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| | In situ structure and proton conductivity studies of ion-conducting self-assembled membranes | Experiment number: MA-4390 |
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Report:

Among amphiphilic liquid-crystalline (LC) compounds, wedge-shaped derivatives sulfonic acid and its sodium, imidazole and pyridine salts, etc., have been well studied. [1] These compounds can form not only lyotropic phases typical for the majority of LC systems in aqueous systems, but thermotropic mesophases in solid state as well. [2,3] The type of the mesophase depends on the mesogens' chemical structure and preparation conditions. Previously, we have shown that the compounds with polymerizable groups are able to organize in cubic (Cub) or columnar (Col_{hd}) supramolecular structures with defined morphology during heating or swelling processes in the water pores [4,5]. The prepared structure can be fixed by photopolymerization of acetylene or methacrylic groups, giving a mechanically stable film with developed polymer network of bound mesogens [6].

For mesogen with linear side chains, we have shown the existence of metastable bicontinuous cubic phases in a wide temperature range due to the local ordering of the alkyl chains. In this case, reversible "activation" of thin films is possible during heating above the melting point of sub-crystals. However, this method has certain disadvantages. First of all, activation occurs only under saturated vapors of methanol, which is able to penetrate through the amorphous alkyl phase at elevated temperature. Second, water evaporation during heating reduces mechanical stability of the polymerized film. Accordingly, a new activation method of self-assembled thin films was developed based on cooling of the samples below 0 °C in humid atmosphere. The effect of water crystallization in the geometric constraints of nanochannels on the activation process was established.

The diffraction pattern of C8Na thin film after swelling upon water vapor for two hours at room temperature demonstrates the presence of two meridional peaks with d-spacings $d_1 = 57.0 \text{ \AA}$ and $d_2 = 61.1 \text{ \AA}$ related to two phases, denoted as 1 and 2, respectively (Fig. 1a). During cooling, a strong increase in the phase 1 parameter and a gradual increase in the phase 2 parameter can be observed (Fig. 1b). At 0 °C the reflection of phase 1 disappears probably because of destruction. On the contrary, the reflex of phase 2 is maintained with constant d_2 below 0 °C. Further cooling to -25 °C did not cause any noticeable changes in the structure (Fig. 1c). Due to the presence of saturated water vapor in the chamber, at -50 °C we detect formation of ice on the film surface and vanishing of the phase 2 (Fig. 1d). Fig. 1e shows the changes in the

parameters of both phases during cooling from 25 ° C to -50 ° C. The d-spacing of the phases 1 and 2 increase by 30% and 7%, respectively. It can be assumed that phase 1 is lamellar one containing two-dimensional water channels. The width of the channels increases during precipitation of water on the film surface below dew point. A weak change of phase 2 parameter indicates that it does not contain water channels. Probably, for these structure hydrophilic regions are not connected to the film surface, that prevents the water vapor diffusion from the atmosphere. In this case, it is the lamellar phase that is equilibrium in the swollen state that is in good agreement with our previous works. [7] Subsequent heating to room temperature leads to recovery of only phase 2 in the region of 71 ° C.

