



Determination of the temperature dependence of the helical pitch in 1.m.7(HH) liquid crystalline compounds

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Abstract: Homologous series 1.m.7(HH) of liquid crystalline compounds, varying in the chiral chain length m ($m=4-9$), were studied. These compounds are characterized by a long helical pitch in an antiferroelectric phase, which is higher than the measuring range of the available instruments. The temperature dependence of the helical pitch of these compounds was determined by the extrapolation of the results obtained for the mixtures of 1.m.7(HH) compounds with 1.4.7(HF) compound of a known helical pitch value. The helical pitch measurements were made by spectrophotometry and phase transition temperatures were measured by polarizing thermomicroscopy. Extrapolation of the results let established that the investigated liquid crystals are characterized by the helical pitch increasing and then decreasing upon heating, which is accompanied by the helical twist sense inversion from the right-handed structure to the left-handed one.

Keywords: liquid crystals, antiferroelectric phase, helical pitch, miscibility study

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1. Introduction

Among liquid crystal smectic phases chiral phases formed by molecules with an asymmetric centre, most commonly formed by an asymmetric carbon atom, can be distinguished. The chirality of liquid crystal compounds results in the formation of phases with macroscopic helical structure. These phases include smectic phases SmC^* and SmC_A^* [1-3]. Fig. 1a shows the structure of the chiral synclinic smectic phase SmC^* . The molecules in the smectic layer are tilted at an angle θ and

the direction of their longer axes (described with the director \hat{n}) changes between the smectic layer and the adjacent one [4]. The distance at which the director rotates by 360° is the helical pitch [1]. Fig. 1b shows the structure of the chiral anticlinic smectic phase SmC_A^* . In the two adjacent layers, the molecules are tilted alternately at angles $+\theta$ and $-\theta$. In the next pair of layers, the director turns by a specific angle so that the phase has a helical structure with the axis perpendicular to the plane of the layers and a repetition period of $p/2$ [1].

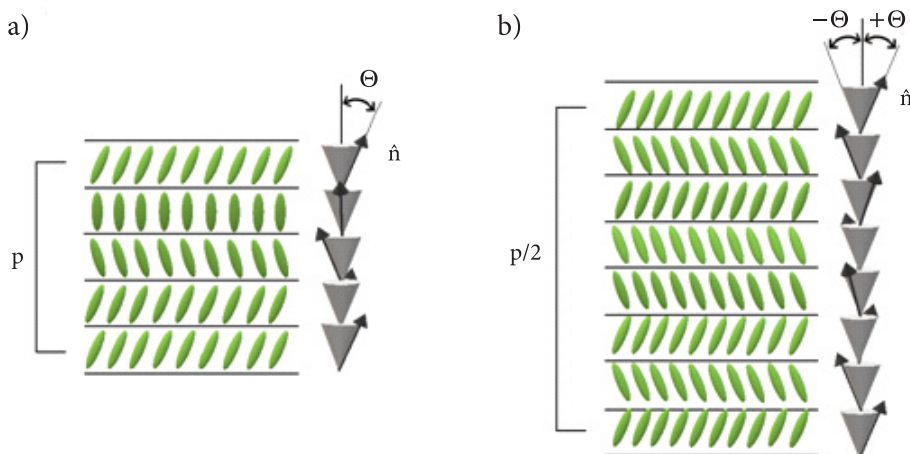


Fig. 1. Schematic diagram of the smectic phases SmC^* (a) and SmC_A^* (b)

Helical pitch is a significant parameter of chiral phases. It is also one of the material parameters optimised in the production of utility mixtures. Multiple techniques of helical pitch measurement exist, and a liquid crystal material can be tested as a thin layer between two microscopic slides, a free standing film, or a drop applied on a glass plate [5-7].

A distinctive property of the macroscopic helical structure is the selective reflection of light at a wavelength proportional to the value of helical pitch [3]. This dependence is expressed with the following equation: $p = \lambda_s / 2n_{av}$, where λ_s is the wavelength of selectively reflected light and n_{av} is the mean refractive index of liquid crystals (its value was 1.5 in the calculations [8]). The dependence is met for SmC^* phase. For SmC_A^* phase, however, the light reflection condition is met for only half of the helical pitch and the equation is reduced to the following form: $p = \lambda_s / n_{av}$.

