

## IDENTIFYING OF THERMOTROPIC LIQUID CRYSTAL PHASE AND ITS INFLUENCE ON LUBRICITY OF IONIC LIQUIDS

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### **Abstract**

*In this article there is discussed a possibility of forming the liquid crystal structure in ionic liquids and its influence on performance characteristics, especially tribological, of these liquids. Formation of such thermal phase might influence on, among other things, easier creation of the boundary lubricating film, which is characterized by high viscous anisotropy. The results of tribological tests showed better lubricity of selected ionic liquids than modern PFPE oils. Identification of mesophase in ionic liquids was necessary. This method is described in the paper. Biolar PL polarizing interference microscope with thermal stabilizing table, with birefracton system, and Brüker Discover 8 powder diffraction instrument with a Cu lamp and monochromator were used. There was being searched the state characterized simultaneously by optical anisotropy properties and liquid state of aggregation. For identification of phase transition temperature, the additional calorimetric tests were carried out during the cycle of heating and cooling. These researches were carried out within the framework of the development and research project no. PBR 15-249/2007/WAT-OR0002904, financed by Ministry of Science and Higher Education during 2007-2011.*

**Keywords:** *mesophase identification, liquid crystals, ionic liquids*

### **1. Introduction**

In recent years, the tribologists have been interested in ionic liquids. So far, there are only few publications about possible uses of ionic liquids as independent lubricants or lubricant additions. In the scientific literature, you can find only several dozen publications about ionic liquid tribological properties. To date there are no any spectacular implementations of any ionic liquid in the lubrication technologies. This time only few fundamental and laboratory researches are being carried out in several science centres (China, Japan, USA, Spain) [1-6].

Ionic liquids (ILs) are liquids consisting of the ions only. Ionic liquids are all salts, but most of them melt at very high temperatures (e.g. sodium chloride NaCl melts at 801°C), so their technological usability is very limited. At the moment, the term “ionic liquid” is not being used for such salts (high temperature molten salts). According to the new definition: “ionic liquids are ionic compounds, which are liquids below 100°C” [1]. The most used ionic salts (liquids) have their melting point (vitrification temperature) below room temperature (25°C), and many of them even considerably below 0°C. This group of ionic liquids is most often called RTILs (room temperature ionic liquids). In scientific literature, in order to emphasise various possible applications of ionic liquids, some their unique properties, e.g. high temperature stability, low vapour pressure and slight volatility, distinct polarity, incombustibility, air and water resistance, wide temperature range for liquid state etc., are being described. Such properties are required for high quality

lubricating oils, but standard lubricating oils sometimes do not meet these requirements [2-6]. Formation of thermal phase may influence on easier creation of the boundary lubricating film of ionic liquids.

Liquid crystals form substances keeping most of liquid properties, simultaneously maintaining mutual molecular order characteristic for a crystal. German botanist F. Reinizter discovered them in 1888 while examining some substances of plant origin under a polarizing microscope. During the examination, he noted they behaved strangely during the melting process. Later, O. Lehman found that they were thermodynamically stable, and they had a transition structure between crystals and traditional liquids. Lehman called that state liquid crystals. Liquid crystals are anisotropic liquids differing from normal isotropic liquids with: viscosity, optical, electrical and acoustic properties. They do not have a stiff crystal lattice, what results in the absence of the shape elasticity and allows the substance to flow. At the same time, liquid crystals have structural properties of solid bodies.

There is a transition phase between crystal and amorphous order, so-called mesophase, liquid crystal phase or mesomorphic phase. Mesophase can come into existence as a results of temperature change, and then it is called thermotropic phase. So, this temperature changes as results of operating conditions, may be caused by the tribological processes.

## 2. Liquid Crystallinity of Ionic Liquids

According to some literature data [1, 7, 8], there is a wide range of possibilities of forming liquid crystalline phases. One of the examples is the instance shown in Fig. 1, described in [1], concerning the series of 1-alkyl-3-methylimidazole tetrafluoroborates.

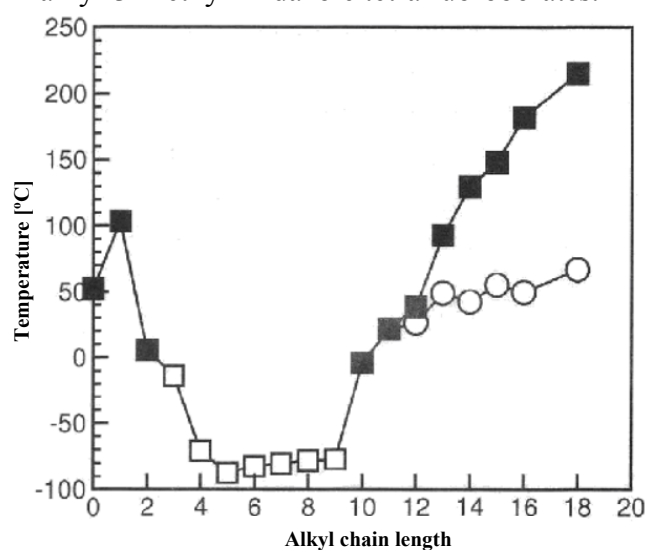


Fig. 1. Change of melting point of  $[RMIM][BF_4]$  ionic liquids against the alkyl chain length; ■ real melting point □ vitrification zone, ○ smectic liquid crystal phase [1]

As can be seen in Fig. 1, with the alkyl chain length increase (the number  $n$  of carbons increase), melting point decreased down to  $0^\circ\text{C}$ . For the values of  $n = 4 - 10$ , the salt vitrification was registered rather than melting. Vitrification symptoms were already registered for three carbons in the alkyl chain. Further increase of the number of carbons, beginning from 8/10, led to salt melting point new increase caused by mutual interaction (van der Waals interaction) between long carbon chains, contributing to the local change of structure, consisting in excitation of microphase separating covalent hydrophobic chains from the zone with charged ions. Initial ( $n = 1 - 3$ ) length change of alkyl substituent was causing decrease of the salt melting point value, thanks to destabilization of close packing caused by Coulomb forces, aiming at the vitrified structure formation. However, further radical length increase, again favoured more efficient interaction of van der Waals' forces between the carbon chains, and crystalline liquid (liquid crystal) structure

reorder for some temperature range. In crystalline phase of ionic liquid, ion-ion Coulomb interactions are dominant, like in typical crystalline salts. Liquid crystal state is being usually obtained by ionic liquids with enhanced amphiphilic cation properties (concurrently hydrophilic and lyophilic), thanks to the substituent with a longer linear alkyl chain. It is an attribute of, for example, soaps and detergents.

