# CRYSTAL GROWTH FROM SUPERSATURATED AQUEOUS SALT SOLUTIONS ON A POLYMER NAFION SUBSTRATE

N. F. Bunkin<sup>1</sup>\*, Y. V. Novakovskaya<sup>2</sup>, P. N. Bolotskova<sup>1</sup>, V. V. Voronov<sup>3</sup>, V. A. Kozlov<sup>1</sup>, S. L. Timchenko<sup>1</sup>, M. T. Khoung<sup>1</sup>, and E. N. Baranova<sup>4</sup>

Features of the crystallization of various compounds on the Nafion polymer substrate from supersaturated aqueous solutions is studied by XRD. The solutions are prepared from natural deionized and deuteriumdepleted water. It was earlier established that the swelling of Nafion in natural deionized water clearly demonstrates effects caused by the partial uncoiling of polymer fibers into the liquid volume, but no such effects were observed in deuterium-depleted water. The ab initio calculations performed in the present work show that the uncoiling of lateral Nafion chains with terminal –SO<sub>3</sub>H groups and the dissociation of these groups with subsequent formation of hydronium ions and -SO3 structural anionic residues are energetically favorable in the case of the contact with a sufficient amount of water molecules. The influence of these factors on the process of crystal formation on polymer substrates is studied. It is established that the effect of partial uncoiling of polymer chains indeed affects the crystallization, and does it in different ways, depending on the crystal structure. Thus, no differences between XRD patterns of crystals grown on smooth and polymer substrates are observed for the monoclinic lattice of sodium acetate trihydrate. In the case of copper sulfate (with either CuSO<sub>4</sub>·5H<sub>2</sub>O pentahydrate crystals (triclinic crystal system) or CuSO<sub>4</sub>·3H<sub>2</sub>O trihydrate crystals (monoclinic crystal system)), copper sulfate trihydrate and pentahydrate are formed on the polymer and smooth substrates, respectively. None of the studied crystals exhibited differences between smooth and polymer substrates for the supersaturated solutions based on deuteriumdepleted water, and in both cases a triclinic crystal system of the CuSO<sub>4</sub>·5H<sub>2</sub>O pentahydrate precipitate is identified for the CuSO<sub>4</sub> aqueous solution. For sucrose, the precipitate amorphization upon the deposition onto the Nafion plate is detected. A theoretical model is proposed to explain the effect of partial polymer chain uncoiling on the growth of crystals, depending on their crystal system, unit cell parameters, and the volumetric ratio of hydrophilic and hydrophobic fragments in the molecular structure.

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<sup>&</sup>lt;sup>1</sup>Bauman Moscow State Technical University, Moscow, Russia; \*nbunkin@mail.ru. <sup>2</sup>Moscow State University, Moscow, Russia. <sup>3</sup>Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia. <sup>4</sup>All-Russia Research Institute of Agricultural Biotechnology, Moscow, Russia. Original article submitted January 27, 2024; revised February 26, 2024; accepted February 26, 2024.

#### INTRODUCTION

A number of properties of the Nafion<sup>™</sup> polymer membrane prepared by the copolymerization of perfluorinated vinyl ether comonomer and tetrafluoroethylene were studied [1]. The following its chemical formula was reported:

$$-[(CFCF_2)(CF_2CF_2)_m] - \\ | \\ OCF_2CFOCF_2CF_2SO_3H \\ | \\ CF_3$$

In the present work, we studied samples of Nafion N117 (m = 6.5) composed of perfluorinated hydrocarbon chains with lateral branches of the perfluorinated ether type and  $-SO_3H$  terminal groups. Thus, the polymer structure includes fragments differently reacting with water and aqueous solutions: a highly hydrophobic skeleton, hydrophilic  $-SO_3H$  terminal groups, and weakly hydrophilic polyester moieties between them. This combination of properties should be manifested in the state of the polymer matrix in an aqueous environment. For example, both direct and reverse micellization was observed upon wetting Nafion in water [1]. When studying specific features of Nafion manifested upon its swelling in water, the dissociation of terminal  $-SO_3H$  groups at the polymer–water interface should be essential:

$$\mathbf{R} - \mathbf{SO}_3\mathbf{H} + \mathbf{H}_2\mathbf{O} \Leftrightarrow \mathbf{R} - \mathbf{SO}_3^- + \mathbf{H}_3\mathbf{O}^+. \tag{1}$$

