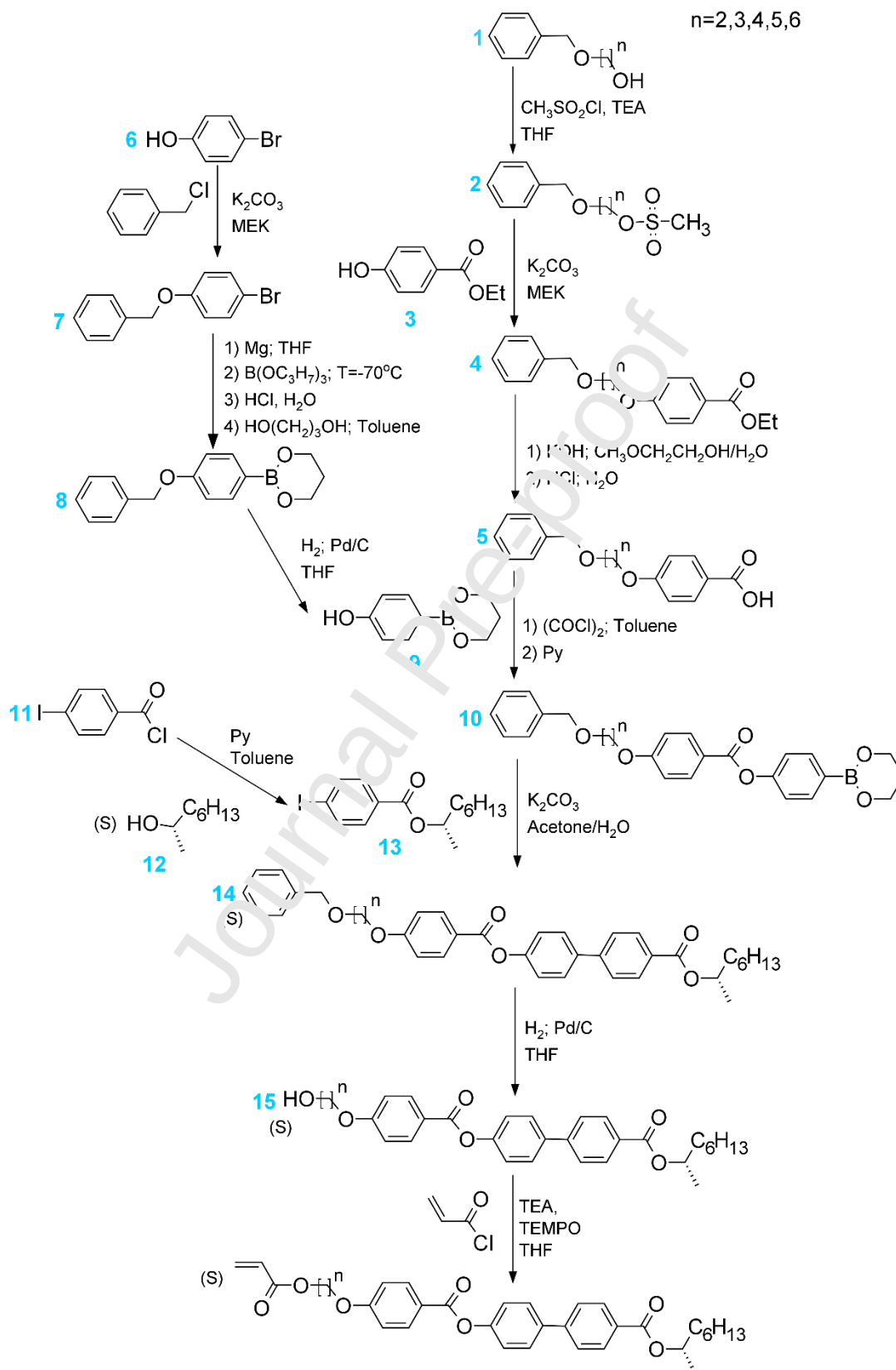
Two series of reactive mesogens were synthesised; the first series is based on biphenyl benzoate core (see the synthesis in Figure 4) and the second series is based on phenyl biphenyl-4-carboxylate core (see the synthesis in Figure 5).

The synthesis scheme of the first series is presented in Figure 4. The synthesis was started from *n*-(benzyloxy)alkan-1-ol (1), where the number of carbons in the chain ranged from *n*=2 to *n*=6. The hydroxyl group of (1) was esterified with mesyl chloride, receiving compound (2) with a good leaving group, which was useful in the reaction of the nucleophilic substitution with ethyl 4-hydroxybenzoate (3). Then carboxylic acid derivative (5) was obtained by reaction of 4-[(benzyloxy)alkyl]-benzoate (4) with KOH, next with HCl and used in the esterification reaction with 4-(1,3,2-dioxaborinan-2-yl) phenol (9). The synthesis of 4-(1,3,2-dioxaborinan-2-yl) phenol (9) was started from 4-bromophenol (6) in which the hydroxyl group was protected by the benzyl group. The next step was the Grignard reaction through which a boronic acid derivative (7) was obtained. Subsequently, the boronic ester derivative was obtained by reaction with 1,3-propanediol. The hydroxyl group was then deprotected by the hydrogenolysis (9). The boronic acid derivative (10) obtained as a result of the esterification reaction was used in the Suzuki-Miyaura cross-coupling reaction with (*S*) 2-octan-2-yl 4-iodobenzoate (13) (this compound was obtained by the esterification reaction between 4-iodobenzoyl chloride (11) and (*S*)-2-octanol (12)). Finally, the hydroxyl group of the coupling reaction product (14) was deprotected by hydrogenolysis and the obtained hydroxyl derivative (15) was used for the esterification reaction with acryloyl chloride. As a result of the synthesis, five final products were obtained and each reactive mesogen in the series differs in the length of the carbon chain in the structure of the molecule (16 for *n*=2, 17 for *n*=3, 18 for *n*=4, 19 for *n*=5, 20 for *n*=6).

