Names and affiliations of applicants (* indicates experimentalists):

D. V. Anokhin[1,2]*, D.A. Ivanov[1,2]*
[1] Moscow Institude of Physics and Technology, Functional organic and hybrid materials, 141700 Institutsky str., 9, Dolgoprudny, Russia
[2] Institut de Science des Matériaux de Mulhouse, LRC CNRS 7228, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse CEDEX, France.

Report:

Wedge-shaped molecules can be considered as building units for design of cubic zeolite-like super-structures [1,2]. Well known, that these mesogens self-organize in different 1D, 2D and even 3D morphologies Fig.1) [3]. The phase behavior of wedge-shaped molecules is determined by combination of mesogenic core and flexible periphery. The formation of cubic phase can be stimulated by choice of counter-ion or by chemical modification of the side groups. Beginn et al. have revealed that mesomorphism in wedge-shaped 2,3,4-trisalkoxybenzenesulfonates is mainly governed by molecular geometry rather than inter-molecular interactions or nature of mesogen [1]. The cubic phase was found for small counter-ions (Li+ и Na+) and was not found for bigger ones (i.e., K+ , Cs+ , pyridinium, and NMe4+). The important role plays the presence of solvent. For example, water is required for cubic phase development in system of wedge-shaped amphiphilic 1,3-dipyrrolyl-1,3-propanedione boron complexes [4]. In addition, phase behavior of mesogens strongly depends on side chain length. Particularly, Ichikawa et al. reported about formation of bicontiniuos cubic phase for (3,4,5- trisalkoxybenzyl)triethylammonium tetrafluoroborate with C10 or C12 chains [5]. For longer tails a columnar hexagonal LC phase appears.

In our group, the self-assembly of wedge-shaped compounds based on sulfonic acid is studied. It was shown that depending on external conditions (temperature and UV-irradiation) such molecules form a variety of LC morphologies like smectic, columnar (hexagonal and rectangular) and cubic (double diamond and gyroid) phases. Particularly, mesogens with polymerizable branched side chains show consequent phase transformation from columnar to cubic as a function of relative humidity (RH) [6-9]. In the result of water absorption, 3D network of ion-conductive water channels is developed. It was shown for Cub_{bi} и Col_{hd} phases of trisalkoxybenzenesulfonates that the topology of channels can be preserved by photopolymerization [6]. Materials in cubic phase demonstrate significantly high ion mobility and considered as perspective organic membranes for fuel cells [10].

Swelling of thin films of mesogens is a complex process. The diffusion of water molecules through the film which is initially organized in columnar phase is limited by in-plane orientation of 1D hydrophilic channels separated by hydrophobic periphery. The swelling kinetics can be enhanced by variation of solvent polarity.

In presented work we report about formation of cubic phase in the system of non-polymerizable wedge-shaped pyridinium salts with linear side groups. The cubic phase in the system is stabilized by non-covalent interaction between alkyl chains [11]. Recently, only few examples of cubic phase formation from wedge-shaped mesogens with pyridinium as counter-ion are discussed in literature [12]. However, heating in the presence of methanol vapors results in formation of the cubic phase. The found cubic morphology is stable in wide temperature range and able to swell in water vapor that important for future applications.
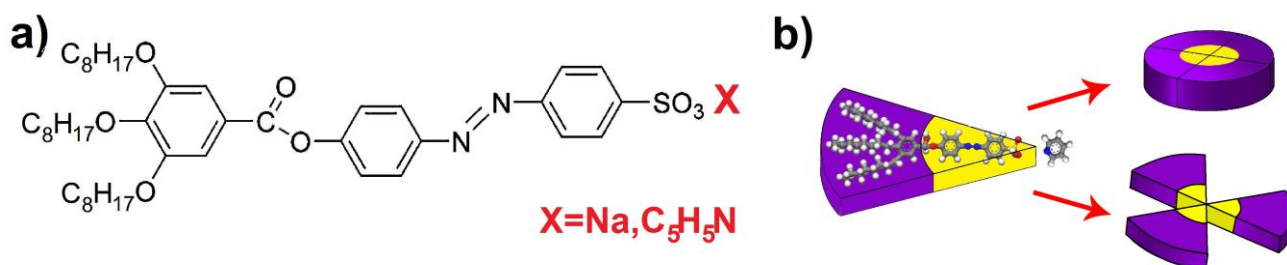

Figure 1. Chemical structure of the C8Pyr compound (a). Examples of self-assembly of wedge-shaped mesogens (b). The violet and yellow colors represented the hydrophobic and hydrophilic parts of the molecules, respectively

Structural evolution of thin film of C8Na and C8Pyr at different temperatures was addressed by GIWAXS technique. According to our previous papers, counter-ion of the compounds plays an important role in structure formation and stability [1]. The substitution of sodium ion by organic pyridinium one results in changes in phase diagram.