As is known (see review [1] and references therein), percolated channels with a diameter of 2-3 nm are formed in the polymer matrix volume as a result of swelling. Negatively charged (as a result of reaction (1)) regions on the inner surface of these channels provide ionic transport through the membrane volume [2]. The nanometer structure of these channels allows separating  $H^+$  and  $OH^-$  ions on both sides of the membrane, which is used in low-temperature hydrogen cells [3]. The physical mechanism of such separation was comprehensively studied (e.g., see review [4]). Ion-exchange processes inside nanometer-size Nafion channels have been broadly studied in recent years [5].

Luminescence spectroscopy is commonly used in Nafion studies (see the recent review [6]). It was established in our photoluminescence spectroscopy experiments that the  $-SO_3H$  terminal groups act as luminescence centers [6, 7]. Placing a Nafion plate in water with deuterium content varying from 3 ppm (deuterium-depleted water, DDW) to  $10^6$  ppm (heavy water) showed that the swelling characteristics of this polymer depend on deuterium content. We estimated the size of the water region adjacent to the Nafion surface and containing luminescence centers. In particular, we measured distance *x* from the Nafion surface to the regions of liquid with a nonzero luminescence signal. It was established that luminescence intensity I(x) remains nonzero up to  $x = 500 \,\mu\text{m}$  during the Nafion swelling in natural deionized water ( $157\pm1$  ppm deuterium content [8]) and vanishes at  $x \approx 10 \,\mu\text{m}$  in the case of DDW. We therefore hypothesized that the coils of polymer fibers are reorganized during the polymer swelling and uncoil into the liquid volume without detaching from the membrane surface. As a result, a specific fixed-size region is formed in the liquid volume, thus determining the detected effect. It can be also concluded [6, 7] that this effect is most pronounced for wetting the membrane in natural water with a deuterium content of  $10^2$ - $10^3$  ppm (obviously, the deuterium content in natural deionized water falls within this range) and to a lesser extent in DDW.

According to [9], the near-surface coils of polymer fibers inside Nafion are mainly oriented perpendicular to the Nafion–water boundary when Nafion contacts natural water and along this boundary when Nafion contacts water vapor. The observations reported in [10] indirectly confirm the effect accompanying the uncoiling of fibers into the liquid volume. The data reported in [10] suggest that the average distance between fibers oriented across the surface can be several nanometers. Assuming that the length of a crystal unit cell edge usually does not exceed 1 nm, the effect of polymer fiber uncoiling can influence the growth of crystals on a polymer substrate from supersaturated aqueous salt solutions based on natural deionized water and DDW and having different isotopic compositions.

The choice of substances for the crystallization study was determined by the following considerations. Obviously, the uncoiling of polymer chains occurs at a certain angle to the middle surface of the Nafion plate, and the highest probability for the formation of crystals with a particular crystal system should be determined by the value of this angle. Since the

process occurs in an aqueous environment, the degree of water participation in the crystal growth is important. Finally, the distances between uncoiled polymer chains should play an essential role that can be revealed using compounds with significantly different molecular sizes and different volume ratios of their hydrophilic and hydrophobic parts.

This work describes X-ray diffraction and refraction experiments to study crystallization on a polymer Nafion substrate in comparison with that on a smooth substrate while taking into account the effect of polymer fiber uncoiling.

## MATERIALS AND METHODS

Nafion N117 plates (Sigma Aldrich, St. Louis, MO, USA) with a thickness of 175  $\mu$ m were studied. The plates were wetted in natural deionized water (157±1 ppm deuterium content) that was purified from ionic admixtures on a Milli-Q apparatus (Merck KGaA, Darmstadt, Germany) with a resistivity of 18 M $\Omega$  ·cm at 25 °C. Deuterium-depleted water (DDW) with deuterium content up to 3 ppm (Sigma Aldrich, St. Louis, MO, USA) was another liquid for the Nafion wetting. The absorption coefficient of Nafion during wetting in deionized water and in DDW was studied using a PB 2201 spectrophotometer (SOLAR, Belarus) in the spectral range of 190-1100 nm with a step of 0.1 nm.