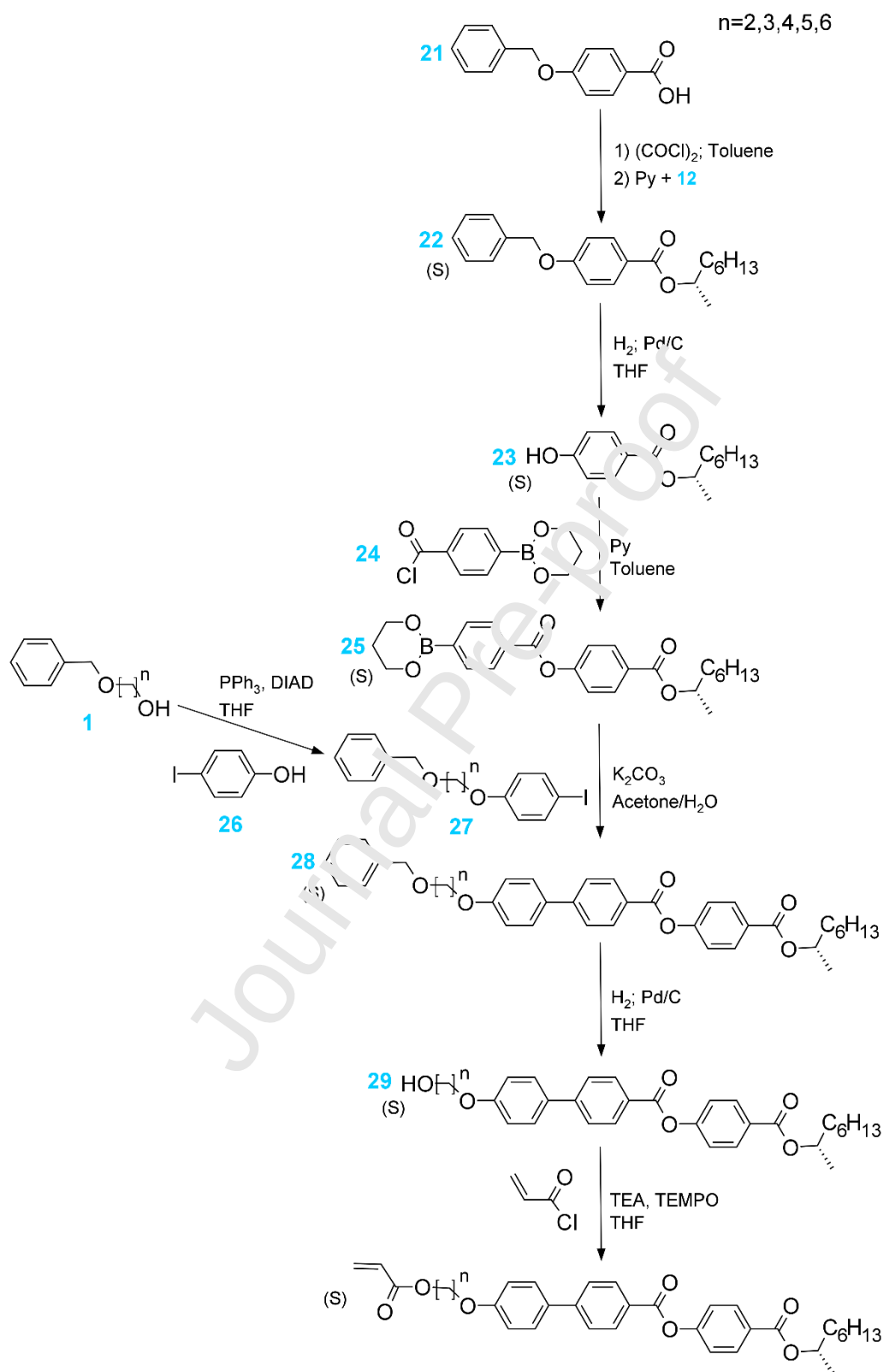
The synthetic pathway of the second series based on phenyl biphenyl-4-carboxylate core is presented in Figure 5. The synthesis was started with 4-(benzyloxy)benzoic acid (21) which was reacted with oxalyl chloride, followed by the esterification with (*S*)-chiral alcohol (12) to get the compound (22). Then, during the hydrogenolysis, the hydroxyl group was deprotected to form a chiral hydroxyl derivative (23). After the esterification with 4-(1,3,2-dioxaborinan-2-yl)benzoyl chloride (24); one of the main reactants (25) to the Suzuki-Miyaura cross-coupling reaction was obtained. Then, the reaction of 2-(benzyloxy)alkan-1-ol (1) with 4-iodophenol (26) gave iodine derivative (27)- the second main substrate for the cross-coupling reaction. The next steps, analogous to the previous series, were the deprotection of the hydroxyl group (28) and the esterification of the hydroxyl derivative (29) with acryloyl chloride respectively. Five final products were obtained (30 for *n*=2, 31 for *n*=3, 32 for *n*=4, 33 for *n*=5, 34 for *n*=6).

The final reactive mesogens were isolated and purified using a multiple crystallisation sequences and liquid column chromatography techniques.

A detailed description of the synthesis and related basic characterisation are given in the Appendix (see Supplementary materials).



16 for $n=2$ 17 for $n=3$ 18 for $n=4$ 19 for $n=5$ 20 for $n=6$

Figure 4. Scheme of the synthesis of the series based on a biphenyl benzoate core.

30 for n= 2 **31** for n= 3 **32** for n= 4 **33** for n= 5 **34** for n= 6

Figure 5. Scheme of the synthesis of the series based on a phenyl biphenyl-4-carboxylate core.

Mesomorphic properties and discussion

The sequence of phases and phase transition temperatures of the designed reactive mesogens determined by POM and DSC on heating cycles are presented and summarised in Table 1. For a better visualisation of the mesomorphic behaviour, Figures 6 and 7 show the phase temperature ranges for all obtained monoacrylates from the first and the second series, respectively.

The monoacrylates with a rigid biphenyl benzoate core (the first series) are characterised by the presence of the orthogonal SmA* phase. In the case of odd homologues, an increase in the length of the terminal chain causes a decrease in the phase transition temperatures and an increase in the temperature range of the smectic phases. For homologues with an even number of carbon atoms in the oligomethylene spacer, the reactive mesogen 18 with the medium chain length exhibits the lowest melting point and simultaneously has the broadest temperature range of the smectic A* phase. The monoacrylate 20 with the longest terminal chain exhibits additionally the liquid ferroelectric SmC* phase. The enthalpies of melting points are the lowest for monoacrylates with intermediate terminal chain lengths in this series.