Spectrophotometric method of helical pitch measurement is based on the detection of the light reflected by helical structure. The light at the selectively reflected wavelength does not reach the detector, as the result a minimum in the transmittance curve appears which position represents the wavelength λ_s [9]. The measurement with this method uses homeotropic arrangement of smectic layers; in this arrangement, the axis of the helix is perpendicular to the glass plate surface on which

the specimen of a liquid crystal is placed. In this case a lower impact of the surface on the helical structure occurs, providing higher measurement accuracy [10]. A limitation of the method is the measuring range of the spectrophotometer.

Helical structures formed by chiral molecules can twist the plane of linearly polarized light to the right or to the left [11]. A right-handed structure is designated “+”; and a left-handed structure is designated “-”. The twist sense of a helix depends on the structure of liquid crystalline compounds, the size and shape of substituents and the absolute configuration of the asymmetric carbon atom (“R” or “S”) [11, 12]. The sense of helical twist changes at the transition from SmC^* to SmC_A^* [13]. Within these smectic phases, a helical twist sense inversion may also occur [14-16]. The structure becomes completely unwound at the helical twist sense inversion temperature.

The temperature dependency of the helical pitch varies between the specific chiral phases. In SmC^* phase, insignificant changes in the helical pitch are most usually observed [16, 17]. SmC_A^* phase features high variations of the helical pitch when the temperature changes. Some homologous series were found with the temperature dependence of the helical pitch upon the length of the terminal non-chiral chain. Hence, three types of temperature dependencies of helical pitch in SmC_A^* phase were distinguished: (a) the increase of helical pitch upon temperature for right-handed helix, which is present for short chain molecules; (b) the decrease of helical pitch upon temperature for left-handed helix, which is present for long chain molecules; (c) both dependencies accompanied with helical twist sense inversion from right- to left-handed which are present for moderately long chain molecules [14].

The aim of this work was to determine the temperature dependence of helical pitch in the smectic SmC_A^* phase for a 1.m.7(HH) homologous series of liquid crystalline compounds. The helical pitch of these compounds is beyond the measuring range of the spectrophotometer used for testing. Hence, to test the temperature dependence of helical pitch, two-component mixtures were prepared; each mixture contained one of tested compounds and a 1.4.7(HF) compound of a known helical pitch. Next, the helical pitch values were determined for the pure 1.m.7(HH) series compounds by extrapolation of the results determined for the specific mixtures.

2. Experiments

Six liquid crystal esters varying in the chiral chain length m were selected for testing their helical pitch. Each compound was designated with acronyms following the formula 1.m.7(HH), with m varying from 4 to 9 [18]. The structure of the molecules is shown in Fig. 2a. Each compound was mixed with a 1.4.7(HF) compound of the structure shown in Fig. 2b [18]. The mixtures were prepared with each at a molar fraction of 0.2, 0.4, 0.6 and 0.8 of the 1.4.7(HF) compound.

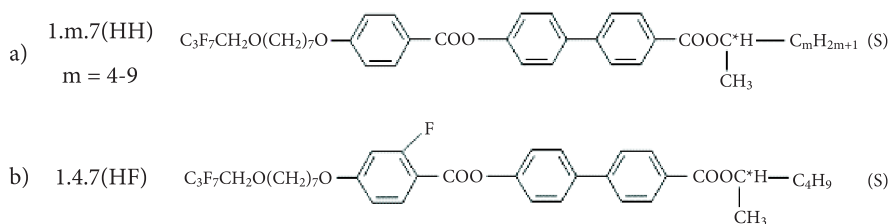


Fig. 2. Structures of the liquid crystal compounds used for testing [18]

The phase transition temperatures of the pure compounds and their mixtures were tested by polarized light thermomicroscopy with a BX51 polarizing microscope and a Linkam THMS 600 heating stage. The heating temperature was controlled with a Linkam CI94 control unit. The test compound specimens were placed between pairs of glass plates. The measurements were made by observation of the liquid crystal textures during temperature changes. The phase transition temperatures shown in the phase diagrams were measured in heating cycles at 2°C/min. The phases formed by the tested compounds are shown in Table 1.