The combination of exposure in atmosphere in saturated vapor of methanol and heating results in transition of the in-plane columns to cubic phase results in orientation of (211) vector of Cub_{gyr} normal to the substrate. Interesting, that the cubic phase is non-equilibrium phase for swollen in methanol sample. However, optimization of swelling time with thermal treatment allows us to fabricate the film with highly-organized gyroid structure. The stability of gyroid phase pyridinium counter-ion plays an important role. According to other authors, cubic phases of different symmetry appear in the films of similar compounds at temperatures above 170 °C [13]. However, these phases are considered to be thermodynamically equilibrium and reversibly transform to columnar structures upon cooling. Probably, for formation of metastable gyroid phase at lower temperature a specific interaction between methanol and pyridinium counter-ion in confined conditions of channel is required. The formed non-equilibrium phase is stabilized at ambient conditions by rigid scaffold of locally organized linear alkyl chains. Stabilization of cubic structure by non-covalent solidification of alkyl chain is an interesting alternative to photopolymerization of diene or methacrilic end groups proposed us elsewhere [14]
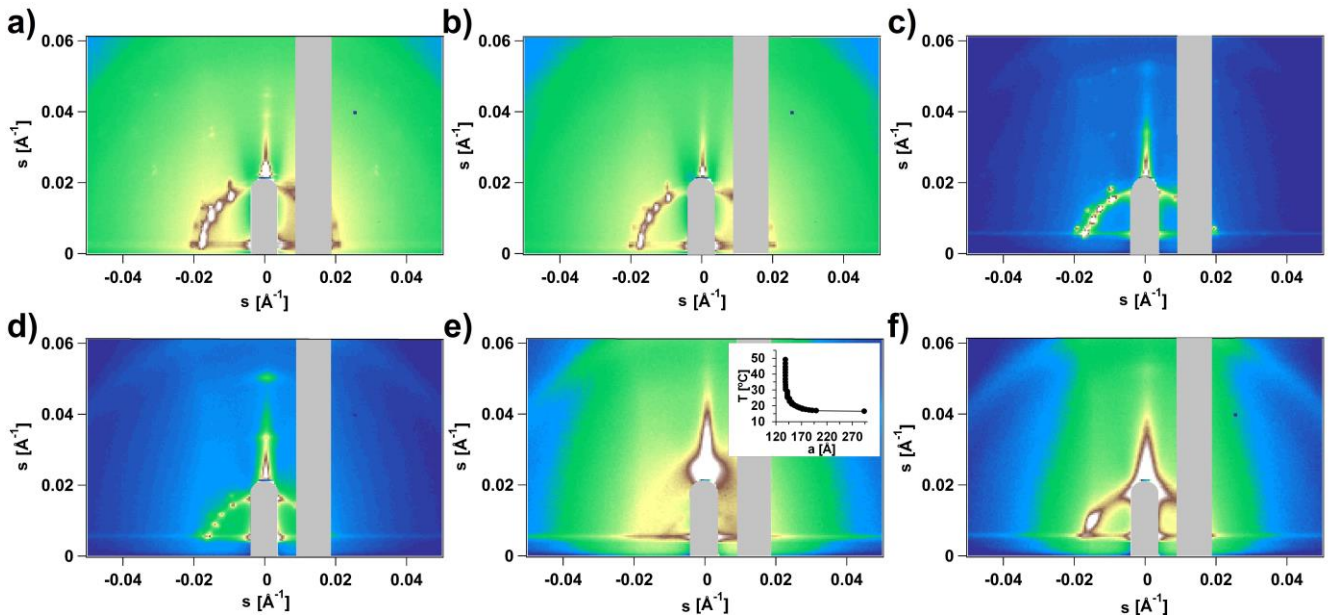
Figure 2. 2D GIWAXS patterns of the C8Pyr thin film in gyroid phase in dry state (a), after storing at ambient humidity and temperature for several months (b), after swelling of dry film in humid atmosphere (c), after cooling to 16 ºC (d) and after heating to 25 ºC (e). Temperature dependence of cubic lattice parameter during cooling (f).