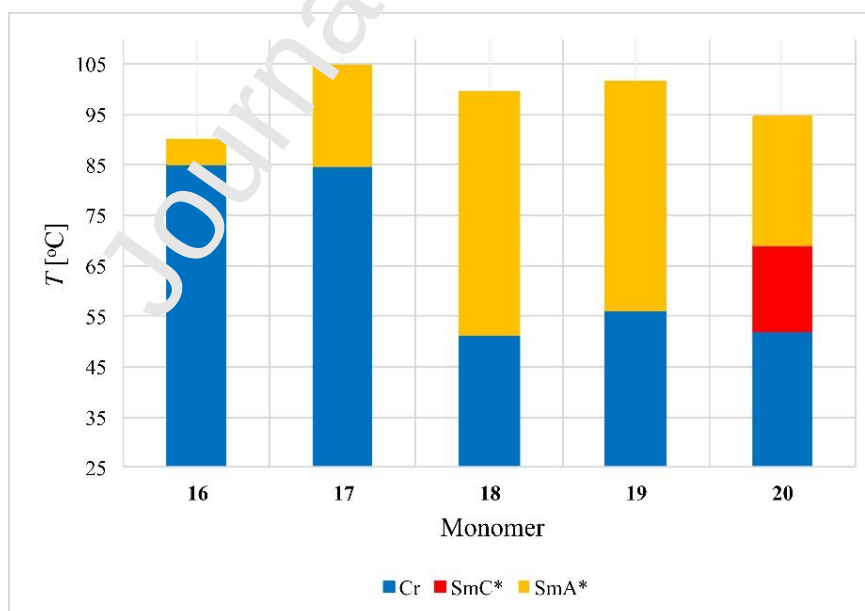
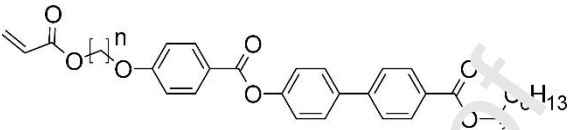
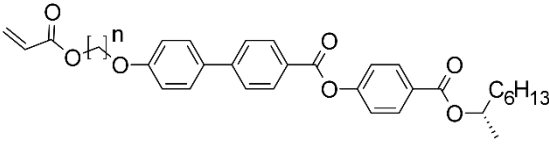


Figure 6. Phase diagram for monoacrylates based on a biphenyl benzoate core (DSC measurements on the heating cycle).

Table 1. Phase sequences and phase transition temperatures **T** [°C] of the studied reactive mesogens obtained by DSC (first row). Enthalpies ΔH [kJ/mol] of the phase transitions are given in italics (second row). \$- monoacrylate that shows an evident tendency for thermal polymerisation just above the clearing temperature.

Compound	Cr	T [°C] ΔH [kJ/mol]	SmC*	T [°C] ΔH [kJ/mol]	SmA*	T [°C] ΔH [kJ/mol]	Iso
 16 for n=2, 17 for n=3, 18 for n=4, 19 for n=5, 20 for n=6							
16	*	84.9 27.85	-	-	*	90.0 3.12	*
17	*	84.7 24.51	-	-	*	104.6 4.64	*\$
18	*	51.2 15.26	-	-	*	99.4 3.92	*\$
19	*	56.0 24.01	-	-	*	101.4 2.93	*
20	*	51.9 32.16	*	69.1 0.07	*	94.6 2.69	*
 30 for n=2, 31 for n=3, 32 for n=4, 33 for n=5, 34 for n=6							

30	*	93.3 29.14	-	-	*	111.9 2.31	*
31	*	47.8 21.10	-	-	*	119.6 4.63	*\$
32	*	73.4 24.87	*	89.9 0.06	*	117.9 4.63	*\$
33	*	97.4 34.17	-	-	*	118.8 4.36	*
34	*	64.9 24.86	Polymerisation above 65.0 in smectic phase				

The monoacrylates with a rigid phenyl biphenyl-4-carboxylate core (the second series) exhibit, similar as previous ones, only the smectic phases within the mesophases. For the even-numbered homologues of this series, a decrease in the melting point is observed with an increase in the length of the terminal alkyl chain. The reactive mesogen 34 with the longest even chain has a very strong tendency towards thermal polymerisation in the smectic phase, while the monoacrylate 32 with an intermediate length of the terminal chain additionally exhibits the tilted ferroelectric SmC* phase. Among compounds with an odd number of the carbon atoms in the alkyl chain, the longest one for monoacrylate 32 has the narrowest temperature range of the smectic phase. It is worth noting the abnormally high melting points and their enthalpies for monoacrylates 30 and 33 compared to other homologues of this series.

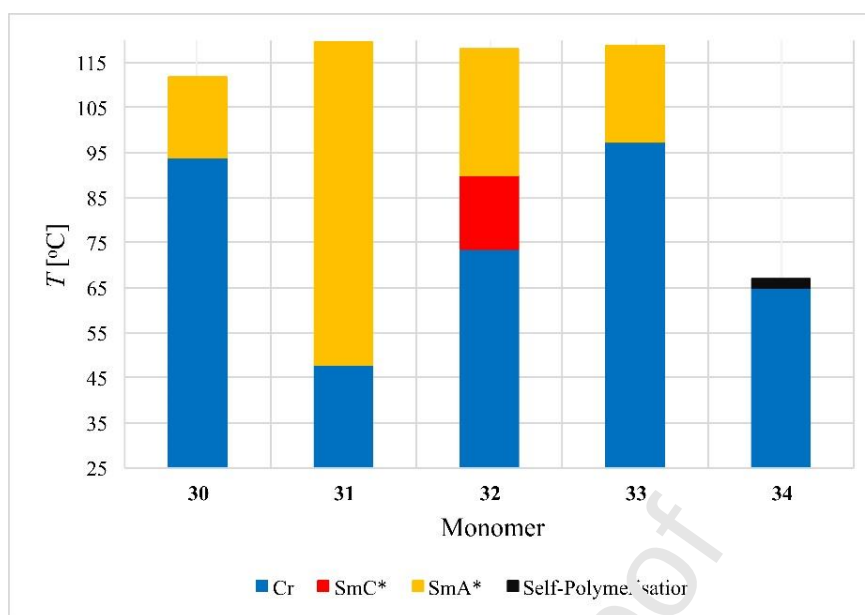


Figure 7. Phase diagram for monoacrylates based on a phenyl biphenyl-4-carboxylate core (DSC measurements on the heating cycle).