TABLE 1

Phase transition temperatures [°C] of tested compounds

Compound	Phase transition temperature [°C]								
	Cr	SmC _A *	SmC*	SmA	Iso				
1.4.7(HH)	*	56.6	*	128.5	*	138.0	*	146.4	*
1.5.7(HH)	*	60.6	*	122.1	*	130.7	*	136.0	*
1.6.7(HH)	*	61.2	*	121.5	*	125.9	*	128.2	*
1.7.7(HH)	*	59.9	*	111.5	*	118.2	*	120.0	*
1.8.7(HH)	*	56.7	*	107.7	*	111.7	*	112.6	*
1.9.7(HH)	*	58.4	*	108.3	*	109.8	*	111.5	*
1.4.7(HF)	*	45.0	*	101.0	*	109.5	*	118.5	*

The helical pitch was measured under a Shimadzu 3600 UV-Vis-NIR spectrophotometer with an MLV U7 temperature controller and a Peltier module. The specimen of each mixture was applied to a glass plate coated with a cetyltrimethylammonium bromide (CTAB) surfactant to produce a homeotropic order. The liquid crystalline layer thickness was not precisely determined but it was definitely above the measured helical pitch. The helical pitch was measured at a wavelength of 360-3000 nm and a temperature of 2-110°C. The spectra obtained at different temperatures provided the minimum position which served to calculate the helical pitch value in the smectic phases SmC* and SmC_A*. The helical twist sense inversion temperature was

determined by comparing the transmittance values within the spectra registered by the spectrophotometer. The transmittance values were the lowest at the helical twist sense inversion temperature.

The helical twist sense was determined under an OPTA-TECH MP-349 polarizing microscope with a Linkam THMS 600E heating stage and a Linkam T95-STD temperature controller. The glass plates were coated with a film of a cetyltrimethylammonium bromide (CTAB) surfactant to produce an organized layer before applying the test specimens. Each test specimen on the glass plate was placed between crossed polarizers. When the microscopic field of view became darker by rotating the analyser clockwise, the structure was left-handed. When the microscopic field of view became darker by rotating the analyser counter clockwise, the structure was right-handed.

3. Results

Fig. 3 presents the phase diagrams for the systems comprising 1.m.7(HH) and 1.4.7(HF) compounds. The tested compounds are immiscible in the crystalline phase, thus eutectic composition is formed. The compounds mix additively in all liquid crystal phases: SmC_A^* , SmC^* and SmA ; this means that across the entire range of concentration the phase transition temperatures change linearly from one pure compound to the other.