We suppose that stability of columnar phases in water and methanol vapors is related to local ordering of linear side groups. In Fig.3a wide angle profile as a function of temperature is presented. At ambient temperature three narrow reflections with d-spacings 5Å, 4.9Å and 4.4Å were detected. These peaks correspond to sub-lattice of alkyl chains typical for wedge-shaped mesogens. Close to 100 °C these peaks disappear that corresponds to transition of monoclinic phase to the hexagonal one. Consequently, the monoclinic phase is stabilized by local crystallization of dodecyl side groups (Fig.3b). In the result, well-organized structure containing 1D hydrophilic cores surrounded by crystalline alkyl chains is formed. Probably, this organized phase is impenetrable for small molecules of water or methanol. In contrast, above 100C density of hydrophobic regions decreases because of disordering of the side groups that enhance diffusion of methanol molecules through the C8Pyr film (Fig.3c). Later, during cooling to room temperature, crystallization of alkyls "freeze" LC structure formed at higher temperature. The presence of Col$_{hd}$ phase at room temperature for compounds with polymerizable side groups can explain their ability to reversible Col$_{hd}$ to cubic phase transition with increase of RH reported by us in previous publications [6]. Presence of functional groups at the ends of molecules prevents local organization of alkyl chains and provides high diffusion of water molecules into hydrophilic regions through liquid state of the alkyl periphery.
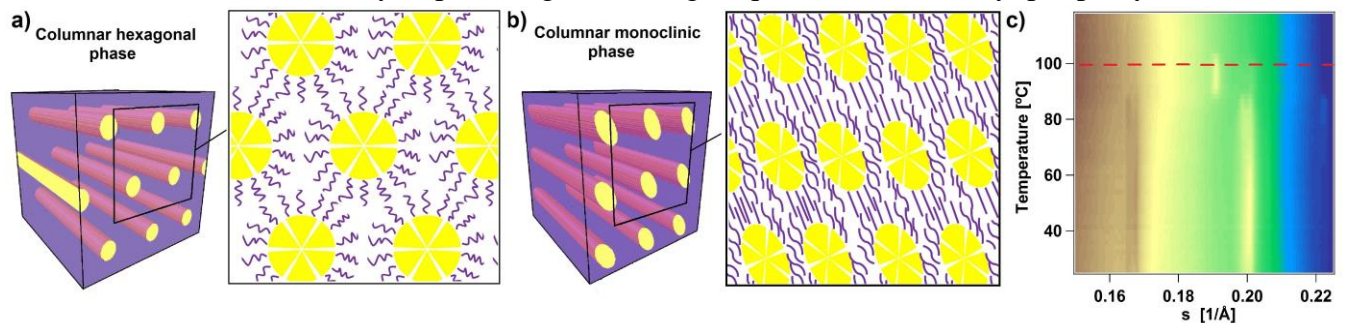

Figure 3. Thermal evolution of wide-angle reflection corresponding to alkyl chain packing (a) Schematic representation of side chains ordering in columnar monoclinic (b) and hexagonal (c) phases. Ксения, поменяйте порядок картинок в соответствие с подписью.

For many applications, 3D network of channels should contain large amount of water. The serious advantage of the obtained gyroid structure is high thermal stability. Particularly, heating of the film in ambient atmosphere 100 ºC results in improvement of the Cub_{gyr} structure (Fig.2a). The evaporation of methanol from 3D channels leads to significant decrease of lattice parameter to 117 Å. As we have discussed in previous paper, the found value of a_{gyr} is the smallest one and corresponds to "dry" cubic phase. Importantly, in the dry state the C8Pyr film becomes accessible for penetration of water molecules to the closed hydrophilic channels. Fig.2b shows the 2D GIWAXS pattern of the pre-heated film after storing in several months at ambient temperature and humidity. One can see that the gyroid structure is well preserved. Additional weak wide angle peaks are attributed to monoclinic phase. However, the parameter of cubic phase recovers to its initial value determined after swelling in methanol – 135 Å. We suggest that this lattice parameter corresponds to an equilibrium state at ambient humidity and temperature with well-developed bicontinuous network of water channels. The further increase of RH to 100% does not effect on the film structure. To increase of water uptake an additional heating to 100C is required. In the result, during cooling of pre-heated "dry" film in saturated water vapors the growth of lattice parameter to 142 Å was detected (Fig.2c).

As it was show above, Cub_{gyr} phase demonstrates relatively good stability during heating up to 100 °C. Above 100 ºC the lattice parameter decrease due to evaporation of water from channels. For practical application it is important to study the behavior of the material below room temperature. It was found that below 25C the lattice parameter dramatically grow and reach maximum value a_{gyr}=19.1 nm at 16 ºC (Fig.2f). This effect can be explained by ultimate film swelling due to condensation of water on the film surface. At lower temperature oversaturation of the C8Pyr film by water results in transition of Cub_{gyr} into Lam phase with a=41 Å (Fig.2d). We expect that similar to swelling in methanol reported previously [9], lamellar phase becomes thermodynamically stable at highest water content. Consequent heating of the film to 25ºC leads to transition of Lam to Col_{hd} phase with a=73 Å (Fig.2e). The growth of lattice parameter of Col_{hd} phase indicates formation of 1D water channels inside the columns.

