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Communication

Synthesis of Calamitic Fluorinated Mesogens with Complex Crystallization Behaviour

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Abstract: This work presents the synthesis and self-organization of the calamitic fluorinated mesogen, 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-4-iodobutoxy)ethanesulfonic acid, a potential model for perfluorosulfonic acid membranes (PFSA). The compound is derived in three steps from 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride, achieving an 78% overall yield. The resulting compound exhibits intricate thermal behavior. At 150 °C, a crystal-to-crystal transition is observed due to the partial disordering of calamitic molecules, which is followed by isotropization at 218 °C. Upon cooling, sample ordering occurs through the formation of large smectic liquid crystalline phase domains. This thermotropic state transforms into a layered crystal phase at lower temperatures, characterized by alternating hydrophilic and hydrophobic layers. Using X-ray diffraction, crystalline unit cell models at both room temperature and 170 °C were proposed. Computer simulations of the molecule across varying temperatures support the idea that thermal transitions correlate with a loss of molecular orientation. Importantly, the study underscores the pivotal role of precursor self-organization in aligning channels during membrane fabrication, ensuring controlled and oriented positioning.

Keywords: DSC; fluorinated compounds; liquid crystals; melting point; smectic

1. Introduction

In recent years, increasing concern has been raised about the growing environmental burden caused by the use of fossil fuels and the overall increase in energy consumption, especially in EU countries [1–3]. Searching for clean energy, particularly decarbonized sources, is relevant, and according to photovoltaics, PV [4,5], Lithium-ion batteries, LIB [6], wind mills [7], and fuel cells [8,9], these appear as innovating and useful means for overcoming such challenges. The fuel cell is a device that converts the electrochemical energy of a fuel's oxidation-reduction into electricity, heat, and water. One of the most important components is the membrane, and among them, perfluorosulfonic acid ones (PFSA) as Nafion®, Flemion®, Aquivion®, and 3M ®membranes are commercially available from Chemours, Fumatech, Solvay, and 3M Innovative, respectively [10]. Many articles have been published on the synthesis, characterization, processing, and electrochemical application into portable, small, and bigger embedded devices (vehicles that are already produced from Toyota [11], Honda, or Hyundai). It has been found that proton transport properties of PFSA membranes strongly depend on their morphology [12]. The self-assembly of fluorinated side-groups determines the volume fraction, topology, and size of water channels. Despite numerous publications on the correlation between chemical structure, preparation conditions, and final supramolecular

morphology of polymeric membranes, this question remains open due to polymer specificity, such as slow structure formation and polydispersity of model ionomers [13–15]. To better understand the self-assembly process in ion-transporting membranes, it would be of interest to propose models (i.e. small molecules) capable of self-assembling under conditions similar to those for fluorinated comb-like copolymers. Such semi-rigid amphiphilic compounds, known as calamitics, are known to form layered, cylindrical, or cubic superstructures as a function of molecular shape, temperature, humidity, etc. [16–18]. For example, Berrod et al. [19] suggested original perfluorosulfonic acid molecules that can reproduce phase-separated morphology of PFSA ionomer membranes used as electrolytes in fuel cells.

Investigation of thermotropic mesogens are also of great interest from the fundamental point of view as the peculiarities of structure and assembly mechanisms of liquid crystals is yet to be fully understood [20–22]. Specific details on molecular level arrangements, conditions of transitions between different phases and so on can be resolved through various simulations techniques [23,24], and comparison between experimental and theoretical data can be used for the refinements of force fields and models, leading to better understanding of physical reasons of mentioned assemblies. Up today there are numerous modeling studies related to thermotropic mesogens [23–27] which show the high ability of modern methods to predict and reveal some features of the structuring of mesogens qualitatively as well as quantitatively.

2. Materials and Methods

Synthesis

1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride was supplied from Appollo while ethylene provided by Air Liquide, France; Perkadox 16S was purchased from Akzo Chemicals and *tert*butanol and Li₂CO₃ from Sigma Aldrich.

Ethylenation of the iodofluorocompounds.