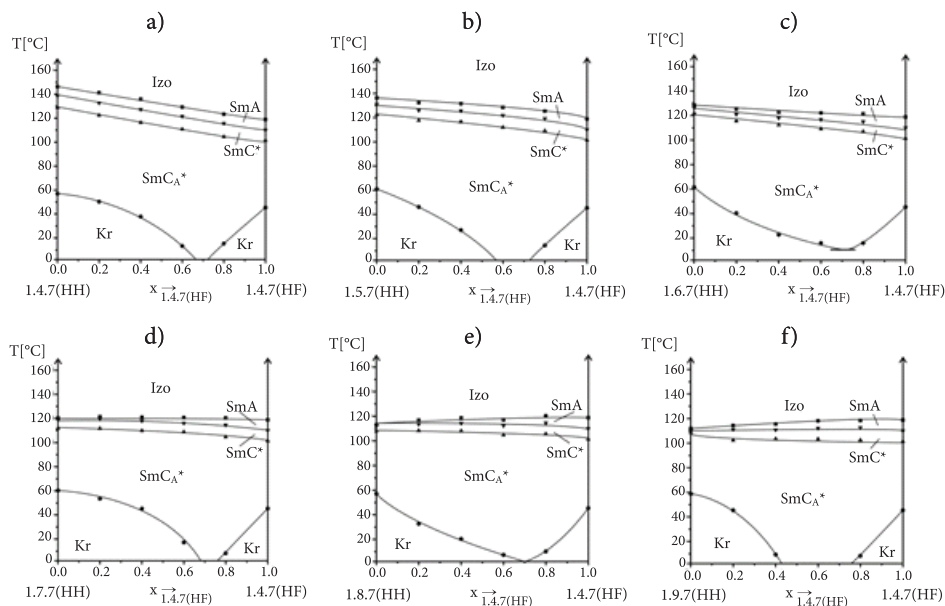


Fig. 3. Phase diagrams for the 1.m.7(HH)-1.4.7(HF) systems

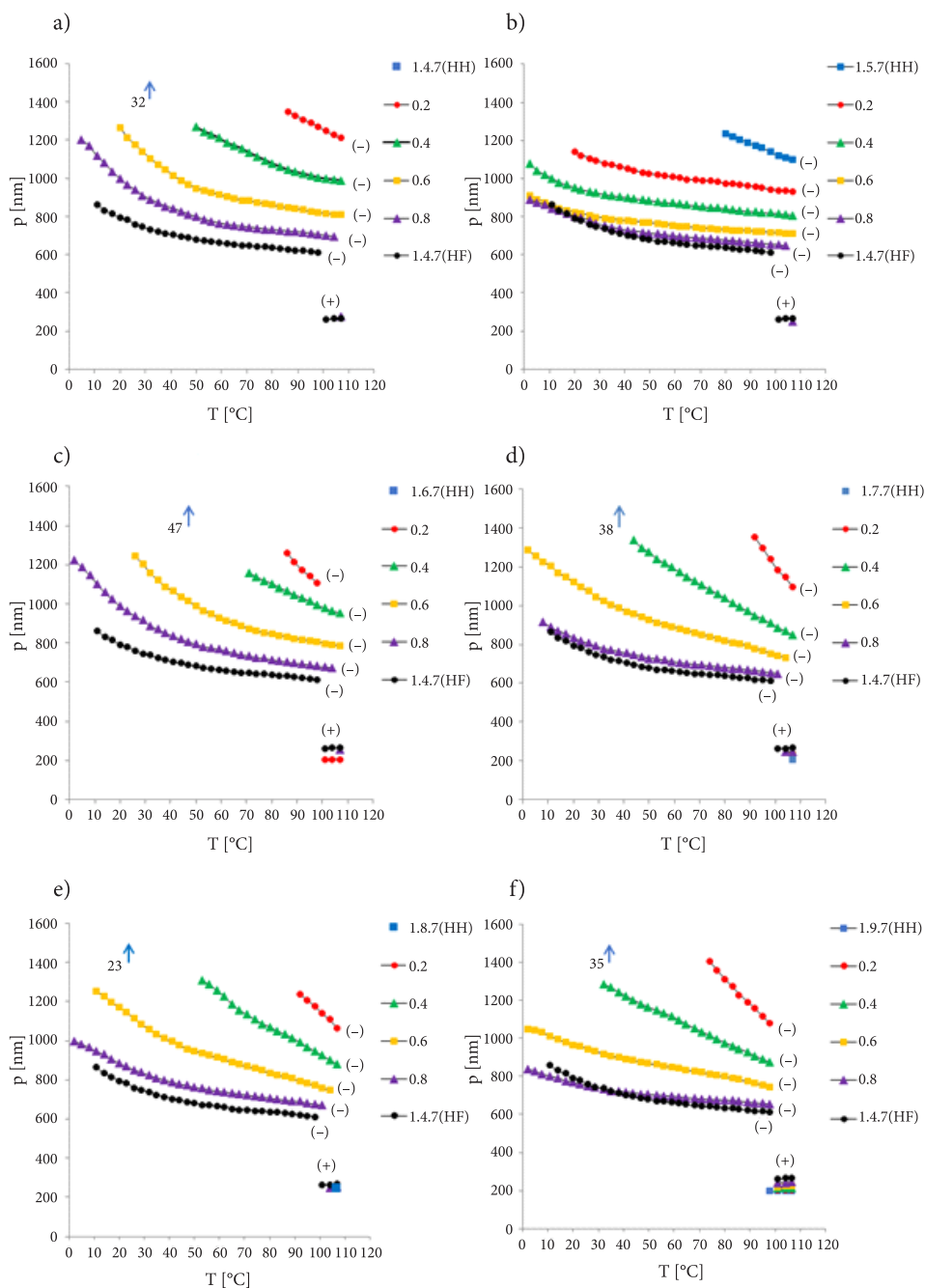


Fig. 4. Helical pitch measurements in the 1.m.7(HH)-1.4.7(HF) systems;
 (+) — right-handed structure; (-) — left-handed structure;
 ↑ — helical twist sense inversion temperature in the 1.m.7(HH) compounds

Fig. 4 shows the helical pitch results determined for the mixtures of the 1.m.7(HH) compound with the 1.4.7(HF) compound in the smectic phases SmC^* and SmC_A^* . In the tested mixtures, the helical pitch values decrease as the temperature increases, and the structure is left-handed in SmC_A^* phase. The transition to SmC^* phase causes the change of the helical twist to right-handed, and the helical pitch changes negligibly as the temperature increases. For the pure 1.m.7(HH) series compounds, it was possible to obtain results of the helical pitch only for the 1.5.7(HH) compound in the temperature range 80-107°C. All other pure compounds have the values of helical pitch over measuring range of the spectrophotometer and only helical twist sense inversion temperatures determined from UV-Vis-NIR spectra are shown with the arrows in Fig. 4.