The reactive mesogens from the first series generally have lower melting and clearing point temperatures than the monoacrylates belonging to the second series. The tilted ferroelectric SmC* phase is detected from the monoacrylate with shorter alkyl chains in the second series based on phenyl biphenyl-4-carboxylate than their first series counterparts. The examples of the observed microphotograph textures of the smectic phases for monoacrylates 20 and 32 are shown in Figure 8.

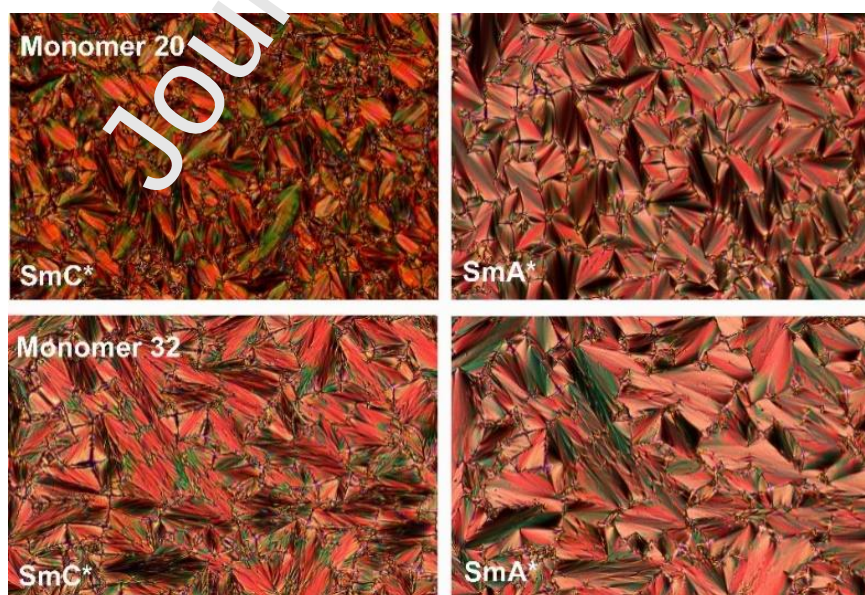


Figure 8. Microphotographs of the characteristic POM textures obtained for different mesophases for monoacrylates 20 (top row: the SmC* at $T = 64^{\circ}\text{C}$ and SmA* at $T = 92^{\circ}\text{C}$) and

32 (bottom row: the SmC* at T=78°C and SmA* at T=114°C) on the cooling cycle. The width all the microphotographs corresponds to $\sim 200\mu\text{m}$.

The presence of the ferroelectric phase for the obtained monoacrylates was also confirmed by dielectric spectroscopy measurements. The real, ϵ' , and the imaginary parts, ϵ'' , of the complex permittivity for monoacrylate 20 versus temperature and versus frequency are presented in Fig. 9a and b as an illustrative result to confirm the ferroelectric character of the polar phase. The obtained dielectric spectra within the whole temperature range of the ferroelectric SmC* phase at zero bias electric field reveal a strong contribution of the Goldstone mode (this is a collective process i.e. the relaxation mode related to azimuthal fluctuations of the molecules in the smectic layer). In the vicinity of the SmA* – SmC* phase transition, a collective mode related to the molecular fluctuations in the direction of the tilt magnitude, the so-called soft mode, was detected. The results of the dielectric spectroscopy fully confirm the polar ferroelectric character of the lower temperature smectic phase detected for monoacrylates 20 and 32. A detailed discussion of the specific behaviour of detected modes, revealed by the broad-band dielectric spectroscopy, with respect to the molecular structure of the monoacrylates is beyond the scope of the present work and will be presented elsewhere.

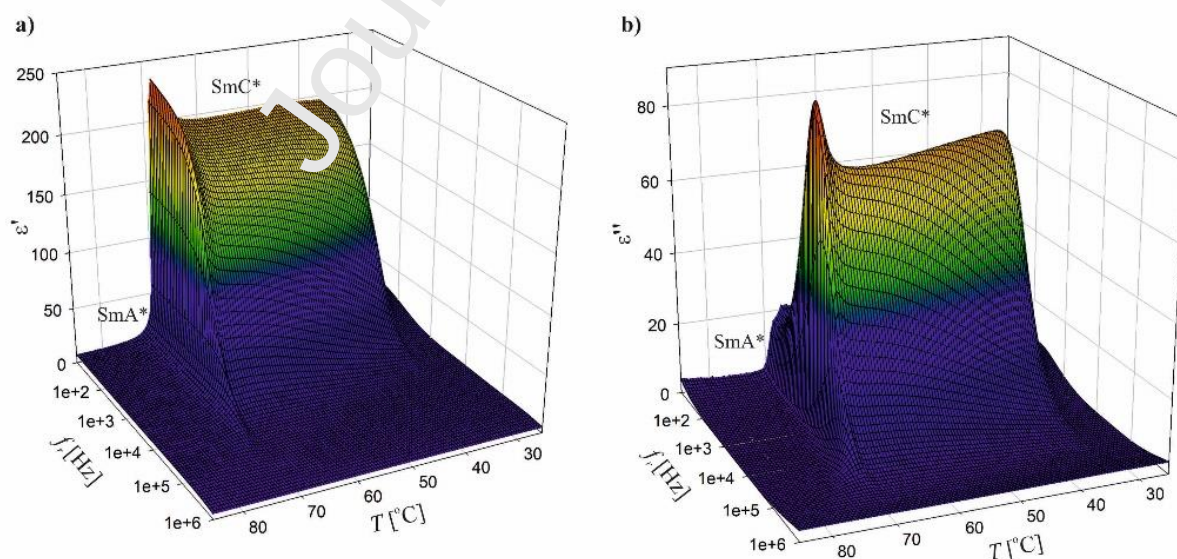


Figure 9. 3D plots of real ϵ' (a) and imaginary ϵ'' (b) parts of complex permittivity versus frequency and temperature for the 20th monoacrylate.