Ethylenation of 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride occurred in 50 mL Hastelloy (HC276) autoclave equipped with inlet and outlet valves, a manometer, a rupture disk, a mechanical stirrer and a controller to check the speeding rate and the temperature. A solution composed of di(*tert*-butylcycloheylperoxy dicarbonate (Perkadox 16S) (0.247 g, 0.63 mmol), 28 mL of *tert*-butanol, and 16.82 g (39.4 mmol) of 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride was degassed by N₂ bubbling for 30 min. During this time, the autoclave was put under vacuum (40×10^{-3} bar) for 30 min to remove the residual traces of oxygen. The above solution was transferred into the autoclave under vacuum *via* a funnel tightly connected to the introduction valve of the autoclave. Then, the vessel was cooled in a liquid nitrogen bath, and ethylene (2 g, 45.5 mmol) was introduced through the autoclave inlet valve while monitoring its amount by double weighing (i.e., the difference of masses before and after filling the autoclave with ethylene). The autoclave was then allowed to warm to ambient temperature and heated to the target reaction temperature (60 °C) under mechanical stirring and the evolutions of pressure and temperature were recorded. Suddenly, ca. after one hour-reaction at 60 °C, a fast high increase of pressure up to 70 bar occurred immediately followed by a drop of pressure as low as 5 bar, considering a complete reaction. The autoclave was then cooled in an ice bath for 30 minutes and no released of unreacted gas was noted, followed by the opening of the vessel. The total product mixture (yellow solid) was recovered from the autoclave and characterized by ¹⁹F NMR. The evidence by the absence of signal at -59 ppm assigned to CF₂CF₂I end-group indicated the quantitative conversion of 5-iodo-3-oxaperfluoropentane-1-sulfonyl fluoride. The crude product was then dissolved in acetone and precipitated from water and finally dried under vacuum (20×10^{-3} bar, 50 °C) for 8 h yielding 17.55 g of a yellowish powder (yield=94%).

Oxidation of the sulfonyl fluoride in I-CH₂CH₂CF₂CF₂OCF₂CF₂SO₂F into SO₃H was carried out in slightly basic conditions in presence of K₂CO₃ to lead to ICH₂CH₂CF₂CF₂OCF₂CF₂SO₃Li (yield not determined). This latter was then acidified to chemically change the -SO₃Li end-group into sulfonic acid, thus producing ICH₂CH₂CF₂CF₂OCF₂CF₂SO₃H as a white powder. The overall yield from 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride was ca. 78%.

Methods of Characterization

The morphology and physical properties of the sample were studied through thermogravimetric analysis, differential scanning calorimetry, polarized optical microscopy, temperature-resolved small- (SAXS) and wide-angle X-ray scattering (WAXS), and computer simulation.

Thermogravimetric experiments were conducted using TGA Q500 from TA Instruments from 25 °C to 900 °C at a heating rate of 10 °C under a nitrogen flow 100 ml/min.

Differential scanning calorimetry (DSC) measurements were carried out using a Polyma 214, Netzsch. Samples were placed in pierced aluminum pans and subjected to two heating – cooling cycles from 20 to 260 °C at a rate of 10 K.min⁻¹.

Microscopic images of thin films were captured using a Carl Zeiss AxioScope A1 POL optical microscope in polarized light with 100x objective. The films, prepared from the melt between two cover glasses, were positioned on a Linkam LTS heating stage. A small amount of the sample was heated to 260 °C, above melting temperature, and then crystallized at two different cooling rates: 1 and 10 K.min⁻¹. Images were captured with a 5 MP CMOS camera.

Temperature-resolved SAXS and WAXS measurements were carried out at the ID02 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The measurements were performed in transmission geometry with X-ray photons at an energy of 11.9 keV. The calibration of the norm of the reciprocal vector s ($|s| = \frac{2\sin\theta}{\lambda}$ where θ is the Bragg angle and λ -wavelength) was done using several diffraction orders of silver behenate (for SAXS) and corundum (for WAXS).

All-atom molecular dynamics (AAMD) simulations of $I(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F$ melt under different temperature conditions were carried out as follows. The initial unit cell configuration was established through Monte Carlo annealing among a set of most common symmetry groups, with geometry optimization using the COMPASS force field [28]. The elementary configuration with the lowest energy was then replicated to form a periodic box measuring 100 Å × 30 Å × 30 Å, containing 288 $I(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F$ molecules. The COMPASS force field was utilized for the AAMD simulations, and electrostatic interactions were computed using the PPPM method [29].