In the X-ray diffraction and refraction experiments, the features of crystallization on a polymer Nafion substrate were studied while taking into account the effect of uncoiling compared to the crystallization on a smooth substrate. A Nafion plate with a thickness of 175  $\mu$ m and an area of 3×2.5 cm was placed into a Petri dish filled with an aqueous solution of the studied salt (25 mL) with a concentration corresponding to the saturation at 20 °C. The solutions were prepared from natural deionized water and DDW. We also conducted control experiments with solutions in a Petri dish without Nafion plates. Fig. 1 shows the process of growing a CuSO<sub>4</sub> crystal on the Nafion surface. Open Petri dishes were placed in a foam box, where water evaporated from a supersaturated solution at a fixed temperature and a crystal was formed.

The rate of crystal growth on smooth and polymer substrates was also estimated. To this aim, the refractive index n(t) of the studied solutions was measured every 10 h. The values of the refractive index n at the wavelength  $\lambda = 589.3$  nm were measured using an Abbe refractometer. In these experiments, a 5 µL drop was taken from a solution surface using an Acura 825 micropipette (Socorex Isba SA, Ecublens, Switzerland) and applied to the surface of the main refractometer prism.

The XRD patterns of the crystal samples were recorded on a Bruker D8 Discover A25 DaVinci Design diffractometer. The radiation source was a Siemens KFL ceramic X-ray tube (focus size =  $0.4 \times 12$  mm). Record modes: Cu $K_{\alpha}$  radiation, K $\beta$ -filter, U = 40 kV, I = 40 mA, Bragg–Brentano geometry, 2.5° Soller collimators, 0.638 mm slit width, LYNXEYE detector, 10-65° 20 scan range, 0.01° scan step, 7.5 s counting time per point. The spectra were processed using the EVA v. 2.1 program. The spectra were interpreted using the PDF-2 2011 database.



Fig. 1. Nation plate in an aqueous  $CuSO_4$  solution in a Petri dish.

The following substances were studied: sodium acetate trihydrate (monoclinic, a = 12.5 Å, b = 10.4 Å, c = 10.4 Å;  $\beta = 112.65^{\circ}$ ); copper sulfate crystallized as a pentahydrate (triclinic, a = 5.9 Å, b = 6.1 Å, c = 10.7 Å;  $\alpha = 77.33^{\circ}$ ,  $\beta = 82.27^{\circ}$ ,  $\gamma = 72.57^{\circ}$ ) and as a trihydrate (monoclinic, a = 5.6 Å, b = 13.03 Å, c = 7.3 Å;  $\beta = 97.1^{\circ}$ ), and sucrose (monoclinic, a = 7.72 Å, b = 8.68 Å, c = 10.82 Å,  $\beta = 102.982^{\circ}$ ). The crystal data were taken from [10]. All the above substances were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as-prepared.

The experimental data were interpreted using ab initio quantum chemical calculations. Model fragments of the Nafion structure were optimized in the DFT approximation using the B3LYP hybrid exchange-correlation functional and the 6-31G(d,p) augmented double-zeta basis set. Dispersion interactions, which are important in the description of perfluorinated regions of the model structures, were considered using the D3+ Grimme correction. As is known (e.g., see, [11, 12]), this approach quite well describes the electron density distribution of substituted hydrocarbons and water clusters by considering in a balanced manner hydrogen bonding, electrostatic, and dispersion interactions. Larger basis sets cannot be used for model systems characterized by such large atomic sizes and spatial compactness because the linear independence parameter of the basis set functions decreases rapidly. In general, no additional functions with larger angular moments or smaller exponents are required, since the same role in this case is played by the tails of the basis functions centered on relatively distant nuclei of the model system. The conformational changes of Nafion in the presence of water were analyzed using combined models composed of up to 60 molecules. Possible formation of salt fragments on the Nafion membrane surface was analyzed for the found structures of the main Nafion model fragment. To prevent aggregation of water molecules typical for small ensembles of particles, constraints were imposed on the distances between oxygen atoms of water molecules and the atoms they are coordinated to in the corresponding hydrates. For the model systems calculated without geometry constraints, the correspondence to the local minima of the adiabatic potential was confirmed by calculating normal coordinates of optimized configurations. Relative stabilities of the systems were estimated by comparing their total electron energies (E) and relative Gibbs free energies ( $\Delta G_{\rm vib}$ ) taking into account thermal corrections due to vibrational degrees of freedom. All calculations were performed using the Firefly 8.2 quantum chemical program [13] and visualized using the Chemcraft package [14].