The temperature dependence of the spontaneous polarisation $P_s(T)$ was measured for monoacrylates 20 and 32 under saturating field 10 V/ μm and is presented in Figure 10. Starting from the SmA* – SmC* phase transition there is a continuous increase of the P_s values without saturation; the maximal amplitude for spontaneous polarisation was 170 nC/cm².

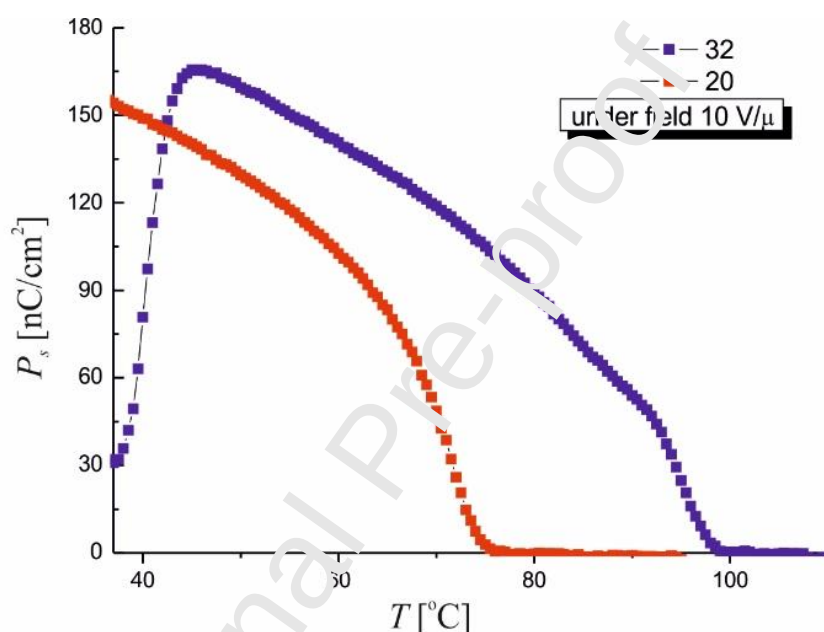


Figure 10. Temperature dependence of the spontaneous polarisation, P_s for monoacrylates 20 and 32 possessing the ferroelectric SmC* phase.

Summary of the results and conclusions

This work presents an advanced synthetic approach for new chiral acrylate-based reactive mesogens build up on the phenyl benzoate and phenyl 4-carboxylate molecular cores. It is important to keep in mind that these reactive mesogens are designed with a specific molecular structure making them more compatible with the components of ferroelectric and antiferroelectric liquid crystalline mixtures possessing well-known properties. This can ensure good miscibility of designed reactive mesogens with LCs bases forming the synclinic and anticlinic phases. All the designed reactive mesogens are highly smectogenic; most of the designed materials possess a relatively broad temperature range of the orthogonal SmA* phase; moreover, materials with longer alkyl chains exhibit the tilted smectic SmC* phase

possessing the ferroelectric order. The existence of ferroelectric behaviour for monoacrylates 20 and 32 was demonstrated by the P_s measurements and dielectric spectroscopy. The latter revealed the presence of the Goldstone mode in the SmC* phase and this is specific for the synclonic phases with a ferroelectric order. The spontaneous polarisation for reactive mesogens 20 and 32 reaches values more than 150 nCcm^{-1} at lower temperatures. Several reactive mesogens show an increased tendency to thermally polymerise just above the clearing temperatures. The reactive mesogen with a rigid phenyl biphenyl-4-carboxylate core and a six-carbon alkyl chain already polymerises in the temperature range of the smectic phase. Such a strong tendency for self-polymerisation is favourable as it can considerably reduce the amount of the reactive mesogen used as dopant for stabilisation of the ferroelectric and antiferroelectric phases; this is very important as it reduces a very common drawback related to the polymer network presence in the LC medium. Further study of reactive mesogens presence on mesomorphic and physicochemical properties of ferroelectric and antiferroelectric liquid crystalline materials and their multicomponent mixtures are in progress and will be presented elsewhere.

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Jakub Herman: Investigation (Organic Synthesis), Writing, Supervision

Michał Czerwiński: Investigation (Mesomorphism), Writing

Sergei Stulov: Investigation (Dielectric data)