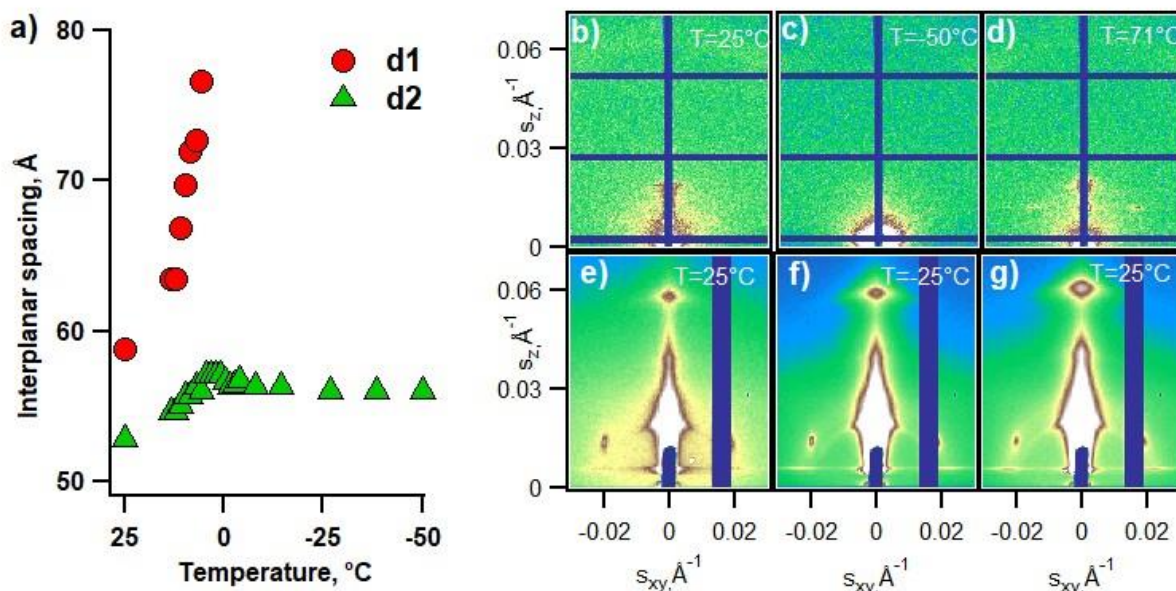


Figure 1 - The change of lamellar phases lattice parameter during cooling of the swollen thin film C8Na (a). Two-dimensional GISAXS patterns of the swollen C8Na sample during thermal treatment: initial structure at 25 ° C (b); after cooling to -50 ° C (c); after subsequent heating to 71 ° C (d); and dry C8Na sample: initial structure at 25 ° C (e); after cooling to -25 ° C (f), after subsequent heating to 25 ° C (g).

To identify phase 2 we have studied the structure of C8Na thin film dried at 200 ° C and measured in a dry nitrogen atmosphere (Fig. 1e, f, g). At room temperature diffractogram reveal pseudo-hexagonal phase with lattice parameters $a_{ph} = 51.0 \text{ \AA}$ and $b_{ph} = 46.8 \text{ \AA}$, $\gamma_{ph} = 66^\circ$ (Fig. 1e). It is important to mention that the position of the meridional peak with $d = 51.0 \text{ \AA}$ corresponds to phase 2 mentioned above for the swollen film. Thus, phase 2 is pseudo-hexagonal columnar, and characterizes the structure of material in the absence of water channels. Cooling the sample to -25 ° C and subsequent heating to room temperature does not lead to significant changes of the structure, which indicates the stability of the columnar phase at temperature below zero (Fig. 1f,g). Based on the evolution of the C8Na thin film structure in the heating and cooling cycles, we conclude that the pseudo-hexagonal phase is stable for the dry film while the lamellar phase – for the swollen one. When the swollen film is cooled down, a sharp increase in the a_{lam} parameter is observed due to intense water absorption below the dew point. In this case, the width of the two-dimensional water channel in the swollen lamellar phase can be calculated as the difference in the d-spacings d_1 and d_2 . Thus, cooling to 0 ° C is an effective way to accelerate the swelling process upon saturated atmosphere of water vapor, providing an increase of the water channel width from 6 to 20 Å. Below 0 ° C water crystallizes in the confined geometry of nanochannels resulting in braking of the soft LC phase. In contrast, cooling of film containing the columnar phase does not have a significant effect.