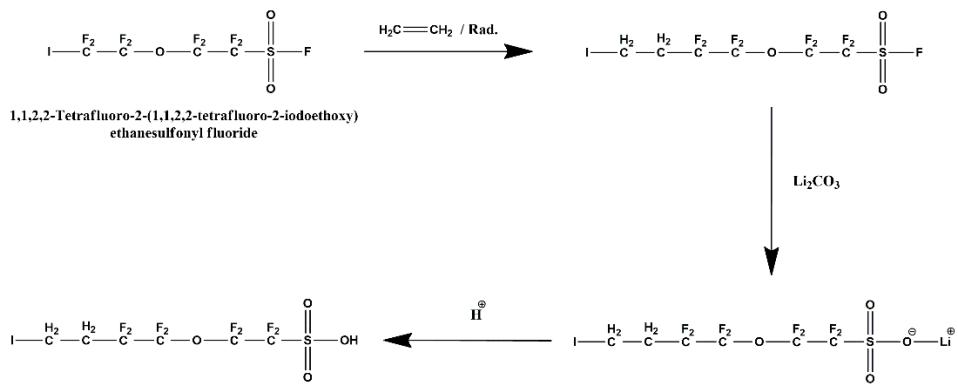
The system was equilibrated in the isobaric-isothermal ensemble (NPT) for 10 ns with a Berendsen barostat [30] and a Nosé -Hoover thermostat [31], at a temperature of T = 25 °C and a pressure of P = 1 atm. Subsequently, the simulation box was heated sequentially by 5 °C every 10 ns up to 280 °C. Statistics were gathered over the last 1 ns of every heating step across three independent heating procedures.

Radial distribution function (RDF) and static structure factor $S(k)$ were utilized for characterizing the translational order of molecules within the box. Orientational ordering was monitored by calculating the first eigenvalue of nematic Q-tensor, $S = <\frac{3\cos^2\gamma - 1}{2}>$ [32], where γ is the angle between molecules' first principal axis and the director. The size of the molecules was estimated based on the calculation of the gyration radius R_g .

3. Results and discussion

1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-4-iodobutoxy)ethanesulfonic acid was synthesized in three steps from 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride (Scheme 1): i) by a quantitative ethylenation initiated by *tert*-butyl cyclohexyl peroxydicarbonate at 60 °C (that generates only the monoadduct as in previous works [33]. The vanishing of the signal at -59 ppm (highlighted by ¹⁹F NMR spectrum) and the presence of two complex multiplets at 2.3 and 3.0 ppm in the ¹H NMR spectrum evidenced the formation of the ethylenated product (with the insertion of one ethylene unit only); ii) the second step enabled to modify the sulfonyl fluoride end group into SO_3Li under mild basic conditions to avoid the dehydroiodination. iii) the final steps dealt with the acidification of that latter into sulfonic acid. These reactions were monitored by ¹⁹F, ¹H and IR spectroscopies. The O-F frequencies (bending modes) centered at 1470 and 810 cm⁻¹ (noted in the spectrum of the product bearing SO_3Li end-group) were absent after the hydrolysis reaction while the -S(O)(O)OH stretching vibrations of the sulfonic acid groups at 3377 cm⁻¹ and 1026 cm⁻¹ were present, indicating the successful hydrolysis reaction. Additionally, the hydrolysis of the -SO₂F

groups was confirmed by the ^{19}F NMR spectrum that does not display any signal at +45 ppm characteristic of the sulfonyl fluoride group [34]. The absence of this peak indicates that the hydrolysis-reaction yield was quasi quantitative.



Scheme 1. General reaction mechanism.

The overall yield was 78 % from 5-iodo-3-oxaperfluoropentane-1-sulfonyl fluoride.

Structural Characteristics of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$

The first DSC heating thermogram shows a double endothermic peak within the temperature range of 80 to 110 °C, which is attributed to the sample's dehydration or dehydroiodination. The peak at 150 °C is likely due to a crystal-to-crystal transition, typical for amphiphilic calamitic molecules [35]. An intense peak at 218 °C corresponds to the sample's isotropization [36]. The second heating curve shows only isotropization, indicating irreversibility of the solid-to-solid transition.