Alexej Bubnov: Investigation (Dielectric data), Writing, Supervision

Przemysław Kula: Supervision

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplementary data

Supplementary material

References

- [1] Castillo-Vallés M, Martínez-Bueno A, Giménez R, et al. Beyond liquid crystals: new research trends for mesogenic molecules in liquids. *J Mater Chem C*. 2019;7:14454-14470. DOI: 10.1039/C9TC04179F.
- [2] Lagerwall JPF, Scalia G. A new era for liquid crystal research: applications of liquid crystals in soft matter nano-, bio-and microtechnology. *Curr Appl Phys*. 2012;12:1387-1412. DOI: 10.1016/J.CAP.2012.03.019.
- [3] Lagerwall JPF, Giesselmann F. Current topics in smectic liquid crystal research. *Chem Phys Chem*. 2006;7:20-45. DOI: 10.1002/cplc.200500472.
- [4] Crissey JT, Fergason JL, Bettenhausen JM. Cutaneous thermography with liquid crystals. *J Invest Dermatol*. 1965;45(5):329–333. DOI: 10.1038/jid.1965.139.
- [5] Wu ST, Yang DK. *Reflective Liquid Crystal Displays*. John Wiley. 2001.
- [6] Coles HJ, Morris SM. Liquid crystal lasers. *Nat Photon*. 2010;4:676–685. DOI: 10.1038/nphoton.2010.184.
- [7] Woltman SJ, Jay GD, Crawford GP. Liquid-crystals materials find a new order in biomedical application. *Nat Mater*. 2007;6:929–938. DOI: 10.1038/nmat2010.
- [8] Brodzeli Z, Silvestri L, Michie A, et al. Sensors at Your Fibre Tips: A Novel Liquid Crystal-Based Photonic Transducer for Sensing Systems. *J Lightwave Technol*. 2013;31(17):2940-1946. DOI: 10.1109/JLT.2013.2274455.
- [9] Shibaev VP, Bobrovsky AY. Liquid crystalline polymers: development trends and photocontrollable materials. *Russ Chem Rev*. 2017;86(11):1024-1072. DOI: 10.1070/RCR4747.
- [10] Cigl M, Bubnov A, Kašpar M, et al. Photosensitive chiral self-assembling materials: significant effects of small lateral substituents. *J Mat Chem C*. 2016;4:5326-5333. DOI: 10.1039/C6TC01103A.
- [11] D'Have K, Dahlgren A, Rudquist P, et al. Antiferroelectric liquid crystals with 45 degrees tilt - A new class of promising electro-optic materials. *Ferroelectrics*. 2000;244(1):115-128. DOI: 10.1080/00150190008228422.
- [12] Lagerwall ST, Dahlgren A, Jagemalm P, et al. Unique electro-optical properties of liquid crystals designed for molecular optics. *Adv Funct Mater*. 2001;11:87-94. DOI: 10.1002/1616-3028(200104)11:2<87::AID-ADFM87>3.0.CO;2-E.

- [13] D'Have K, Rudquist P, Lagerwall ST, et al. Solution of the dark state problem in antiferroelectric liquid crystal displays. *Apply Phys Lett*. 2000;76:3528-3530. DOI: 10.1063/1.126696.
- [14] Lagerwall ST. *Ferroelectric and antiferroelectric liquid crystals*. Wiley-VCH. 1999.
- [15] Kim Y, Lee YJ, Kim DH, et al. Fast response time of fringe-field switching liquid crystal mode devices with reactive mesogens in a planar alignment layer. *J Phys D: Appl Phys*. 2013;46:485306. DOI: 10.1088/0022-3727/46/48/485306.
- [16] Nepal S, Mondal S, Sinha A, et al. Fast switching behaviour and dielectric parameters of two chiral ferroelectric mesogens. *Liq Cryst*. 2020;47(10):1464-1472. DOI: 10.1080/02678292.2020.1735547.
- [17] Chung HK, Lee WK, Park HG, et al. Polarized UV cured reactive mesogens for fast switching and low voltage driving liquid crystal device. *Opt Express*. 2014;22(18):21551-21559. DOI: 10.1364/OE.22.021551.
- [18] Liu D. Surface Dynamics at Photoactive Liquid Crystal Polymer Networks. *Adv Optical Mater*. 2019;1900255. DOI: 10.1002/adom.201900255.
- [19] Broer DJ. Creation of Supramolecular Thin Film Architectures with Liquid-Crystalline Networks. *Mol Cryst Liq Cryst*. 1995;261(1):513-523. DOI: 10.1080/10587259508033494.
- [20] Broer DJ, Gossink RG, Hikmet RAM. Oriented polymer networks obtained by photopolymerization of liquid-crystalline monomers. *Angew Makromol Chem*. 1990;183(1):45-66. DOI: 10.1002/apmc.1990.051830103.
- [21] Bobrovsky A, Shibaev V, Bubnov A, et al. Effect of molecular structure on chiro-optical and photo-optical properties of smart liquid crystalline polyacrylates. *Macromol*. 2013;46(11):4276-4284. DOI: 10.1021/ma401010t.
- [22] Woon KL, Liedtke A, O'Neill M, et al. Photopolymerization studies of a light-emitting liquid crystal with methacrylate reactive groups for electroluminescence. *Proc of SPIE*. 2008;7050:E500. DOI: 10.1117/12.724248.
- [23] Bobrovsky A, Shibaev V, Cigl M, et al. Azobenzene-containing LC polymethacrylates highly photosensitive in broad spectral range. *J Polym Sci Part A: Polym Chem*. 2016;54:2962-2970. DOI: 10.1002/pola.28181.
- [24] Bobrovsky A, Shibaev V, Cigl M, et al. The effect of spacer and alkyl tail lengths on the photoorientation processes in amorphous films of azobenzene-containing liquid crystalline polymethacrylates. *Liq Cryst*. 2020;47(3):377-383. DOI: 10.1080/02678292.2019.1655171.
- [25] Achten R, Koudijs A, Giesbers M, et al. Non-symmetric bent-core mesogens with one terminal vinyl group. *Liq Cryst*. 2005;32(3):277-285. DOI: 10.1080/02678290500031756.
- [26] Tóth-Katona T, Cigl M, Fodor-Csorba K, et al. Functional photochromic methylhydrosiloxane-based side-chain liquid-crystalline polymers. *Macromol Chem Phys*. 2014;215(8):742-752. DOI: 10.1002/macp.201300729.
- [27] Bubnov A, Domenici V, Hamplová V, et al. First liquid single crystal elastomer containing lactic acid derivative as chiral co-monomer: synthesis and properties. *Polymer*. 2011;52(20):4490-4497. DOI: 10.1016/j.polymer.2011.07.046.
- [28] Petrova I, Gaj A, Pocięcha D, et al. Design and self-assembling behaviour of comb-like stereoregular cyclolinar methylsiloxane copolymers with chiral lactate groups. *Liq Cryst*. 2019;46(1):25-36. DOI: 10.1080/02678292.2018.1461265.