## **RESULTS AND DISCUSSION**

Sodium acetate crystallizes with the participation of water molecules, and the environment of each sodium atom contains five molecules at an average Na···O distance of 2.42 Å, but the local coordination is not highly symmetrical, since the six oxygen atoms (from five water molecules and one acetate group) around the sodium atom form a distorted octahedron with Na···O distances ranging from 2.34 Å to 2.50 Å, quite typically for sodium [10]. Copper sulfate hydrates are very regular. In addition, the counterion in this case is complementary to the Nafion HSO<sub>3</sub> terminal groups. In the trihydrate, the first shell of each copper atom contains three water molecules and three sulfate groups, whereas the first shell in the pentahydrate contains four water molecules and two sulfate groups in an elongated octahedral configuration. Thus, copper sulfate pentahydrate can be considered to have the highest local symmetry among the three considered hydrates CuSO<sub>4</sub>·5H<sub>2</sub>O, CuSO<sub>4</sub>·3H<sub>2</sub>O, and CH<sub>3</sub>COONa·3H<sub>2</sub>O. Finally, sucrose is a relatively large molecule containing penta- and hexamolecular rings with numerous hydroxyl groups, which can cause certain spatial effects.

Typical sizes of Nafion surface regions in aquatic environments were determined and the experimental data were interpreted by conducting a nanoscale modeling. The basic Nafion fragment chosen for the modeling included a region of the perfluorocarbon skeleton with two lateral perfluoroether chains ended by SO<sub>3</sub>H groups and two terminal methyl groups. The chemical formula of this fragment (Fig. 2) is

$$CF_{3}C(F)(O - CF_{2}CF(CF_{3})OCF_{2}CF_{2}SO_{3}H)(CF_{2})_{14}C(F)(O - CF_{2}CF(CF_{3})OCF_{2}CF_{2}SO_{3}H)CF_{3}.$$
(2)

First, possible conformations of the basic fragment were considered. The comparison of various structures (differing mainly by their conformations and orientations of lateral chains ended by  $SO_3H$  groups) showed that the more twisted the chains and the closer their terminal  $SO_3H$  groups to each other, the lower the total energy of the system. It is virtually



Fig. 2. Three main conformations of the Nafion model fragment (formula (2)). See comments in the text.

impossible to find the absolute energy minimum of the system and all possible conformers because of a large number of degrees of freedom due to internal rotations around all single bonds. However, this is not a problem in this case. In any real system, numerous interactions between neighboring functional groups inevitably generate numerous distorted configurations. Their averaging over finite time periods gives structures within the existence energy ranges that were determined by analysing a small number of fundamentally different conformers.

The highest energy is exhibited by configurations where perfluoroether chains with terminal SO<sub>3</sub>H groups are most distant from each other (since the real structure is extended and any chain has neighbors on both sides, the average angle between the direction of the hydrophobic skeleton and perfluoroether lateral chains should not exceed 90°) and are most strongly elongated (Fig. 2*a*). The initially twisted chains tend to get closer to each other to minimize the total dipole moment (Fig. 2*b*), and the resulting electronic energy decrease compared to the first case is ~15 kcal/mol. Finally, the system is most stable when terminal groups can form H-bonds. The energy of the fragment shown in Fig. 2*c* is 10 kcal/mol lower than that of the system in Fig. 2*b*, so this conformation is more favorable than the structure with elongated non-interacting terminal chains (with an energy difference of about 25 kcal/mol). If thermal energy contributions due to the main chain bending are additionally considered (the chain becomes more compact as the interaction between the chains with terminal SO<sub>3</sub>H groups increases), the energy differences between conformations decrease but are still significant: relative Gibbs free energies  $\Delta G_{vib}$ of the studied structures are equal to 0 (conformation *a*), -11 kcal/mol (*b*), and -19 kcal/mol (*c*) (Fig. 2).