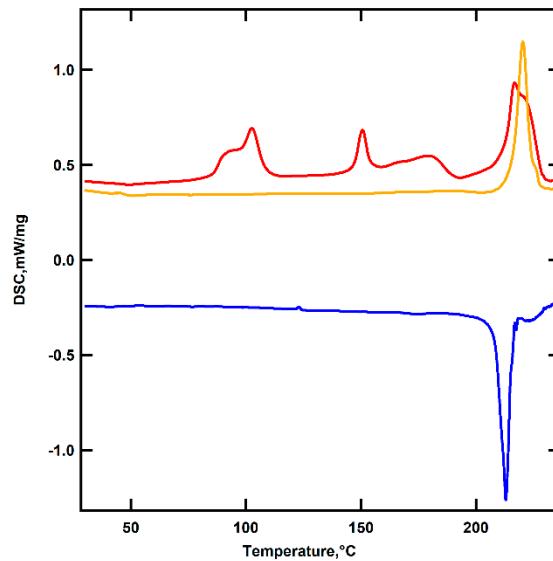


Figure 1. DSC thermograms of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$: 1st heating (yellow), cooling (blue) and 2nd heating (red). Exo processes are down.

Polarized optical microscopy of thin films of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$ at 216 °C reveals crystalline spherulites and rod-like domains of the smectic liquid crystalline (LC) phase (Figure 2a). It is plausible that the LC phase is thermotropic, which signifies that it is in equilibrium in a certain temperature range. During cooling, the nucleation rate increases, leading to the emergence of a grainy polycrystalline texture at room temperature (Figure 2b).

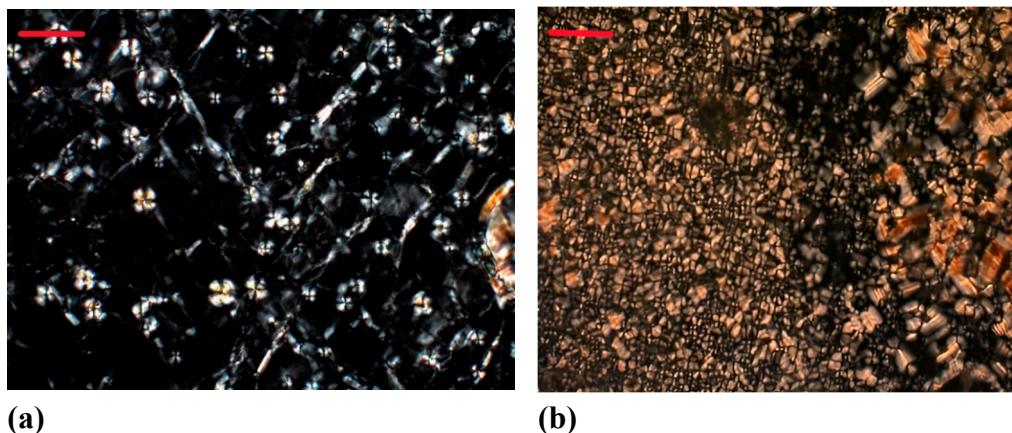


Figure 2. POM images of the studied sample during isothermal crystallization 216 °C (a) and after cooling to room temperature (b) Scale bar is 50 μ m.

Structural analysis was performed using temperature-resolved small- (SAXS) and wide-angle (WAXS) X-ray scattering. At room temperature, powder diffraction indicates a highly ordered crystalline structure with numerous peaks in the WAXS region (Figure 3). The SAXS region shows peaks typical for a layered structure. The complete table of the peaks is presented in Table S1. According to SAXS, the longest inter-layer distance is 2.72 nm. The high-intensity peaks at $s=4.3$ and 4.9 nm^{-1} are associated with aluminum foil used as a sample container.