3.1. Determination of the temperature dependence of helical pitch in 1.m.7(HH) compounds

Fig. 5 shows the concentration dependence of helical pitch for the specific two-component systems at different temperatures. The helical pitch decreases as the reference compound 1.4.7(HF) is added. Generally, the change in the helical pitch as a function of concentration in mixtures is rarely linear; because it depends on many factors, including intermolecular forces, the value of helical pitch of pure compounds and the temperature dependence of helical pitch. The results of this work were used in the calculation of the helical pitch of the 1.m.7(HH) series by extrapolation with a second-degree polynomial, due to the best match of the function to the measurement data. The 1.5.7(HH) compound was not extrapolated; its helical pitch was within the measuring range of the spectrophotometer. The calculations were performed within temperature range 86-98°C because for these temperatures the results for most mixtures were determined (between 1 and 0.2 of a molar fraction). If the temperature range had been extended, the extrapolation of the results would have been valid only within a concentration range of 1-0.4 of molar fraction, or even smaller at lower temperatures. Table 2 shows the polynomial equations derived for the temperature of 95°C. Fig. 6a shows the temperature dependence of helical pitch for the homologous series 1.m.7(HH) compounds; the extrapolated results are shown with open points. The helical pitch of these compounds decreases with the increase of temperature above 86°C, where the structure is left-handed.

The temperature dependence of inverted helical pitch was used to determine the temperature dependence of helical pitch in a wider temperature range. The temperature dependence of inverted helical pitch is a linear function for which the zero value corresponds to the helical twist sense inversion temperature, the positive values correspond to the right-handed structure, and the negative values correspond to the left-handed structure [19]. The extrapolated results, the values measured for 1.5.7(HH) compound and the helical pitch inversion temperatures were superimposed on the chart