Salts melting point is relatively low, near room temperature, when alkyl chain length  $C_n$  is small ( $n \leq 10$ ), while mesomorphism manifests within them, when  $n > 12$ . Extensive researches on liquid crystal phase formation were being performed for many years by Neve and the team [5] on N-alkyl pyridine salts with alkyl chains, when  $n = 12-18$ , and with tetrachlorometallic anions based on Pd (II), Cu (III) Co (II), Ni (II) Zn (II) and Cd (II). Various liquid crystal phases were found, strongly dependent on the kind of the metal contained in the salt.

Liquids not containing metals are also being tested in the context of liquid crystal phases forming. For example, Bradley and the team [6] tested 1-alkyl-3-methylimidazole salts containing anions: chloric, bromide, trifluoromethylsulfonyl [OTf]<sup>-</sup>, bis(trifluoromethylsulfonyl)imide [Tf<sub>2</sub>N]<sup>-</sup> and tetrafluorobromic [BF<sub>4</sub>]<sup>-</sup>. Within mesophase, they found, because of X-ray tests (X-ray diffraction), the presence of smectic phase (A) with interlayers 22 and 61 Å away, which grew evenly with the alkyl chain length increase (n). For the given cations, distances between mesophase layers were decreasing in the following anions order: Cl<sup>-</sup> > Br<sup>-</sup> > [BF<sub>4</sub>]<sup>-</sup> > [OTf]<sup>-</sup> – when bis(trifluoromethylsulfonyl)imide salt was not forming any mesophase structure.

Anions influence on the distance between mesophase interlayers is the greatest, when they show the highest ability to shape three-dimensional spatial crystal lattices with hydrogen bonds. It arises from the researches carried out by Neve [9] with the use of X-ray diffraction method, that in case of every salt melted into isotropic liquid a clear peak occurs on the diagram of X-rays intensity against dispersion angle  $2\Theta$  – X-rays intensity temporary increase for a very low value of angle  $2\Theta$ . That peak means that, even in isotropic liquid phase, within some narrow range, ordered structural action is still possible (Fig. 2).

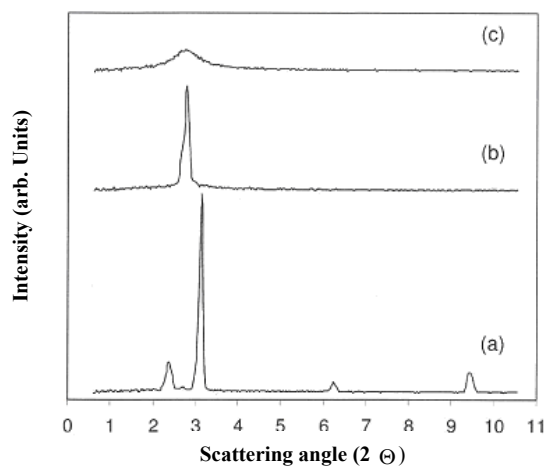


Fig. 2. Small X-ray diffraction angle for  $[C_{16}MIM]^+[OTf]^-$  at the temperature of: a) 50°C, b) 70°C, c) 90°C, accordingly in crystalline  $SmA_2$  and isotropic phase, during cooling [10]

During these researches, it was found that distances between smectic phase interlayers were strongly decreasing during cooling, from 50-60 Å to 25-31 Å. Similar researches on other salts were being performed in few countries. It appears from them that both main cation member and alkyl chains connected with it, including their length, are responsible for the possibility of liquid crystal phase forming [10]. Whereas temperature is the most important determinant of mesophase occurrence within ionic liquid, Hamaguchi and the team [8] proved that mesophase occurrence was also possible in case of very short imidazole salt alkyl chains. They were examining 1-butyl-3-methylimidazole halide salt, finding strong dependence of structure of that salt solid body on the prior temperature interactions.

### 3. Identification Tests of Liquid Crystal Thermal Phase within Selected Ionic Liquids

#### 3.1. Tested Ionic Liquids and Reference Oils

As a part of the development, project no. PBR/15-249/2007/WAT-OR00002904 founded by the Ministry of Science and Higher Education during 2007 – 2011, the research works were carried out with the goal of, among other things, checking possibilities of the application of selected ionic liquids in the lubrication technologies [11-13]. It were, first of all, patented in 2009, new Polish ionic liquids [14] based on 1-alkyl-3-alkoxymethylimidazole, from POCH S.A. [15]. These liquids were never fully examined yet. A few other liquids, with different cations or anions and insoluble in water, were selected for comparative tests, from Sigma Aldrich [16].

- CJ001 – tetrafluoroborate 1-methyl-3-octyloxymethylimidazole –  $C_{13}H_{25}BF_4N_2O$ ,
- CJ002 – bis(trifluoromethylsulfonyl)imide 1-methyl-3-octyloxymethylimidazole –  $C_{15}H_{25}F_6N_3O_5S_2$ ,
- CJ003 – bis(trifluoromethylsulfonyl)imide 1-butoxymethyl-3-methylimidazole –  $C_{11}H_{17}F_6N_3O_5S_2$ ,
- CJ004 – bis(trifluoromethylsulfonyl)imide 1-butoxymethyl-3-butylimidazole –  $C_{14}H_{23}F_6N_3O_5S_2$ ,
- CJ005 – tetrafluoroborate 1-benzyl-3-methylimidazole –  $C_{11}H_{13}BF_4N_2$ ,
- CJ006 – bis(trifluoromethylsulfonyl)imide 3-methyl-1-propylpyridyne –  $C_{11}H_{14}F_6N_2O_4S_2$  ( $T_{melt} = 0^\circ C$ ),
- CJ007 – bis(trifluoromethylsulfonyl)imide 1.2-dimethyl-3-propylimidazole –  $C_{10}H_{15}F_6N_3O_4S_2$ ,
- CJ008 – bis(trifluoromethylsulfonyl)amide trihexyltetradecylphosphonium –  $C_{34}H_{68}F_6NO_4S_2P$ ,
- CJ009 – tetrafluoroborate trihexyltetradecylphosphonium –  $C_{32}H_{68}BF_4P$ .

The lubricity properties of the ionic liquids we decided to confront with the results for modern perfluoropolyethers oils (PFPE) from Solvay Solexis [17]. These oils are used among others things, for lubrication of some parts in the space engineering, on account of their insignificant evaporativity like ionic liquids, and other machines lubricated elastohydrodynamically [18, 19]. There were selected four PFPE oils: Fomblin PFPE YPL 1500, Fomblin PFPE YO4, Fomblin PFPE M60 and Fomblin PFPE M15 [17]. During preliminary tests, fundamental physical properties of all ionic liquids and reference PFPE oils were identified. The selected tests results are presented in table 1.