- [29] Bubnov A, Cigl M, Sedláčková N, et al. Self-assembling behaviour of new functional photosensitive cinnamoyl-based reactive mesogens. *Liq Cryst.* 2020. DOI: 10.1080/02678292.2020.1783586.
- [30] Baxter BC, Gross BJ, Gin DL, Correlation of structure and phase behaviour for a series of modular, chiral liquid crystal diacrylates based on lactic acid. *Liq Cryst.* 2000;27(10):1317-1323. DOI: 10.1080/026782900423368.
- [31] Herman J, Dmochowska E, Czerwiński M. Synthesis of new chiral mono- and diacrylates for ferro- and antiferroelectric liquid crystals. *J Mol Liq.* 2018;271:353-360. DOI: 10.1016/j.molliq.2018.09.017.
- [32] Shakila A, Ravikumar S, Pandiyan V. Influence of temperature on thermo physical properties of binary mixtures of ethyl acrylate and alkyl amines: An experimental and theoretical approach. *J Mol Liq.* 2018;265:544-555. DOI: 10.1016/j.molliq.2018.05.130.
- [33] Peralta RD, Infante R, Cortez G. Density, excess volumes and partial volumes of the systems of p-xylene + ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K. *Termochim. Acta* 421. 2004:59-68. DOI: 10.1016/j.tca.2004.02.019.
- [34] Dierking I. A Review of Polymer-Stabilized Ferroelectric Liquid Crystals. *Materials.* 2014;7(5):3568-3587. DOI: 10.3390/ma7053568.
- [35] Thiem H, Stroehriegel P, Shkunov M, et al. Photopolymerization of Reactive Mesogens, *Macromol Chem Phys.* 2005;206:2153-2159. DOI: 10.1002/macp.200500272.
- [36] Kumagai T, Yoshida H, Ozaki M. Dielectric Properties of Dual-Frequency Reactive Mesogens before and after Photopolymerization. *Materials.* 2014;7(2):1113-1121. DOI: 10.3390/ma7021113.
- [37] Liu D, Broer DJ. Liquid Crystal Polymer Networks: Preparation, Properties, and Applications of Films with Patterned Molecular Alignment. *Langmuir.* 2014;30(45):13499-13509. DOI: 10.1021/la500454d.
- [38] Lee KM, Ware TH, Tondiglia VP, et al. Initiatorless Photopolymerization of Liquid Crystal Monomers. *ACS Appl Mater Interfaces.* 2016;8(41):28040-28046. DOI: 10.1021/acsami.6b09144.
- [39] Feng Y, Zhu Z, Zhang H, et al. Chiral polymer network stabilised blue phase liquid crystals. *Liq Cryst.* 2020. DOI: 10.1080/02678292.2020.1735545.
- [40] Kikuchi H, Yokota M, Hisakado Y, et al. Polymer-stabilized liquid crystal blue phases. *Nat Mater.* 2002;1:64-68. DOI: 10.1038/nmat712.
- [41] Yoshizawa D, Okumura Y, Yamamoto J, et al. Decreasing the operating voltage of a polymer-stabilized blue phase based on intermolecular affinity. *J Polym.* 2019;51:667-673. DOI: 10.1038/s41428-019-0183-6.
- [42] Lu Hongbo, Yang L, Xia L, et al. Band-edge-enhanced tunable random laser using a polymer-stabilised cholesteric liquid crystal. *Liq Cryst.* 2020. DOI: 10.1080/02678292.2020.1774085.
- [43] Rumi M, Bunning TJ, White TJ. Polymer stabilization of cholesteric liquid crystals in the oblique helicoidal state. *Soft Matter.* 2018;14:8883-8894. DOI: 10.1039/C8SM01278D.
- [44] Zhang W, Lub J, Schenning A, et al. Polymer Stabilized Cholesteric Liquid Crystal Siloxane for Temperature-Responsive Photonic Coatings. *Int J Mol Sci.* 2020;21(5):1803. DOI: 10.3390/ijms21051803.

- [45] Bobrovsky A, Boiko N, Shibaev V. Unusual electro-optical behaviour of the nematic polyacrylate. *Liq Cryst.* 2017;44(12-13):1870-1876. DOI: 10.1080/02678292.2017.1342004.
- [46] Rudquist P, Elfström D, Lagerwall ST, et al. Polymer-Stabilized Orthoconic Antiferroelectric Liquid Crystals. *Ferroelectrics.* 2006;344(1):177-188. DOI: 10.1080/00150190600968116.
- [47] Baliyan VK, Lee SH, Kang SW. Optically and spatially templated polymer architectures formed by photopolymerization of reactive mesogens in periodically deformed liquid crystals. *NPG Asia Mater.* 2017;9:e429. DOI: 10.1038/am.2017.151.
- [48] Czerwiński M, Urbańska M, Bennis N, et al. Influence of the type of phase sequence and polymer-stabilization on the physicochemical and electro-optical properties of novel high-tilt antiferroelectric liquid crystalline materials. *J Mol Liq.* 2019;288:111057. DOI: 10.1016/j.molliq.2019.111057.
- [49] Dierking I. Polymer Network Stabilized Liquid Crystals. *Adv Mater.* 2000;12(3):167-181. DOI: 10.1002/(SICI)1521-4095(200002)12:3<167::AID-ADMA167>3.0.CO;2-I.
- [50] Hikmet RAM, Lub J. Anisotropic networks with stable dipole orientation obtained by photopolymerization in the ferroelectric state. *J Appl Phys.* 1995;77:6234. DOI: 10.1063/1.359153.
- [51] Lagerwall ST. *Ferroelectric and Antiferroelectric Liquid Crystals.* Weinheim; NewYork; Chichester; Brisbane; Singapore; Toronto. Wiley-VCH, 1999.
- [52] Lagerwall JPF, Giesselmann F, Osipov M. On the change in helix handedness at transitions between the SmC* and phases in chiral smectic liquid crystals. *Liq Cryst.* 2006;33(6):625-633. DOI: 10.1080/02678290500371392.
- [53] Gąsowska J, Dąbrowski R, Drzewiński W, et al. Synthesis and Mesomorphic Properties of Achiral and Chiral Esters with High Tilted Synclitic and Anticlinic Phases. *Mol Cryst Liq Cryst.* 2004;411:231-241. DOI: 10.1080/15421400490435224.
- [54] Gąsowska J, Dąbrowski R, Drzewiński W, et al. Comparison of Mesomorphic Properties in Chiral and Achiral Homologous Series of High Tilted Ferroelectrics and Antiferroelectrics. *Ferroelectrics.* 2004;309:82-92.
- [55] Novotná V, Hamplová V, Kašpar M, et al. Variety of mesophases in compounds with an increasing number of lactate units in the chiral chain. *Liq Cryst.* 2013;40;14-21. DOI: 10.1080/02678292.2012.730638.
- [56] Bubnov A, Novotná V, Hamplová V, et al. Effect of multilactate chiral part of liquid crystalline molecule on mesomorphic behaviour. *J Mol Struct.* 2008;892:151-157. DOI: 10.1016/j.molstruc.2008.05.016.
- [57] Bubnov A, Novotná V, Pociecha D, et al. Effect of alkyl chains length on properties of ferroelectric liquid crystals with the keto group attached to the molecule core. *Phase Transit.* 2012;85:849-860. DOI: 10.1080/01411594.2012.684880.
- [58] Nishiyama I, Goodby JW. Effect of Polymerization on the Stability of Antiferroelectric Liquid-crystalline Phases: Liquid-crystalline Properties of some Chiral Acrylates and their Corresponding Polyacrylates. *J Mater Chem.* 1993;3(2):169-182. DOI: 10.1039/JM9930300169.