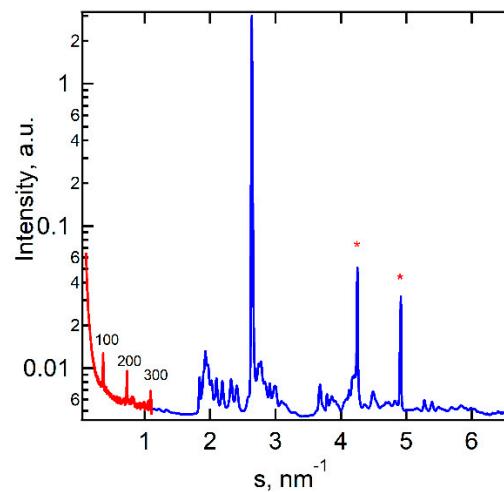


Figure 3. SAXS (red) and WAXS (blue) 1D diffractograms measured at room temperature. Several orders of 100 peak are denoted on the SAXS curve (* peaks at 4.3 and 4.9 nm^{-1} are assigned to Al foils).

The crystalline structure observed can be assigned to a monoclinic unit cell with lattice parameters: $a = 27.5 \text{ \AA}$, $b = 5.2 \text{ \AA}$, $c = 5.0 \text{ \AA}$, and angles $\alpha = 81^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$. Temperature-dependent SAXS and WAXS measurements are presented in Figure 4(a) and Figure 4(b), respectively. During heating, distinct changes in both peak positions and intensities are noticeable in the SAXS and WAXS regions. Specifically, shifts observed at 90 °C and 150 °C are attributed to dehydration and a crystal-to-crystal transition, respectively. The isotropization process at 220 °C becomes evident with the fading of sharp crystalline peaks.

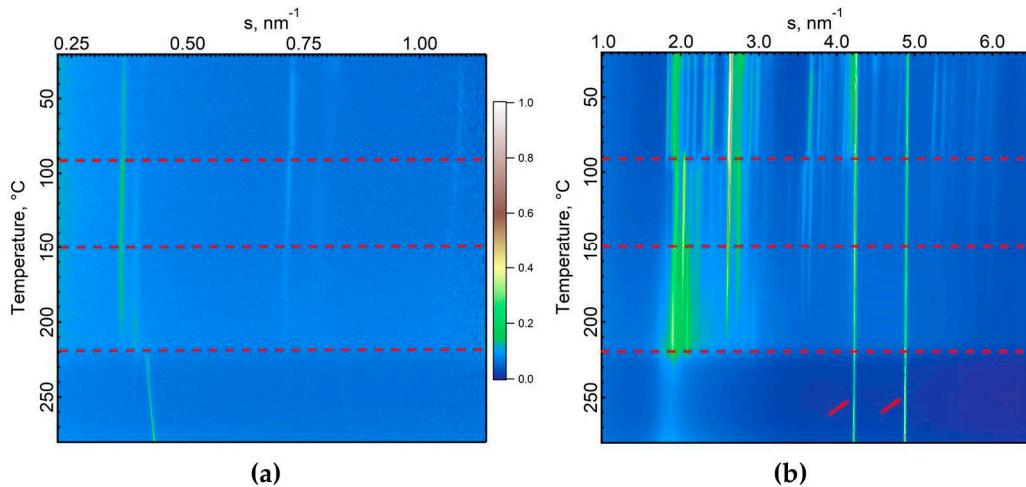


Figure 4. Temperature-resolved SAXS (a) and WAXS (b) curves corresponding to a heating ramp. Color table indicates the peak intensity of 1D diffractograms as a function of the norm of the scattering vector \mathbf{s} . Two intense reflections marked by arrows are attributed to aluminum foil.

Indexation of the high-temperature phase indicates the formation of a triclinic unit cell with the following parameters: $a=25.6 \text{ \AA}$, $b=5.12 \text{ \AA}$, $c=4.96 \text{ \AA}$, $\alpha=95^\circ$, $\beta=97^\circ$, $\gamma=88^\circ$.

To gain insights into the arrangement of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$ at different temperatures, all-atom molecular dynamics simulations of a box sized $100 \text{ \AA} \times 30 \text{ \AA} \times 30 \text{ \AA}$, filled with 288 molecules, were conducted at room temperature, followed by a heating procedure with a temperature increase up to $280 \text{ }^\circ\text{C}$. A detailed description of the modeling methodology is provided in the Materials and Methods section.

Initially, after system equilibration at $T=25 \text{ }^\circ\text{C}$, the molecules are elongated and retain crystal ordering. Approximation of the lattice parameters, obtained through identification of the minimal symmetric parallelepiped [37] and averaged over the system, yielded the following values: $a = 27.2 \text{ \AA}$, $b = 5.0 \text{ \AA}$, $c = 5.0 \text{ \AA}$, $\alpha = 81.1^\circ$, $\beta = 89.6^\circ$, $\gamma = 90.4^\circ$. These parameters correspond to a cell with monoclinic symmetry and are in good agreement with experimental data (Figure S1).