Tab. 1. Selected Physical Properties of Ionic Liquids and Reference PFPE Oils

Liquid lubricant	Molecular weight [g/mol]	Density at 25°C $\rho_{25}$ [g/cm <sup>3</sup> ]	Absolute viscosity at 25°C $\eta_{25}$ [mPas]	Kinematic viscosity at 25°C $\nu_{25}$ [mm <sup>2</sup> /s]	Viscosity index VI [-]	Flow temperature or melting point $T_f/T_{mel}$ [°C]
001 Ionic liquid	311.20	1.116	552.42	495.00	110	+10.8
002 Ionic liquid	504.50	1.308	102.02	78.00	104	-34.0
003 Ionic liquid	448.40	1.354	76.01	56.14	156	-40.7
004 Ionic liquid	490.50	1.334	72.53	54.37	170	-45.9
005 Ionic liquid	260.04	1.242/100°C	18.37/100°C	14.79/100°C	-	+77.0
006 Ionic liquid	416.36	1.447	51.53	33.61	138	0
007 Ionic liquid	419.36	1.449	86.61	59.77	134	+15.0
008 Ionic liquid	764.00	1.061	327.24	308.43	-	-50.0
009 Ionic liquid	570.66	0.936/40°C	292.49/40°C	312.49/40°C	156	+17.0
Fomblin 1500YPL	6600	1.908	1879.72	985.18	134	-24
Fomblin Y04	1500	1.868	60.04	32.14	56	-54
Fomblin M60	12500	1.828	697.42	381.52	392	-57
Fomblin M15	8000	1.822	224.49	123.21	306	-72

The possibility of forming liquid crystal structures at determined temperature can affect improvement of properties, including the tribological ones.

Selected standard lubricity parameters for ionic liquids and reference PFPE oils presented in table 2.

Tab. 2. Lubricity parameters of ionic liquid and reference PFPE oils

Liquids lubricant	Seizure load $P_t$ [N]	Time to obtain $P_t$ under loading 409 N/s [s]	Wear limiting load capacity $G_{oz}$ [N/mm <sup>2</sup> ]	Avg. scar diameter $\bar{d}$ after 60 s under load 1471.5 N, [mm]
CJ001	4601.3	11.25	3186.9	0.49
CJ002	3435.6	8.40	3616.2	0.46
CJ003	2842.6	6.94	2941.9	0.51
CJ004	3006.2	7.35	3060.7	0,50
CJ006	2658.5	6.50	2724.0	0.53
CJ007	3026.6	7.40	3060.7	0.50
CJ008	3967.3	9.70	3060.7	0.50
CJ009	3272.0	8.00	2528.5	0.55
YPL 1500	1840.5	4.50	1324.8	0.76
Y 04	940.7	2.30	1811.1	0.65
M 60	613.5	1.50	1607.2	0.69
M 15	531.7	1.30	1517.9	0.71

The investigations were realized on Four-Ball Apparatus [20]. Two parameters were estimated: seizure load  $P_t$  [N] for increasing continuous loading (409 N/s) and wear limiting load capacity  $G_{oz}$  [N/m<sup>2</sup>] for load  $P = 150$  kgf (1471.5 N). The comparison of parameters for ionic liquids and PTFE Fomblin shows that the tribological properties of ionic liquids are better, particularly CJ001.

### 3.2. Methodology of the Tests

The analysis of the source literature, especially information given by Katanayagi and Hamaguchi [8], indicates that there is the possibility of mesophase forming even within ionic liquids with relatively short alkyl chains. When anions are less hydrophobic, that possibility is higher, e.g. [BF<sub>4</sub>]<sup>-</sup> in CJ001, CJ005 and CJ009 liquids.

Preliminary analysis was made with the use of the thermal microscopy method. For this purpose, the gauge cells consisting of two glasses internally covered with SE130 polyamide, which ensured homogeneous (planar) molecules orientation on the surface, had been made. The glasses were separated with glass microballs (so-called spacers) of diameter  $d \cong 5$   $\mu$ m. The thin layer of tested liquids was obtained by filling the cells, using capillary action. Then the cells with the thin layer of tested liquids were put on a thermostatic stage of a polarizing microscope in a birefracton system, i.e. between crossed polarizers (Fig. 3).

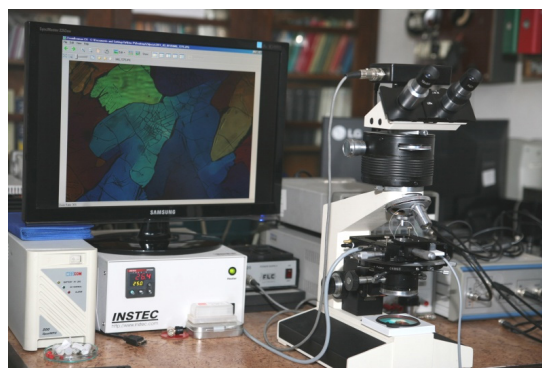


Fig. 3. Biolar PL polarizing interference microscope with the thermal stabilizing table (on the right), with birefracton system, which allows for visualisation of anisotropy of optical properties of the thin transparent layers in visible and infrared spectrum. On the monitor (on the left), the texture of a molecular crystal (exemplary) is visible on the screen of the monitor (on the left)

The observation of the samples was carried out for each of ionic liquids, within the temperature range from the isotropic phase temperature to the temperature of  $-15^{\circ}\text{C}$  (the range of the equipment capabilities). There was being searched the state characterized simultaneously by optical anisotropy properties and liquid state of aggregation. Besides the direct observation of the samples, there was also being registered transmission of the light with  $\lambda = 535\text{ nm}$  wavelength through the birefracton system, in order to find possible phase transitions.

For every sample the X-ray test was performed, with the use of Brüker Discover 8 powder diffraction instrument with a Cu lamp, monochromator and a thermal adapter. The test was complementary to the microscopic examination of the thin layers, and it was to confirm the presence of signs of molecular aggregates in the liquid structure. The test was carried out with the use of thin ( $< 100\ \mu\text{m}$ ) liquid samples with one free surface, imposed on the glass substrate vectoring homeotropically, made of optical flat glass. The divergent beam geometry was applied in order to increase intensity of the beam reflected from liquid surface, and recorded by the detector (Fig. 4).