An increase in the length of alkyl groups from octyl to dodecyl result in change of the phase behavior of the amphiphilic mesogen (Fig. 2,3). The initial state of the C12Na thin film in the swollen state shows a lamellar phase ($a_{lam} = 53.1 \text{ \AA}$) (Fig. 2a). Cooling the sample from room temperature to -25 ° C causes a slight decrease of the lattice parameter (Figure 2b). Reheating to room temperature leads to the recovery of the

original structure (Fig. 2c). A weak change in the parameters of the swollen lamellar phase can be explained by hydrophobic nature of the film surface formed by alkyl chains. The regular hydrophobic surface limits diffusion of water molecules to polar regions of the LC phase. Assuming normal orientation of the C12Na molecules in respect to the lamellar layer, we can estimate water channel width r as:

$$r = a_{lam} - 2l$$

where a_{lam} is the parameter of the lamellar phase, l is the length of the molecule (24 Å). The found channel width is 5 Å, which is significantly less than critical nuclei size of ice at -50 °C — about 13 Å [8,9]. Thus, the small width of water channels in the swollen C12Na structure prevents the formation of ice nuclei down to -50 °C and provides high stability of the lamellar phase at low temperature.

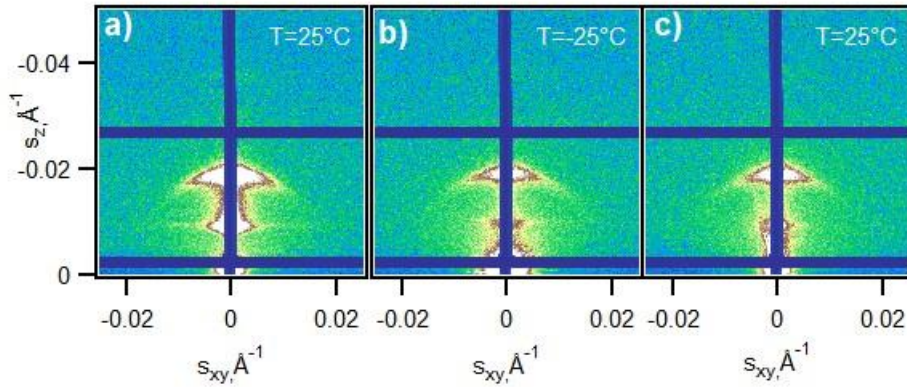


Figure 2 - Two-dimensional GISAXS patterns of swollen C12Na samples during thermal treatment: initial at 25 °C (a); after cooling to -25 °C (b), after subsequent heating to 25 °C (c).

The dry film structure of C12Na at 25 °C is similar to C8Na (Fig. 3a). A characteristic texture of the monoclinic columnar phase is observed with the following parameters: $a_{mon} = 57.6\text{Å}$, $b_{mon} = 51.4\text{Å}$, $\gamma = 55^\circ$. Cooling of dry C12Na film leads to certain disordering of the columnar phase and insignificant change of the lattice parameters (Fig. 3c). During heating from -25 to 25 °C the initial structure is fully restored (Fig. 3d, e). Thus, thermodynamically stable at room temperature columnar phase does not undergo changes upon cooling.