In conclusion we demonstrate a new approach for designing zeolite-like structure from small wedge-shaped mesogens. It was shown that a specific combination of exposure in methanol vapors with thermal treatment is required for development of bicontinuous gyriod phase from columnar hexagonal one for pyridinium salt. In contrast, for sodium salt only columnar phases were observed in the same preparation conditions. Probably, complexation of large pyridinium ion by solvent plays an important role for cubic phase formation. The key role of linear alkyl chains in structure formation was revealed. We suggest that local ordering of linear side groups prevent efficient diffusion of polar solvents like water or methanol through non-polar matrix. This diffusion is significantly increased for liquid alkyl chains in columnar hexagonal phase above 100C. The gyroid phase stabilized by alkyl chains can be dried from methanol by heating to 100C. After cooling of dry Cub_{gyr} phase to room temperature the material can efficiently swell in water vapors resulting in increase of lattice parameter by 18% compare to initial phase formed in methanol vapors. Developed bicontinuous network of 3D water channels with average radius 28 Å and water uptake up to 16 is expected to provide high proton mobility irrespective to structure orientation. Interesting to mention that designed gyroid phase is thermodynamically unstable both in dry state (stable phase is monoclinic) and in fully swollen state (stable phase is lamellar). However, in humid atmosphere the transformation to equilibrium lamellar phase occurs only below room temperature after precipitation of water into film surface. Heating back to room temperature results in irreversible transition to columnar hexagonal phase with large water channel. Consequently, by variation of relative humidity one can control stability of cubic phase in wide temperature range. Based on two-phase and three-phase models proposed by us earlier, structural models of gyroid phase in dry, partially swollen and fully swollen state were proposed. The volume fraction and distribution of water, hydrophilic and hydrophobic fragments of mesogens gives an important

information about water channels topology as a function of external factors. The obtained results about stabilization of zeolite-like morphology by local ordering of alkyl periphery can help in development of new approaches of design of functional organic supramolecular materials.

References

[1] Beginn, U.; Yan, L.; Chvalun, S. N.; Shcherbina, M. A.; Bakirov, A.; Möller, M. Liq. Cryst. 2008, 35, 1073−1093.

[2] Albrecht, K.; Mourran, A.; Zhu, X.; Markkula, T.; Groll, J.; Beginn, U.; de Jeu, W. H.; Möller, M. Macromolecules, 2008, 41 (5), pp 1728–1738

[4] H.Maeda, N. Eifuku, Y. Haketa, Y. Ito, E.Lee and M. Lee/ Phys. Chem. Chem. Phys., 2011, 13, 3843–3850

[5] Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Mukai, T.; Ohno, H.; Kato, T. J. Am. Chem. Soc. 2007, 129 (35), 10662−10663

[6] Zhang, Heng; Li, Lei; Moller, Martin; Zhu, Xiaomin; Hernandez Rueda, Jaime J;Rosenthal, Martin;Ivanov, Dimitri A. Advanced Materials 2013, 25,26 3543-3548

[7] K. N. Grafskaia, J. J. Hernandz Rueda, X. Zhu,V. M. Nekipelov, D. V. Anokhin, M. Moellerd and D. A. Ivanov Phys.Chem.Chem.Phys.,2015,17,30240

[8] Grafskaia Kseniia N. , Anokhin Denis V. , Hernandez Rueda Jaime J. , and Ivanov Dimitri A. Applied Mechanics and Materials Vol. 792 (2015) pp 623-628

[9] Kseniia Grafskaia, Boris Zimka, Xiaomin Zhu, Denis Anokhin and Dimitri Ivanov AIP Conference Proceedings 1748, 040009 (2016)

[10] Y. Chen, M. D. Lingwood, M. Goswami, B. E. Kidd, J. J. Hernandez, M. Rosenthal, D. A. Ivanov, J. Perlich, H. Zhang, X. Zhu, M. Möller, and L. A. Madsen, Journal of Physical Chemistry B, 2014, 118, 11, 3207-3217

[11] Boris Rybtchinski, ACS Nano, VOL. 5 ' NO. 9 ' 6791–6818 ' 2011

[12] Mihelj, T.; Tomasic, V. J. Dispersion Sci. Technol. 2014, 35, 581−592

[13] Maxim A. Shcherbina, Artem V. Bakirov, Andrei N. Yakunin, Uwe Beginn, Linglong Yan, Martin Möller, Sergei N. Chvalun, Soft Matter, 2014, 10, 1746

[14] X. M. Zhu, A. Mourran, U. Beginn, M. Moller, D. V. Anokhin and D. A. Ivanov, Phys. Chem. Chem. Phys., 2010, 12, 1444–1452.