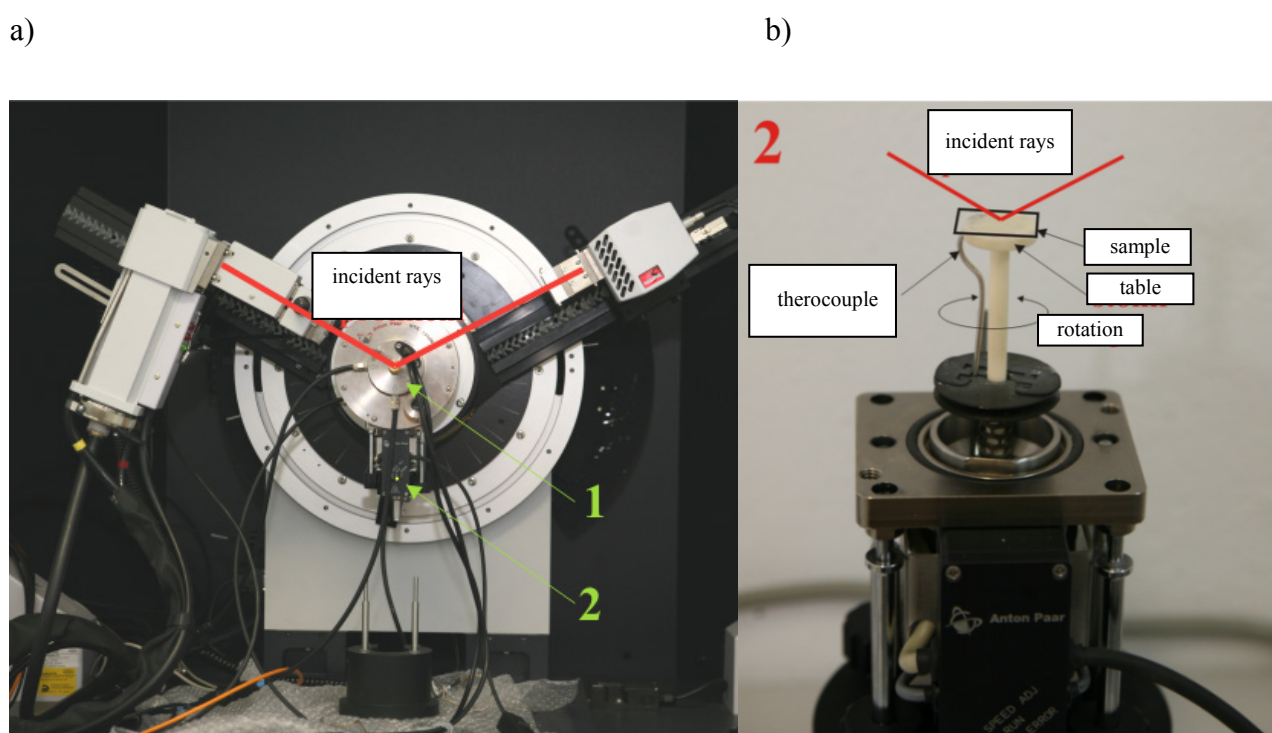


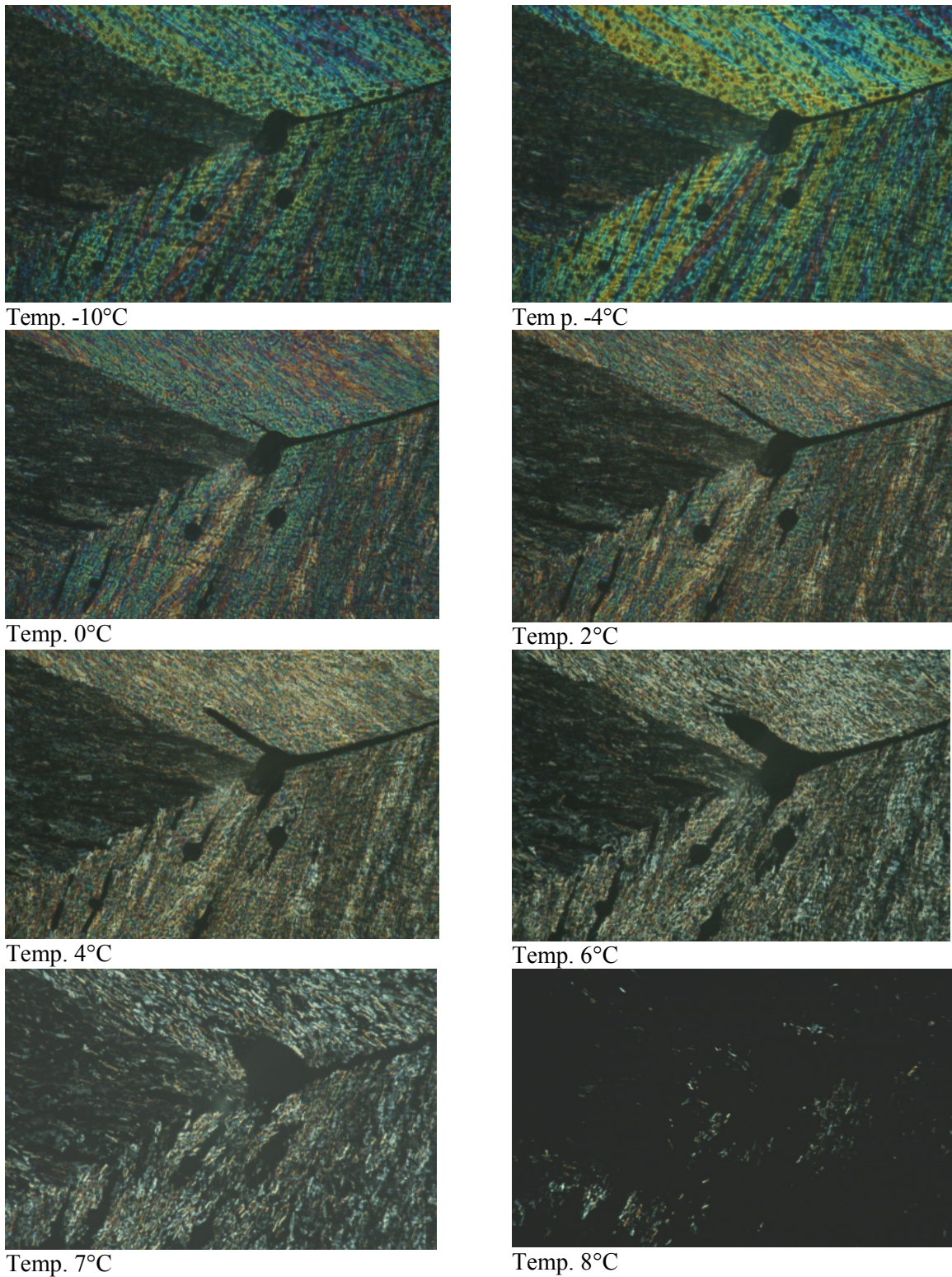
Fig. 4. a) Powder diffraction instrument with a thermal chamber: 1 – liquid sample location inside the chamber, 2 – head with ceramic heating element (rotary); b) the sample on the glass substrate was located on the head object stage and put into the chamber stabilized thermally

### 3.3. The Tests Results and Analysis

In further figures (Fig. 5, 6) there are shown selected results of the thermal microscopy examinations, carried out with Biolar PL polarizing interference microscope (Fig. 3), and the X-ray structural tests (Fig. 7-9) made with Brüker Discover 8 powder diffraction instrument (Fig. 4).

For example, the thermal microscopy examination of CJ001 ionic liquid (i.e. tetrafluoroborate 1-methyl-3-octyloxymethylimidazole) in the birefracton system showed the molecular crystal, which occurred at temperature below  $8^{\circ}\text{C}$ . Melting into isotropic phase was homogeneous, without signs of mesogenic properties (Fig. 5).