The results of our study suggest that fibers in dry (anhydrous) Nafion are packaged in such a way that their perfluoroether chains containing terminal  $SO_3H$  groups are twisted and approach the main skeleton, while  $SO_3H$  groups are interconnected by H-bonds, thus enclosing such segments within the hydrophobic matrix. The number of chains (and  $SO_3H$  groups) within one H-bonded coil may be more than two, but not much more due to spatial constraints. Additional chains belong to adjacent fibers or to adjacent segments of the same fiber, so that the entire structure is highly intertwined.

The interaction with water molecules can be studied only for one half of the basic Nafion fragment (formula (2)), i.e. we can consider only one lateral chain attached to the perfluorinated skeleton and analyze changes associated with a gradual increase in the number of water molecules. If the number is small, the molecules are aggregated around the  $-SO_3H$  hydrophilic group (Fig. 3*a*). In the case of 16 molecules, which are sufficient to form the first hydration shell around the  $-SO_3H$  group, the energy of the system decreases by 49 kcal/mol compared to the separated Nafion fragment and a cluster of water molecules. At the same time, the number of stabilizing hydrogen bonds increases only by one: from 25 hydrogen bonds in the relaxed water cluster to 26 in the cluster connected with the hydrophilic group of the Nafion model fragment. Note that the reference structure in these calculations was a cluster of water molecules formed during the relaxation of the aqueous shell after removing the Nafion fragment from it. If we consider the lowest-energy water cluster consisting of the same number of molecules, the energy gain from the Nafion fragment hydration will be smaller, albeit insignificantly (only 5 kcal/mol), and the total number of hydrogen bonds stabilizing the cluster is larger only by 1. It means that the H-bonds as such are enhanced by the reorganization of water molecules around  $-SO_3H$  group, and the average hydration energy per one such group for low water contents can be estimated as 45 kcal/mol. As the number of water molecules increases almost doubly times while maintaining their initially quite uniform distribution around the Nafion model fragment (Fig. 3*b*), the number of molecules in the immediate environment of the  $-SO_3H$  group does not increase. Other water molecules are



Fig. 3. Optimized hydration shells around the Nafion model fragment for *n* water molecules: n = 16 (*a*); n = 28 (*b*); n = 50 (*c*).

oriented in such a way that only some of the peripheral molecules have free OH groups, while most protons participate in the formation of H-bonds. This expansion of the water shell corresponds to the formal total hydration energy of the model Nafion fragment equal to 24.5 kcal/mol compared with the compact cluster of water molecules chosen as the reference cluster. At the same time, the energy gain is much larger (~50.4 kcal/mol) for the cluster obtained by the relaxation of the hydration shell of the Nafion model fragment. This means that significant energy is required to distort the initial network of water H-bonds when water molecules are rearranged around fluorocarbon chains. If these energy loss is counteracted by effective hydration of  $-SO_3H$  groups, the process is thermodynamically possible though becomes less favorable with increasing length of hydrated fluorocarbon chains.

As the number of water molecules increases to fifty (Fig. 3*c*), they can form a monomolecular layer around the SO<sub>3</sub>H-containing Nafion model fragment, and the fluorocarbon skeleton is located inside kind of a "tunnel". In spite of the fact that a continuous closed network of 85 H-bonds was constructed, such hydration is energetically unfavorable, since the resulting strongly distorted H-bond network (obtained instead of a compact ensemble of water molecules) is not stabilized by interactions with the structure it encompasses, except for the coordination with the SO<sub>3</sub>H group. As a result, the energy difference between the hydrated Nafion model fragment and the "individual Nafion fragment + relaxed water cluster" combination is 48 kcal/mol. Formally, this difference can be explained by the smaller number of H-bonds stabilizing the 3D cavity (85 versus 94) in the 3D ensemble. Approximately the same energy is required for the system to reorganize the H-bonds. Note that it is virtually equal to the energy released due to the hydration of HSO<sub>3</sub> groups, meaning that the hydration shell expansion towards fluorocarbon chains is thermodynamically possible only due to the hydration of hydrophilic segments. The case when only SO<sub>3</sub>H groups are hydrated is most energetically favorable. This conclusion is also supported by the fact that the SO<sub>3</sub>H group dissociates to form a H<sub>3</sub>O<sup>+</sup> fragment even for the smallest number of water molecules (see formula (1)).