- [59] Mery S, Lotzsch D, Heppke G, et al. Antiferroelectric and ferroelectric liquid crystalline low molar mass materials and polymers. *Liq Cryst.* 1997;23(5):629-644. DOI: 10.1080/026782997207902.
- [60] Kühnpast K, Springer J, Scherowsky G, et al. Ferroelectric liquid-crystalline side group polymers. Spacer length variation and comparison with the monomers. *Liq Cryst.* 1993;14(3):861-869. DOI: 10.1080/02678299308027763.
- [61] Bolton EC, Lacey D, Smith PJ, et al. Twisted smectic A phases in side chain liquid crystal polymers. *Liq Cryst.* 1992;12(2):305-318. DOI: 10.1080/02678299208030399.
- [62] Ruth J, Naciri J, Shashidhar R. Ferroelectric properties of mixtures of a liquid crystalline polymer and its side-group mesogen. *Liq Cryst.* 1994;16(5):883-892. DOI: 10.1080/02678299408027859.
- [63] Scherowsky G. Fast switching ferroelectric liquid crystalline polymers. *Makromol Chem Makromol Symp.* 1993;69:87-98. DOI: 10.1002/masy.19930690111.
- [64] Madhuri PL, Prasad SK, Nair GG. Influence of polymer stabilization on the dielectric relaxations of an antiferroelectric liquid crystal. *RSC Adv.* 2014;4:3121-3130. DOI:10.1039/c3ra43343a.
- [65] Labeed A, Gleeson HF, Hegmann T. Polymer stabilization of the smectic C- α^* liquid crystal phase—Over tenfold thermal stabilization by confining networks of photopolymerized reactive mesogens. *Appl Phys Lett.* 2015;107:232903.
- [66] Atorf B, Hoischen A, Ros MB, et al. Switching performance of a polymer-stabilized antiferroelectric liquid crystal based on bent-core molecules. *Appl Phys Lett.* 2012;100:223301. DOI: 10.1063/1.4722594.
- [67] Rudquist P. Orthoconic antiferroelectric liquid crystals. *Liq Cryst.* 2013;40(12):1678-1697. DOI: 10.1080/02678292.2013.828031.
- [68] Krup K, Czerwiński M, Tykarska M. Ferroelectric compounds with chiral (S)-1-methylheptyloxycarbonyl terminal chain – their miscibility and a helical pitch. *Liq Cryst.* 2015;42(2):248-254. DOI: 10.1080/02678292.2014.982222.
- [69] Piecek W, Perkowski P, Raszewski Z, et al. Long pitch orthoconic antiferroelectric binary mixture for display applications. *Mol Cryst Liq Cryst.* 2010;525:140-152. DOI: 10.1080/15421401003753223.
- [70] Czapryński K, Gąsowska J, Tykarska M, et al. Orthoconic antiferroelectric liquid crystalline materials. *J Opt Technol.* 2005;72(9):655-658. DOI: 10.1364/JOT.72.000655.
- [71] Dzik E, Mieczkowski J, Górecka E, et al. Ferroelectric, ferroelectric and antiferroelectric mesophases in compounds with a polybenzyloxycarbonyl mesogenic core. *J Mater Chem.* 2005;15:1255-1262. DOI: 10.1039/B417144F.
- [72] Dąbrowski R, Drzewiński W, Dziaduszek J, et al. Orthoconic antiferroelectric liquid crystals containing biphenyl, terphenyl, or naphthyl mesogenic unit. *Opto-Electron Rev.* 2007;15(1):32-36. DOI: 10.2478/s11772-006-0052-7.
- [73] Essid S, Rihab Z, Nguyen HT. Synthesis and characterisation of a novel chiral smectic liquid crystal compound. 2012;39(7):865-872. DOI: 10.1080/02678292.2012.686634.
- [74] Krup K, Czerwiński M, Tykarska M, et al. Design of advanced multicomponent ferroelectric liquid crystalline mixtures with submicrometre helical pitch. *Liq Cryst.* 2017;44(4):748-756. DOI: 10.1080/02678292.2016.1239774.

[75] Żurowska M, Czerwiński M. The new high tilt mixtures with antiferroelectric phase at a broad temperature range and a long helical pitch. *Liq Cryst.* 2017;44(6):1044-1049. DOI: 10.1080/02678292.2016.1256443.

[76] Kurp K, Czerwiński M, Tykarska M, et al. Design of functional multicomponent liquid crystalline mixtures with nano-scale pitch fulfilling deformed helix ferroelectric mode demands. *J Mol Liq.* 2019;290:111329. DOI: 10.1016/j.molliq.2019.111329.

[77] Czerwiński M, García de Blas M, Bennis N, et al. Polymer stabilized highly tilted antiferroelectric liquid crystals - the influence of monomer structure and phase sequence of base mixtures. *J Mol Liq.* 2020;114869. DOI: 10.1016/j.molliq.2020.114869.

Graphical abstract

Highlights

- The design and mesomorphic properties of new chiral calamitic reactive mesogens.
- Monoacrylates that are structurally compatible with N5FL's mixture components.
- Low values of transition temperatures connected with chirality and reactivity.