After equilibration at room temperature, the box of $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$ was slowly heated in the NPT (isobaric-isothermal ensemble) ensemble from $T=25 \text{ }^\circ\text{C}$ to $T = 280 \text{ }^\circ\text{C}$. Within this temperature range, the system undergoes a series of transitions, analyzed using nematic order parameter S [32], which indicates whether the molecules' main axis is oriented in one direction ($S=1$) or their orientations are distributed isotropically ($S=0$). The presence of a layered structure was monitored through the calculation of the static structure factor $S(k/k^*)$.

Figure 5 shows the dependency of the nematic order parameter S on temperature, the insets provide typical snapshots of the system under different states and the normalized static structure factor for the chosen T . The latter was plotted against k/k^* , where k^* is the location of the first maximum. For the layered structure, positions of consequent peaks $k(1):k(2):k(3):k(4)$ should satisfy the relations 1:2:3:4 [38], indicating the periodicity of layers. This relation breaks when layered ordering is disrupted. Positions of these peaks are marked with vertical lines.

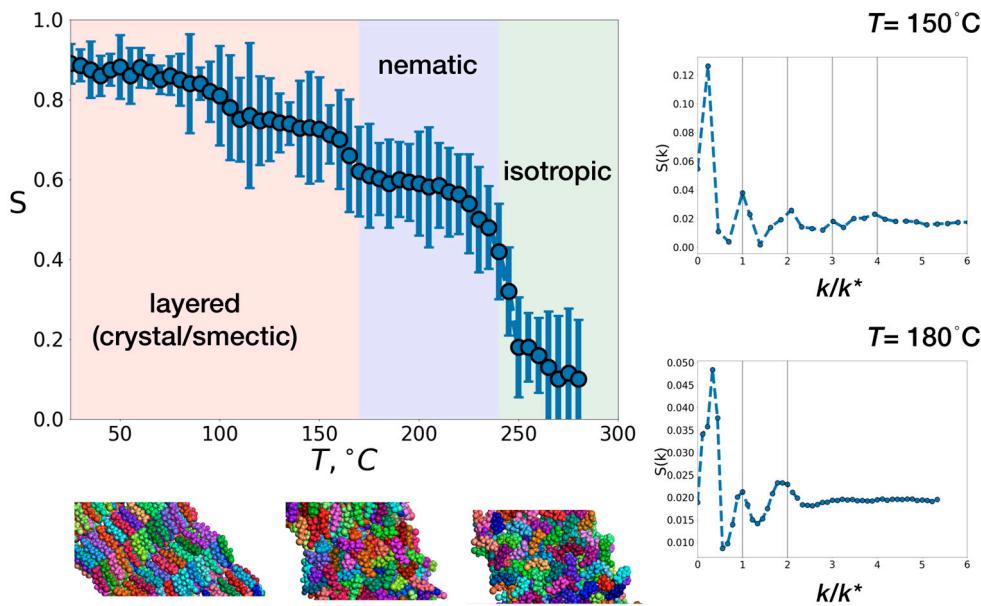


Figure 5. Orientational order parameter S as a function of temperature T , obtained from simulations; snapshots of the system, corresponding to layered, nematic and isotropic state; and normalized structure factor, plotted against k/k^* , where k^* is the location of the first meaningful peak at the vicinity of smectic - nematic transition. Within every molecule atoms are colored in the same way, neighboring molecules are colored differently.

Overall, the dependency of the nematic order parameter on temperature is qualitatively similar to what is expected for ellipsoidal mesogens [39,40], with S close to 1 at low temperatures (crystal) and decreasing monotonically as T increases. Sharp changes in the order parameter S indicate transitions between different states (crystal, smectic, nematic, isotropic), with the most pronounced drop at the nematic-isotropic transition.