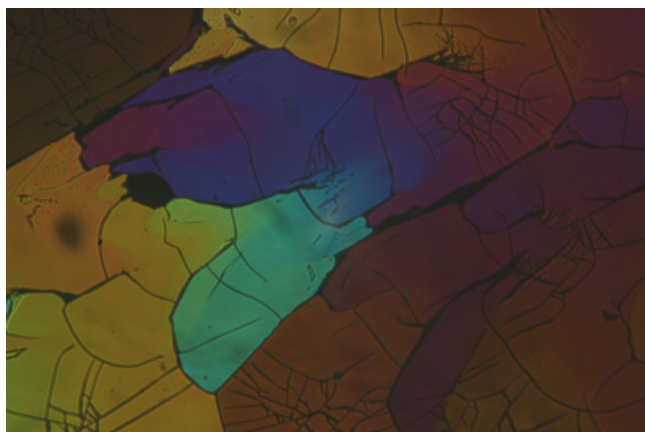
*Fig. 5. View of optical anisotropic textures of CJ001 molecular crystals, observed under the polarizing microscope. At the temperature of 8°C, melting of the isotropic crystals is visible (black fields)*

During CJ001 X-ray tests carried out at three different temperatures within the range of 28-30°C, periodic structure in the liquid sample was not observed too. Only background spectrum of the lamp radiation was exposed. The results of the tests of CJ002, CJ003 and CJ004 liquids were similar to CJ001 results. Thermal microscopy examinations of the thin material layer in the birefractance system, carried out within the entire possible to obtain temperature range, i.e. from -15°C to +60°C when

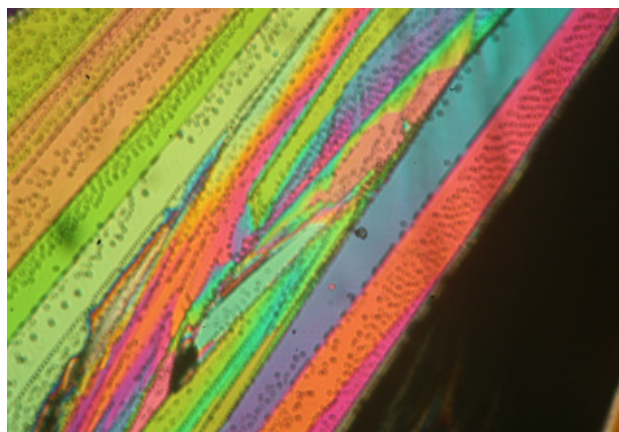


samples were remaining in liquid state, did not prove optical anisotropic properties occurrence. Radiographic measurements of the sample, at three temperatures within the range of 28-30°C did not also show periodic structure in the liquid sample. Only background spectrum of the lamp radiation was exposed.

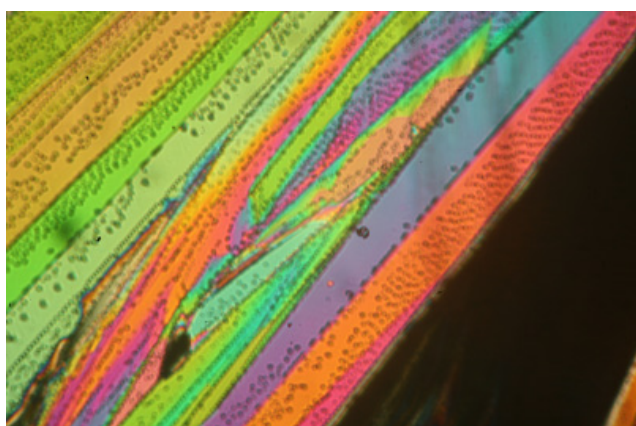
The results of the tests of CJ005 ionic liquid were slightly different. Thermal microscopy examination of the thin material layer in the birefringence system were being carried out within the temperature range from room temperature 25°C up to the temperature of 72°C. At the temperature of 72°C, a gradual transition from isotropic liquid to a molecular crystal was performed. Observed textures are shown in Fig. 6, where the following phases of the solid body transition to liquid are visible.