The obtained data show that hydration of lateral Nafion chains is energetically favorable when water molecules do not penetrate directly to the perfluorinated main chain. The energy required to uncoil and partially straighten the lateral chains can be effectively compensated by the hydration energy, provided that water molecules in this situation can be located at a larger distance from the perfluorocarbon skeleton. It is also energetically favorable. The calculation data indicate that hydration of Nafion plates should lead to the uncoiling of lateral chains with terminal SO<sub>3</sub>H groups, in agreement with the experimental results reported in [10]. On average, the chains should be oriented perpendicularly to the skeleton part of the polymer, and the distances between them in N117 should be  $\sim$ 15 Å. The conclusions suggest that the studied substances should exhibit different types of crystal formation.

Fig. 4, 6, 9 present the XRD data obtained for the crystals grown from salt solutions and natural deionized water with and without using Nafion plates in a Petri dish. In all the graphs, black and red curves correspond to the absence and presence of Nafion plates in the Petri dish. The abscissa and the ordinate show the doubled XRD beam diffraction angle and the number of photo counts (spectral line intensity), respectively. Note that no difference was observed between the XRD



**Fig. 4.** XRD patterns of NaCH<sub>3</sub>COO· $3H_2O$  crystals grown from a supersaturated solution of natural deionized water: crystal grown on a Nafion plate in a Petri dish (red curve) and without a Nafion plate (black curve). See the electronic version.

patterns of crystals grown from solutions based on natural deionized water and on DDW in the absence of Nafion. Also, no difference was observed between the XRD patterns of crystals formed on a polymer substrate and in the absence of a polymer substrate in DDW based solutions. Therefore, the results for DDW based solutions are not discussed here.

The XRD patterns of sodium acetate show peaks corresponding to the formation of its crystal trihydrate. The recorded XRD patterns are almost identical for the cases when a Nafion plate was and was not placed into the Petri dish (Fig. 4).

Note that the salt counterion of sodium acetate contains a hydrophilic carboxyl moiety and a hydrophobic methyl group. In the crystal lattice, these CH<sub>3</sub> groups are facing each other. The C···C distance is equal to 3.56 Å (Fig. 5*a*) and therefore significantly limits the possibilities for the arrangement of the species, and the acetate groups are oriented in the crystal lattice alternately in two orthogonal directions. The distances between carbon atoms of oppositely orientated acetate groups are 6.23 Å, 6.48 Å, and 9.16 Å, and no direction coincides with any lattice vector (Fig. 5*b*). This means that the direction of crystal growth cannot be determined by nearly parallel Nafion chains if they are extended most strongly and form a symmetrically repeating brush perpendicular to the Nafion surface. However, in the case of two equally orientated acetate groups is 5.24 Å and 5.93 Å. The  $3 \times$  magnification gives values 15.72 Å and 17.79 Å. The considered conformers of the model Nafion fragment with a similar configuration of lateral chains, the O···O distances between  $-SO_3^-$  groups vary from 15 Å to 16 Å (Fig. 5*c*). Since the Nafion chains are quite flexible due to numerous internal rotations in any perfluorinated chain and since their terminal groups can also change their position, especially under the influence of surrounding water molecules, the distance between terminal  $-SO_3^-$  groups can kind of "adapt" to the growing crystal. The lower part of the crystal (one-two monolayers) may be defective, but in general a completely ordered structure can be formed. Apparently, polymer chains can act in this situation as weakly coordinating elements.

The CuSO<sub>4</sub> solutions based on deionized natural water exhibited differences in their crystal formation. As already mentioned, CuSO<sub>4</sub> crystals grown from a supersaturated aqueous solution can be either CuSO<sub>4</sub>·5H<sub>2</sub>O pentahydrates (triclinic crystal system) or CuSO<sub>4</sub>·3H<sub>2</sub>O trihydrates (monoclinic crystal system). Fig. 6 shows that CuSO<sub>4</sub> trihydrate crystals grow on the polymer Nafion substrate, and pentahydrate is formed in the absence of Nafion plates. Note again that a crystalline CuSO<sub>4</sub>.