In the interval between 25 °C and ~ 170 °C, the molecules maintain a layered arrangement (peaks at $k/k^* = 1, 2, 3, 4$ at $T = 150^\circ\text{C}$, Figure 5 upper right, Figure S2(left)) and retain a high orientational ordering parameter, which decreases from $S = 0.9$ to $S = 0.64$ upon heating. At $T \sim 170^\circ\text{C}$, layers begin to overlap, leading to the destruction of the smectic phase - at $T = 180^\circ\text{C}$, only the first two peaks of $S(k/k^*)$ remain (Figure 5 bottom right, Figure S2(middle)). However, the system maintains high orientational order for $\text{I}(\text{CH}_2)_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{OH}$ ($S \sim 0.64$). Thus, at $T \sim 170^\circ\text{C}$ the smectic to nematic transition can be observed. The model temperature for this transition to the nematic phase was found to lie within the interval between 170 and 245 °C, with a monotonic decrease of S upon heating from 0.64 to 0.42. A subsequent increase in T leads to a sharp drop in the nematic order parameter to 0.19 at $T = 250^\circ\text{C}$, with the nematic-to-isotropic transition temperature occurring approximately at $T \sim 245^\circ\text{C}$, Figure S2 (right).

Therefore, within the all-atom molecular dynamics framework, two pronounced transition temperatures were identified: smectic-to-nematic at $T \sim 170^\circ\text{C}$ and nematic-to-isotropic at $T \sim 245^\circ\text{C}$, both of which are in good agreement with experimental data (Figure 3). The fact that the values derived from simulations are slightly higher than those observed experimentally (i.e., 150 and 230 °C, respectively) can be attributed to finite-size effect or to inaccuracies within the chosen force field.

4. Conclusions

Initially, a model of the membrane was proposed based on ethylenation and chemical modification. The formation of the structure of ionomer comb-like polymer precursors was carried out, and the dependencies of their self-organization on thermal history were established through both experimental and theoretical considerations. It was discovered that at room temperature, the compound exhibits a highly ordered crystal structure with a monoclinic lattice formed by almost

extended molecules. Heating to 150 °C results in partial disordering of fluorinated tails and a transition to a triclinic unit cell. During cooling from the isotropic state, the molecules form large domains of the smectic LC structure. This smectic phase acts as a pre-ordered state for crystallization into a layer-like monoclinic phase at room temperature. Experimental findings on the formation of the crystalline phase and crystal-to-crystal phase transitions were validated by computer modeling using molecular mechanics approaches. The emergence of a smectic phase for relatively short linear fluorinated molecules is significant for the synthesis of self-organizing comb-like ionomers with controlled morphology of ion-conductive channels. The formation of the smectic phase was confirmed through all-atom molecular dynamic simulations, and the temperatures of smectic-nematic and nematic-isotropic transitions upon heating were determined. It was demonstrated that theoretical results are in good agreement with experimental findings. The insights presented in this work can be utilized for the development of new types of fuel cells with enhanced control over their morphology and improved performance.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figure S1: Possible symmetries of unit cell of $I(CH_2)_2(CF_2)_2O(CF_2)_2SO_2OH$ used in simulation; Figure S2: Model of P1 unit cell of $I(CH_2)_2(CF_2)_2O(CF_2)_2SO_2OH$ at different temperatures; Table S1: Experimental and theoretical peak positions for $I(CH_2)_2(CF_2)_2O(CF_2)_2SO_2OH$ at room temperature; Figure S3: ^{19}F -NMR spectrum of $ICF_2CF_2OCF_2CF_2SO_2F$ recorded in d6-acetone; Figure S4: 1H -NMR spectrum of $ICH_2CH_2CF_2CF_2OCF_2CF_2SO_3H$ recorded in d6-acetone. Figure S5: ^{19}F -NMR spectrum of $ICH_2CH_2CF_2CF_2OCF_2CF_2SO_3H$ recorded in d6-acetone. Figure S6: FT-IR spectra of $ICH_2CH_2CF_2CF_2OCF_2CF_2SO_3H$.

Author Contributions: Conceptualization, D.V.A. and B.M.A.; methodology, D.V.A.; formal analysis, A.V.M. and A.I.B.; investigation, D.V.A.; data curation, A.V.M.; writing—original draft preparation, D.V.A.; writing—review and editing, B.A.M., D.A.I and UUO.; visualization, A.I.B.; supervision, D.A.I. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds are available from the authors.

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