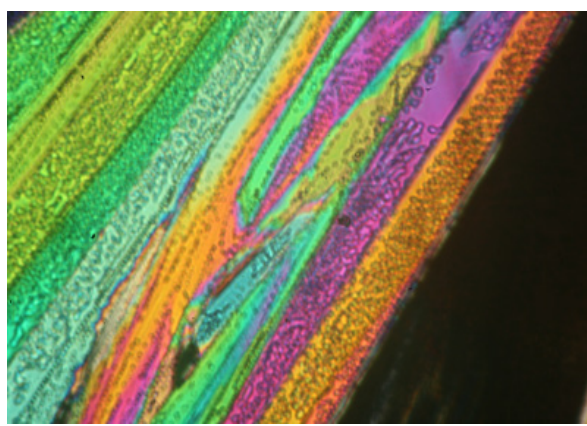
Temp. 25°C



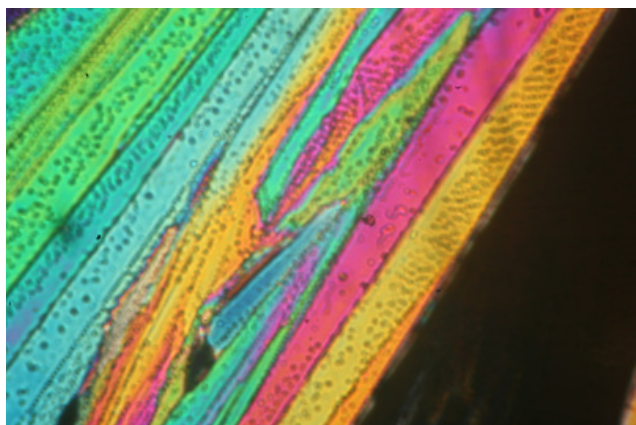
Temp. 30°C



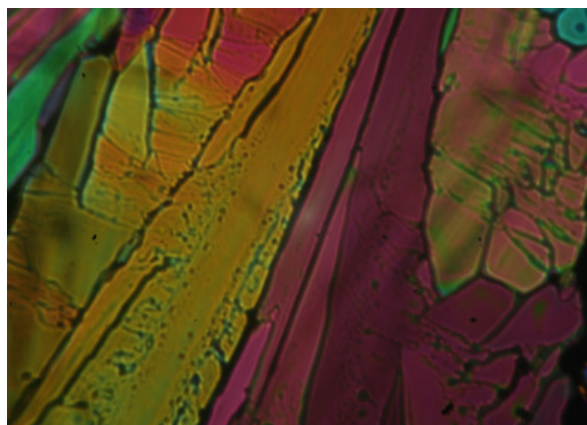
Temp. 40°C



Temp. 60°C

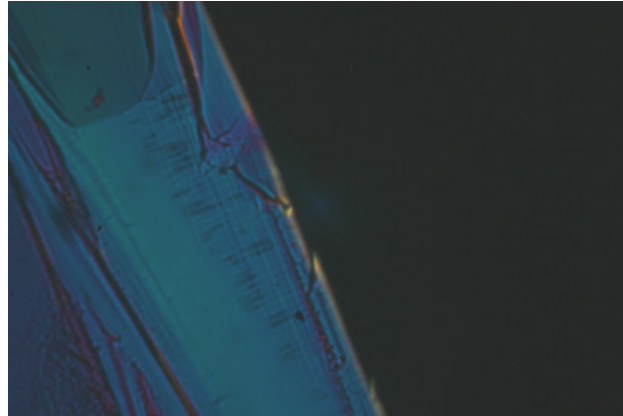


Temp. 68°C



Temp. 71.5°C



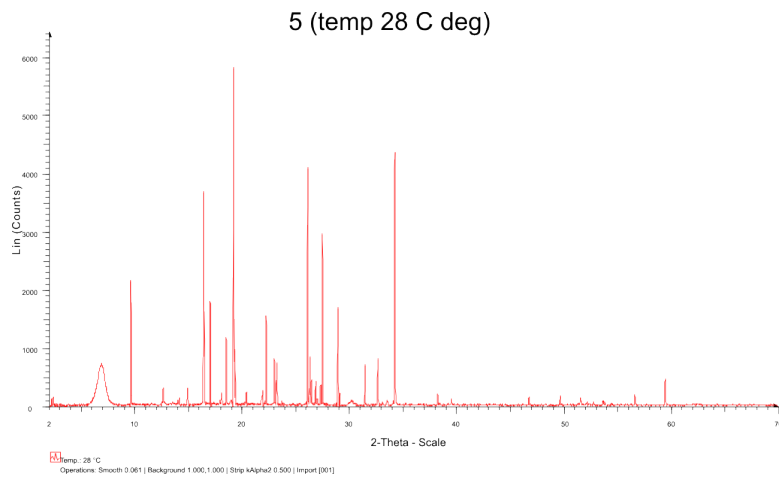


Temp. 72°C

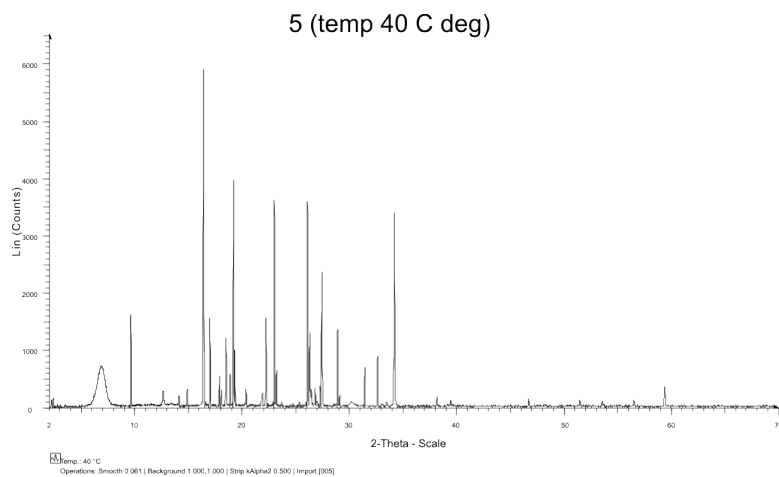
Fig. 6. View of optical anisotropic textures of CJ005 molecular crystal observed under the polarizing microscope. Clear textures changes under the influence of temperature were exposed. At the temperature of 68°C material melting into isotropic phase began

This transition showed some features indicating mesophase existence (textures view change under the influence of pressure on the tested layer – mild phase mixture, not solid nor liquid), so detailed tests of this material were carried out. In further figures there are shown the radiographic tests results (Fig. 7, 8).

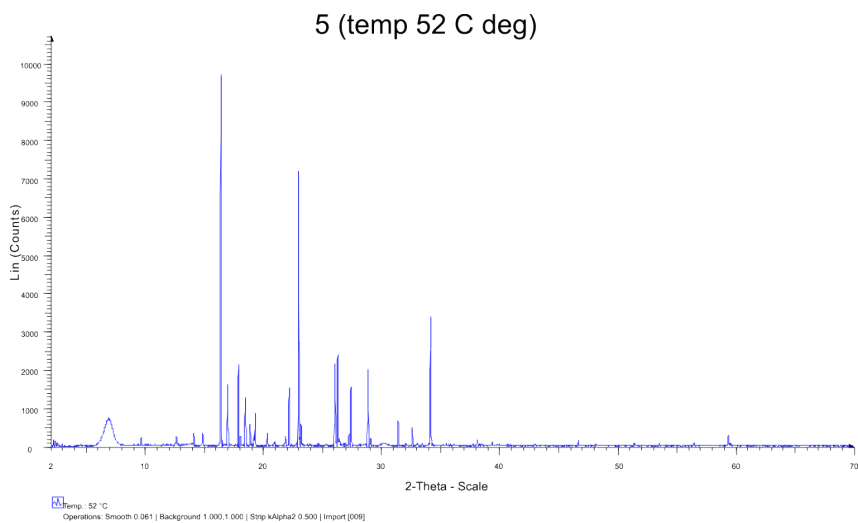
a)



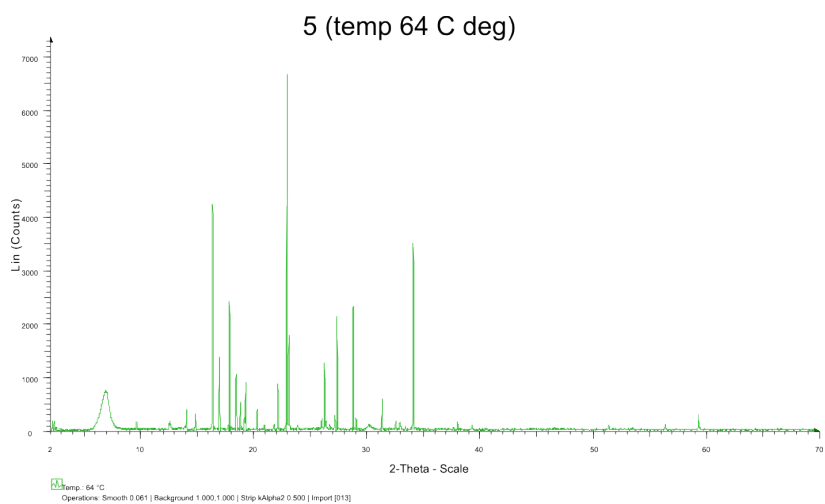
b)



c)



d)



e)