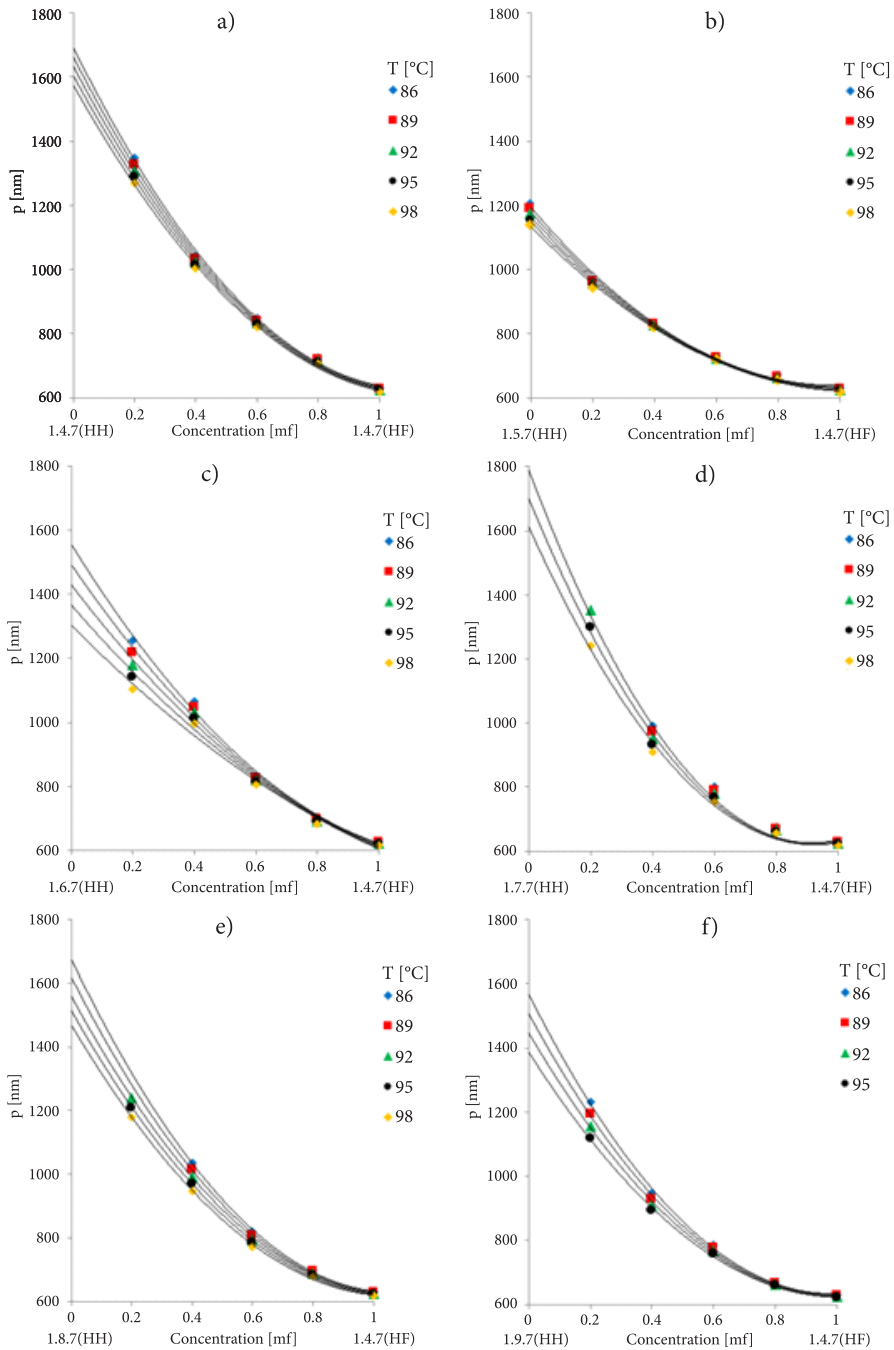


Fig. 5. Graphs of concentration dependence of helical pitch in the 1.m.7(HH)-1.4.7(HF) systems at different temperature values

of the temperature dependence of inverted helical pitch (Fig. 6b). Next, line equations were derived for the individual liquid crystal compounds and summarized in Table 3. The obtained functions were used to determine the temperature dependence of helical pitch of tested compounds in wider temperature range of 10-100°C (Fig. 6c). The helical pitch in the tested compounds increases with temperature and next decreases above the helical twist sense inversion temperature, with the exception of the compound $m=5$, the helical pitch of which decreases with temperature.

TABLE 2

Extrapolation polynomial equations at 95°C for the 1.m.7(HH) compounds

Compound	Extrapolation polynomial	Correlation factor
1.4.7(HH)	$y = 785.47x^2 - 1761.7x + 1602.8$	0.9986
1.6.7(HH)	$y = 357.39x^2 - 1112.3x + 1364.8$	0.9896
1.7.7(HH)	$y = 1277.3x^2 - 2344.7x + 1699$	0.9928
1.8.7(HH)	$y = 784.75x^2 - 1673.9x + 1512$	0.9995
1.9.7(HH)	$y = 743.3x^2 - 1507x + 1385.9$	0.9989