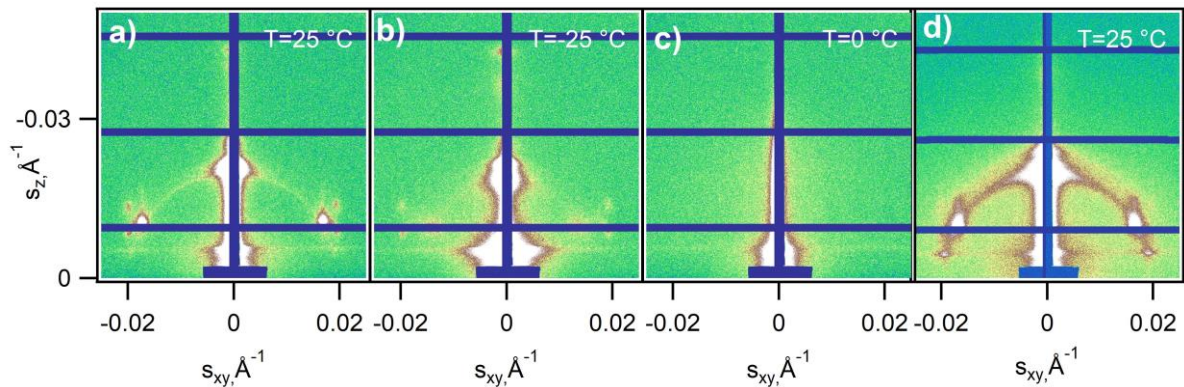


Figure 3 - Two-dimensional GISAXS patterns of dry C12Na samples during thermal treatment: initial at 25 °C (a); after cooling to -25 °C (b), after subsequent heating to 0 °C (d), to 25°C (e).

The reason for the stability of the lamellar phase of C12Na during cooling can be understood from the analysis of wide-angle reflections (Fig.4). On the WAXS pattern of the swollen film one can see equatorial reflections with d -spacings of 4.5 and 4.0 Å (Fig. 4a). In our previous work, we have observed these reflections in the columnar monoclinic and cubic gyroid phase [10]. For wedge-shaped mesogens, they correspond to the local ordering of the alkyl chains with formation of nanometer-sized crystals in the total supramolecular cell [11]. In this case, the alkyl chains are oriented perpendicular to the substrate.

Thus, in the lamellar phase of the swollen thin film we observe crystallization of the alkyl chains providing formation of a rigid physical network and stabilization of the supramolecular structure at low temperature. During following heating to 25 °C, wide-angle reflections are not observed, which indicates the destruction of alkyl nanocrystals caused by water freezing on the film surface. (Fig. 4b). However, the supramolecular lamellar structure of the C12Na film remains up to 100 °C, where transforms to hexagonal phase with parameter $a_{\text{hex}} = 58.0 \text{ \AA}$. Probably due to the lack of a selected orientation of the alkyl chains in the columns, the formation of a regular physical network in the dry film does not occur.