**Fig. 5.** Partial complementarity of the sodium acetate crystal structure and the Nafion fragment: fragment of the CH<sub>3</sub>COONa·3H<sub>2</sub>O crystal structure (*a*), its unit cell with indicated directions of lattice vectors (*b*), model Nafion fragment with the corresponding orientation of lateral chains (*c*).



**Fig. 6.** XRD patterns of  $CuSO_4 \cdot 5H_2O$  (black curve) and  $CuSO_4 \cdot 3H_2O$  crystals (red curve) grown from a supersaturated solution based on natural deionized water: crystal grown on a Nafion plate in a Petri dish (red curve) and crystal grown without a Nafion plate (black curve).

pentahydrate (triclinic crystal system) was formed during the growth from supersaturated DDW-based solutions in both cases (with and without Nafion plates in the Petri dish).

Fragments of both crystal structures are shown in Fig. 7. In the trihydrate, the first shell of any copper atom contains three water molecules and three sulfate groups, so the Cu···O distances are different (vary within 1.96-1.98 Å for the oxygen atoms of water and within 1.96-2.45 Å for the sulfate oxygen atoms), but the bond directions are quite regular, taking into account the crystal unit cell periodicity. In the pentahydrate, the first shell of copper contains four water molecules and two sulfate groups, and the sulfates are arranged along a local symmetry axis close to  $C_4$  (if only oxygen atoms without water molecules are considered). As a result, the local O-symmetry of copper atoms corresponds to an elongated octahedron: the Cu···O distances to the sulfates are equal to 2.41 Å and the Cu···O distances to the water oxygen atoms in opposite pairs are equal almost equal with a small difference between the pairs (1.97 Å and 1.94 Å). A higher local symmetry of the pentahydrate imposes significant restrictions on the possible boundaries of the crystallization region due to Nafion chains.

Fig. 8 illustrates almost exact incorporation of such fragments between the polymer chains. Two cases were considered: cluster  $(Cu)_3(SO_4)_3(H_2O)_9$  (Fig. 8*a*) and cluster  $(Cu)_4(SO_4)_3(H_2O)_{16}$  (Fig. 8*b*). Relative positions of copper ions, sulfo groups, and water molecules in both systems corresponds to the lattice of copper sulfate pentahydrate. Two systems of different sizes were studied to demonstrate that rotation of the hydrate relative to Nafion chains can compensate for the



Fig. 7. Fragments of copper sulfate crystal structures: trihydrate (a) and pentahydrate (b).



**Fig. 8.**  $(Cu)_3(SO_4)_3(H_2O)_9$  (*a*) and  $(Cu)_4(SO_4)_3(H_2O)_{16}$  clusters (*b*) illustrating wide possibilities for copper sulfate crystal unit cells to embed between Nafion chains.

changes in distances between  $-SO_3^-$  groups. The S···S distances in the considered clusters were 12.7 Å and 11.5 Å, respectively, meaning that polymer Nafion chains in this case can be possibly arranged in the manner most efficient for the crystal growth, so that the formation of copper sulfate trihydrate becomes significantly more probable in the presence of Nafion plates.

Finally, fundamental differences in the precipitate formation from a supersaturated solution were observed in the case of sucrose. It is known that sucrose in its pure form is composed of monoclinic crystals. When the molten sucrose hardens, an amorphous transparent mass, caramel, is formed. Our data indicate that caramel is formed also in the growth from a supersaturated sucrose solution on a polymer substrate (Fig. 9). Apparently, in this case, the presence of polymer chains in the region of precipitate nucleation caused some disorder of crystal unit cells and amorphization.