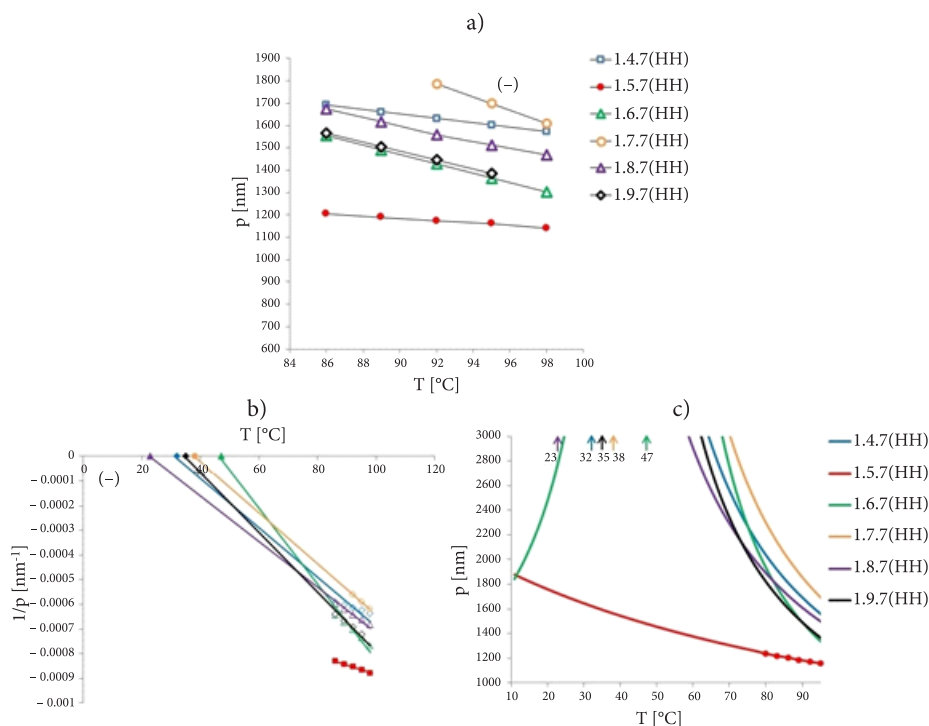


Fig. 6. Helical pitch at temperatures 86-98°C (a), inverted helical pitch (b) and helical pitch at temperatures 10-100°C (c) for the 1.m.7(HH) compounds; the open points were determined by extrapolation

TABLE 3

Function equations for the temperature dependence of inverted helical pitch for the 1.m.7(HH) compounds

Compound	Function equation $f = p^{-1}(T)$	Linear correlation factor
1.4.7(HH)	$y = -1.142 \cdot 10^{-5}x + 3.631 \cdot 10^{-4}$	0.9970
1.5.7(HH)	$y = -3.411 \cdot 10^{-6}x - 5.988 \cdot 10^{-4}$	0.9896
1.6.7(HH)	$y = -1.637 \cdot 10^{-5}x + 7.662 \cdot 10^{-4}$	0.9968
1.7.7(HH)	$y = -1.305 \cdot 10^{-5}x + 4.951 \cdot 10^{-4}$	0.9996
1.8.7(HH)	$y = -1.073 \cdot 10^{-5}x + 2.459 \cdot 10^{-4}$	0.9995
1.9.7(HH)	$y = -1.411 \cdot 10^{-5}x + 4.924 \cdot 10^{-4}$	0.9993

4. Conclusion

The temperature dependence of helical pitch in SmC_A^* phase of liquid crystal compounds of the homologous series 1.m.7(HH), which varied in the terminal chiral chain length, was tested. Polarizing thermomicroscopy was applied to measure the phase transition temperatures of the mixtures of the 1.m.7(HH) compounds with the 1.4.7(HF) compound; next phase diagrams were constructed. The compounds featured additive miscibility in the individual liquid crystal phases and immiscibility in the crystalline phase.

The helical pitch measurement results, determined with the spectrophotometer and extrapolated with a second-degree polynomial provided the temperature dependence of helical pitch. At temperatures between 86–98°C, the helical pitch of the 1.m.7(HH) compounds decreases as temperature increases and a helical structure is left-handed. An extrapolation-based determination of helical pitch in liquid crystal compounds, which cannot be measured by spectrophotometry, is effective when compounds with the same sense of helical twist are mixed together. The results allowed a conclusion that the 1.m.7(HH) compounds are characterised by a helical pitch which increases at lower temperatures and decreases at higher temperatures with a change of the helical twist sense from right- to left-handed. The chiral chain length has a minor effect on the temperature dependence of helical pitch in 1.m.7(HH) compounds.

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**Wyznaczanie zależności skoku helisy od temperatury
dla związków ciekłokrystalicznych 1.m.7(HH)**

Streszczenie: Przedmiotem badań był szereg homologiczny związków ciekłokrystalicznych 1.m.7(HH) różniących się długością łańcucha chiralnego m ($m = 4-9$). Związki te charakteryzują się długim skokiem helisy w fazie antyferroelektrycznej, większym niż zakres pomiarowy dostępnej aparatury. Zależność skoku helisy od temperatury wyznaczono, ekstrapolując wyniki pomiarów skoku helisy otrzymane dla mieszanin związków 1.m.7(HH) ze związkiem 1.4.7(HF) o znanym skoku. Pomiar skoku helisy wykonano metodą spektrofotometryczną, natomiast temperatury przemian fazowych zmierzono za pomocą polaryzacyjnego mikroskopu optycznego. Ekstrapolacja wyników pozwoliła ustalić, że badane ciekłe kryształy charakteryzują się skokiem helisy zwiększającym się, a następnie zmniejszającym ze wzrostem temperatury, czemu towarzyszy inwersja skrętności helisy z prawoskrętnej na lewoskrętną.

Słowa kluczowe: ciekłe kryształy, faza antyferroelektryczna, skok helisy, badania mieszalności

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