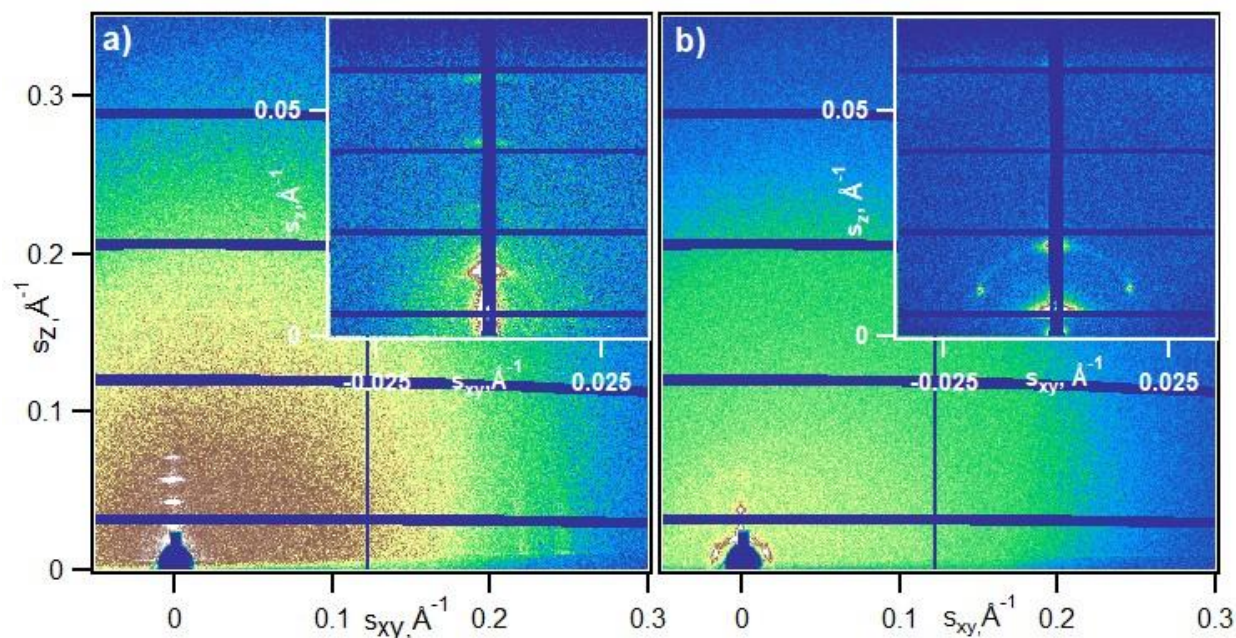


Figure 4 - Two-dimensional GISAXS and GIWAXS (inset) patterns of the swollen (a) and dry (b) sample C12Na at room temperature.

It is worth mentioning that subsequent cooling of the film from 100 °C to 25 °C in the presence of water vapor leads to the recovery of the lamellar structure with wide-angle equatorial reflections. Probably, the diffusion of water vapor through the amorphous alkyl matrix occurs much faster than through the crystalline regions.

In conclusion by X-ray diffraction analysis and atomic-force microscopy the phase behavior of thin films of wedge-shaped mesogens at low temperatures in dry and swollen state was investigated for the first time. Dry samples are characterized by the presence of a columnar phase, whereas in the swollen thin films reveal lamellar phase containing two-dimensional water channels. For a sample with octyl side groups, cooling below room temperature results in an increase in the width of the water channel from 6 to 20 Å followed by LC structure vanishing 0 °C due to water freezing. Mesogen bearing dodecyl groups show excellent channel stability down to -50 °C due to the presence of physical network formed by nanocrystals of the alkyl chains. The rigid framework prevents film swelling during cooling and suppress ice nucleation in narrow (5 Å) channels. The obtained results are important for understanding of supramolecular systems formation at different hierarchical levels and help in developing of new approaches in fabrication of self-organized films with required morphology.

References

- [1] K. Binnemans, *Ionic Liquid Crystals*, Chem. Rev. 105 (2005) 4148–4204.
- [2] C. Tschierske, *Progr. Polym. Sci.* 21 (1996) 775-852.
- [3] J.W. Goodby, *Mol. Cryst. Liq. Cryst.* 110 (1984) 205-219.
- [4] J.J. Hernandez, H. Zhang, Y. Chen, M. Rosenthal, M.D. Lingwood, M. Goswami, M. Möller, L.A. Madsen, D.A. Ivamov, *Macromolecules*. 14 (2017) 5392-5401.

- [5] 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, L.A. Madsen, *Journal of Physical Chemistry B*. 11 (2014) 3207-3217.
- [6] H. Zhang, L. Li, M. Moller, X. Zhu, J.J. Hernandez, M. Rosental, D.A. Ivanov, *Advanced Materials*. 25 (2013) 3543-3548.
- [7] A. Dolgoplov, K.N. Grafksaia, D.V. Anokhin, D.E. Demco, X. Zhu, D.A. Ivanov, M. Möller, *Phys.Chem.Chem.Phys.* 19 (2017) 7714.
- [8] J. Liu, C.E. Nicholson, S.J. Cooper, *Langmuir*. 23 (2017) 7286-7292.
- [9] T. Mizuguchi, *Physical Review E*. 95 (2017) 042804
- [10] K.N. Grafksaia, D.V. Anokhin, B.I. Zimka, I.A. Izdelieva, X. Zhu, D.A. Ivanov, *Chem. Commun.* 99 (2017) 13217-13220.
- [11] K.N. Grafksaia, J.J. Hernandez Rueda, X. Zhu, V.M. Nekipelov, D.V. Anokhin, M. Moeller, D.A. Ivanov, *Phys.Chem.Chem.Phys.* 17 (2015) 30240-30247.