Note that pure sucrose crystals are stepped brushes of alternating methylene groups and hydroxyls (Fig. 10) containing no distinct regions of predominantly hydrophilic or hydrophobic nature. Also, due to the large size of sucrose molecules (though smaller than the distances between the uncoiled SO<sub>3</sub>H terminal groups of Nafion chains), no regular distribution of sucrose molecules between these chains is possible. The only possibility is when some two neighboring polymer chains are separated by a large distance (~16 Å between them terminal groups), thus allowing two sucrose molecules to embed between them, whereas the distances to their next left and right lateral neighbors are small enough to encompass only one sucrose molecule. This is possible only if the uncoiled Nafion chains are tilted at different angles with respect to the average polymer surface rather than are normal to it. However, such "freely oriented" chains are no longer a regular brush that can stabilize the orthorhombic or monoclinic lattice. Instead, this is a heavily crumpled brush that can only distort the molecular order of the growing crystal. Thus, taking into account the size of sucrose molecules, their crystal packing cannot be realized on the regular orientation of Nafion chains; therefore, the sucrose precipitate is formed only in the disordered mode, as is manifested in its amorphization.

The relative rate of crystal growth on a polymer substrate and without it in a Petri dish was preliminary estimated using a refractometry experiment. The object of study was copper sulfate, for which the structuring role of Nafion plates was definitely revealed. Fig. 11 shows plots of the refractive index n(t) for an aqueous CuSO<sub>4</sub> solution based on natural deionized water in the presence of a polymer substrate in a Petri dish and in its absence during the precipitate formation. The obtained experimental dependences n(t) are well approximated by the function



 $Y = 1.4[1 - 0.14 \cdot \exp(-t/\tau)].$ (3)

**Fig. 9.** XRD patterns of sucrose precipitates formed from a supersaturated solution based on natural deionized water: crystal grown on a Nafion plate in a Petri dish (red curve), crystal grown without a Nafion plate (black curve).



Fig. 10. Fragment of the sucrose crystal lattice and the structure of its individual molecule.



**Fig. 11.** Time dependence of refractive index on the surface of a supersaturated aqueous  $CuSO_4$  solution when growing a crystal on the Nafion surface (red curve) and without using a Nafion plate (black curve).

According to theoretical and experimental estimations [15], the refractive index of pentahydrate CuSO<sub>4</sub> is n = 1.514, and the maximum *n* value in supersaturated aqueous CuSO<sub>4</sub> solutions [15] is n = 1.35 (see Table 1 in [15]), i.e. very close to our value n(t) = 1.4 at  $t \rightarrow \infty$  (see formula (3)). The characteristic time of refractive index exponential growth is  $\tau = 40$  h in the absence of Nafion plates in a Petri dish and  $\tau = 109$  h in the presence of Nafion plates, i.e. the refractive index on the solution surface increases faster without Nafion plates. This means that the surface layer exhaustion due to the involvement of ions in the precipitate growth is slower in the presence of Nafion plates in the Petri dish. Assuming that water evaporates from the solution surface at the same rate under identical physical conditions, the copper sulfate precipitate should be formed faster in the presence of Nafion.

#### **CONCLUSIONS**

The Nafion substrate can provide selective formation of the same type of crystals (in the case of copper sulfate) or promote amorphization of the precipitate structure (in the case of sucrose). The influence of the polymer template on the precipitate formation is due to the partial uncoiling of polymer chains. This is confirmed by fundamentally different results obtained in crystal growth experiments with supersaturated solutions based on deionized natural water (the effect of polymer chain uncoiling into the liquid volume was observed) and from DDW based solutions (no such effect observed). At the nanoscale, the effect of uncoiling of lateral fluorinated ether Nafion chains with –SO<sub>3</sub>H terminal groups in an aqueous environment was confirmed by quantum chemical calculations of model Nafion fragments in the free state and those surrounded by various numbers of water molecules.

In our further works, the crystal growth will be studied in the conditions when the Nafion substrate is irradiated by counterpropagating ultrasonic waves. The ultrasound is absorbed by the layer of uncoiled polymer chains, thus generating acoustic currents (see our recent article [16]), which in turn can distort the orientation of polymer chains that were initially arranged perpendicular to the main fluorinated Teflon skeleton. This effect can be realized in the structure of crystals grown on a polymer substrate, in particular, in the degree and nature of their defects. Also, the dependence of refractive index n(t) will be studied more comprehensively, until reaching the actual asymptotics, to characterize the kinetics of precipitate formation in more detail.

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## **CONFLICT OF INTERESTS**

The authors of this work declare that they have no conflicts of interest.

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