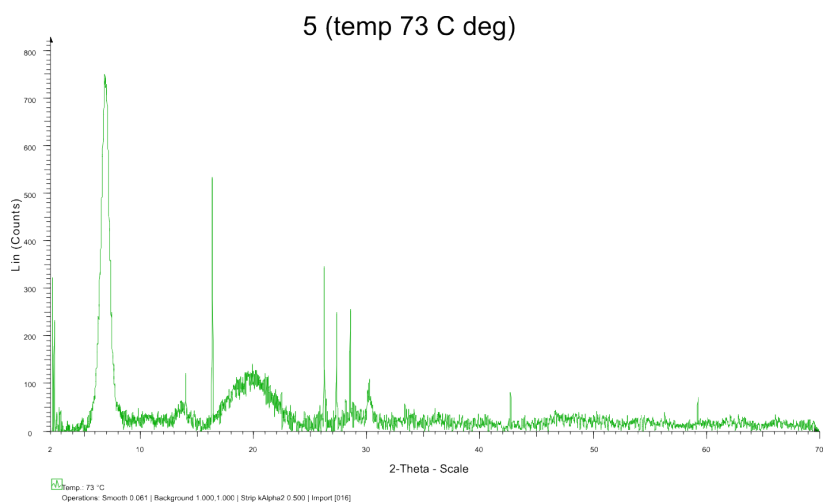


Fig. 7. CJ005 X-ray powdered-crystal patterns for selected temperatures The last result (e), with a peak for the angle  $2 - \theta \sim 7^\circ$  and diffusion maximum for the angle  $2 \theta \sim 20^\circ$ , indicates the possibility of smectic phase induction. The low intensity of peaks indicates that it could be induction of smectic order only on the free surface of the liquid

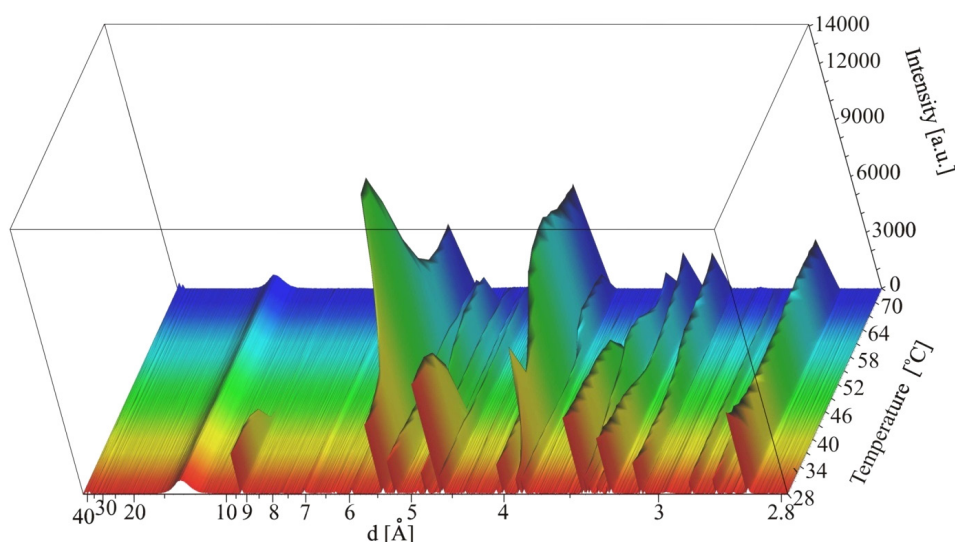
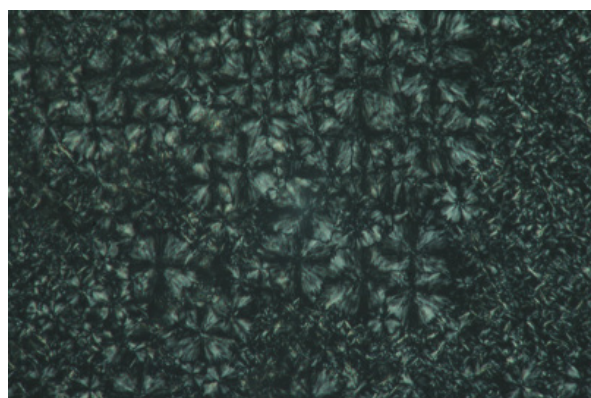


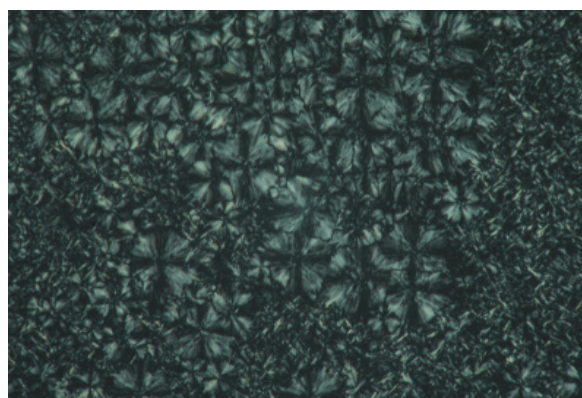
Fig. 8. X-ray powdered-crystal pattern of CJ005 sample against temperature

Then CJ006, CJ007 and CJ008 ionic liquids were tested in the order. For all mentioned materials similar tests results were obtained. Thermal microscopy examinations of the thin material layer in the birefrance system, realized within the temperature range as above, from  $-15^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ , when samples were in liquid state, did not prove optical anisotropic properties occurrence. The radiographic measurements at three temperatures within the range of  $28\text{--}30^{\circ}\text{C}$  did not also show periodic structure in the liquid sample. Only background spectrum of the lamp radiation was exposed, just like during the previous tests.

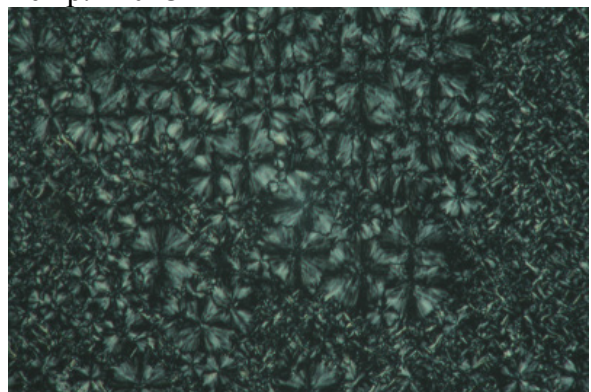
In case of CJ009 ionic liquid, during thermal microscopy examinations of the thin layer of this liquid in the birefrance system, clear texture changes under the influence of temperature were registered, and at the temperature of  $26^{\circ}\text{C}$  heterogeneous melting was visible (Fig. 9).



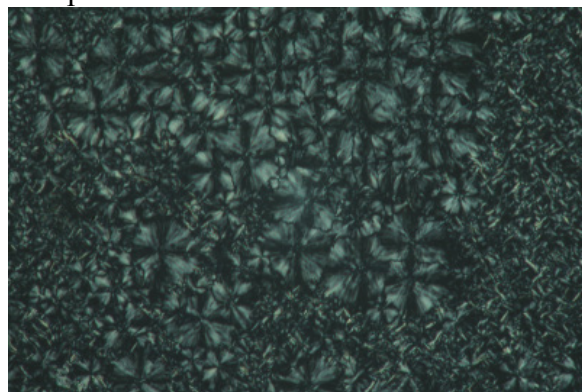
Temp.  $-10^{\circ}\text{C}$



Temp.  $0^{\circ}\text{C}$



Temp.  $10^{\circ}\text{C}$



Temp.  $20^{\circ}\text{C}$



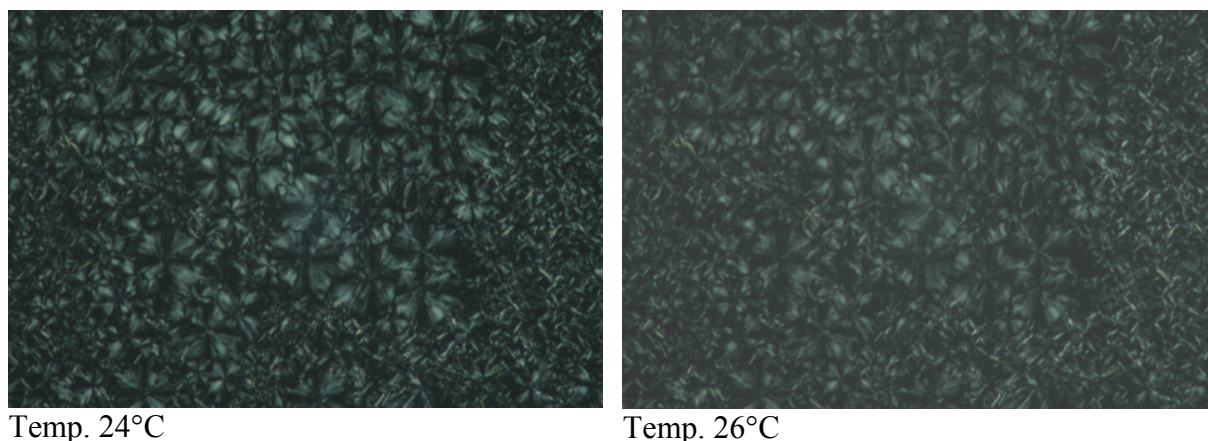


Fig. 9. View of optical anisotropic textures of CJ009 molecular crystals observed under the polarizing microscope. Clear textures change under the influence of temperature when exposed. At the temperature of 26°C heterogeneous melting was visible.

In this case, for identification of phase transition temperature, the additional calorimetric test was carried out during the cycle of heating and cooling (Fig. 10).

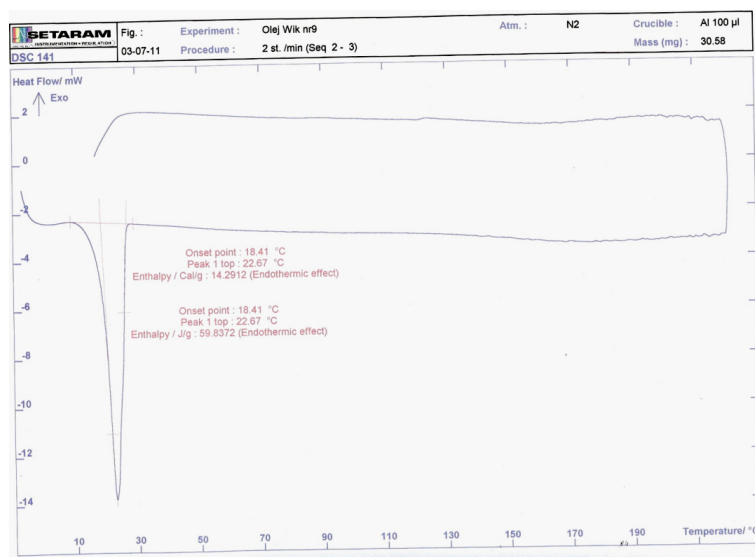


Fig. 10. The results of the calorimetric test of CJ009 liquid during the cycle of heating and cooling. The phase transition was exposed at the temperature of 18.41°C during the cooling cycle.

However, during the radiographic measurements nothing was observed except for background X-ray powdered-crystal pattern. This examination was made like before, i.e. within the temperature range of 28-30°C.

#### 4. Summary

Concluding, it should be said that none of tested liquids showed mesogenic (liquid crystal) properties. Observed optically active phases were the phases in the solid state of aggregation, and it is possible to define them as so-called molecular crystal. Melting of these materials into isotropic phase was being directly observed. Biphasic zone (i.e. zone, where optical isotropic phase and molecular crystal coexisted) for tested liquids was within the range of -2 to 4 degrees. The radiographic tests carried out at room temperature unambiguously excluded mesophases existence in the material structure sequence, observed during cooling cycle (except CJ005

liquid). In case of this ionic liquid, heterogeneous transition from the crystal phase into the liquid phase with extent of 4 K was being observed. That is why more detailed tests of CJ005 liquid were carried out with the use of DSC (differential scanning calorimetry) calorimetric method and XRD (X-ray diffraction) method, within temperature domain. At the temperature of 68°C, considerable decrease of intensity of radiation diffracted on the tested substance structure was observed. At the same time, relatively high diffraction maximum was observed for a period range of 13 Å, and fuzzy zone of diffuse scattering for a period of 4.5 Å. This type of scattering can be specific for smectic structure; however, obtained spectrum can be treated as a result of testing the non-homogeneous melting material being a mixture of isotropic liquid, molecular crystal and, maybe, smectic phase. Weak indication about smectic phase existence in this mixture could be justified by forming ordered molecular structure (here: smectic) on the free surface of isotropic liquid. Suspicion of mesophase existence between isotropic phase and crystal phase, is not justified by calorimetric observation of the cooling process from isotropic phase into the molecular crystal of this sample. One phase transition between crystal and liquid phase – isotropic, was exposed there.

In case of CJ009 ionic liquid, non-congruent material melting, observed under the polarizing microscope, was the reason for carrying out the calorimetric test (Fig. 10), which also did not prove additional phase transition existence between isotropic phase and a molecular crystal.

Therefore, none of the tested ionic liquids CJ001 – CJ009 showed mesogenic (liquid crystalline) properties and, on account of this fact, did not confirm Katayanagi's and Hamaguchi's suggestions [8] about such a possibility in comparison with ionic liquid, especially imidazole, with relatively short alkyl chains. As a result, good tribological properties of these liquids do not have any connection with possible mesophase existence.

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