RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

Structure characterization of perfluorosulfonic short side chain polymer membranes

Yu. V. Kulvelis,[a] S. S. Ivanchev (RSC member 518622),[b] V. T. Lebedev,[a] O. N. Primachenko,[b] V. S. Likhomanov[b] and Gy. Török[c]

Small-angle neutron scattering has been used to study the structure of dry and wet perfluorinated short side chain membranes first synthesized by new aqueous emulsion method. These membranes are new perspective materials for hydrogen fuel cells and have advantages over long side chain Nafion-type membranes. Experiments enabled to recognize the subtle features of membranes structure being responsible for the proton conductivity. The parameters of pores interconnected and forming the channels for diffusion of water molecules and protons were determined as dependent on chemical composition of membranes. It was discovered the influence of molecular weight and equivalent weight, varied during synthesis, on the polymer structure.

Introduction

The development of hydrogen power has initiated the recent studies of perfluorinated membranes with –SO_3H groups for hydrogen fuel cells, based on copolymers with different side chain length. While earlier the attention was focused on almost only Nafion® membranes, which were positioned as having best structure and properties, the recent studies have a tendency to use perfluorinated membranes with short side chains with sulfonic acid groups in fuel cells[1-6]. Basically these are researches of Solvay Solexis Company, which introduced short side chain (SSC) membranes under the trade mark Aquivion®. The shortened side chain with sulfonic acid group in Aquivion® membrane provides higher glass transition temperature of the copolymer, larger water uptake and higher electrical conductivity and protons mobility in the low humidity conditions. Aquivion® membranes permit to rise the operating temperature of the fuel cell to near critical 130°C, when equilibrium between H_2 and CO in the catalyst layer allows to reduce or eliminate poisoning of catalyst by CO. High temperature tests have shown that long side chain (LSC) Nafion® membranes lose their features after 20 hours of work, while Aquivion® membranes remain in a good performance[1]. Such temperature of operating fuel cells allows to reduce negative influence of carbon oxide in the fuel (hydrogen) on fuel cell efficiency and to use less pure hydrogen.

SSC membranes for the current work were synthesized at St. Petersburg Department of Boreskov Institute of Catalysis SB RAS (Russia) by new aqueous emulsion copolymerization method[7], having advantages over traditional solution method of synthesis LSC Nafion-type membranes[8,9].

To improve the functional properties of complicated porous membranes it was necessary to evaluate the protons diffusion paths and to find their structure features by the small-angle neutron scattering studies which were carried out in the present work.

Experiment

We have implemented an original method, based on aqueous emulsion technology, for synthesis of SSC membranes[7]. Monomer 2-fluorosulphonyl perfluoroethylvinyl ether (PFEVE) was synthesized by a patented method[10]. Fig. 1 demonstrates the synthesis route. Copolymer of PFEVE with tetrafluoroethylene (TFE) was prepared using emulsion copolymerization, leading to obtain copolymer of constant composition to high degrees of PFEVE conversion[7]. Copolymerization was carried out with the use of perfluorinated emulsifier and non-reactive perfluorinated modifying additive, providing optimal equivalent weight and molecular weight of the resulting copolymers. Equivalent weight (EW) is the major structural parameter for perfluorinated membranes such as Nafion® and characterizes the concentration of sulfonic acid groups in the polymer volume. The physical meaning of EW corresponds to molecular weight of polymer chain fragment per one sulfonic acid group. Copolymers with low EW synthesized without modifying additive seem not suitable for manufacturing of membranes with optimal characteristics, but may be used to prepare catalyst layers for membrane-electrode units.

[a.] Neutron Researches Department, B.P. Konstantinov Petersburg Nuclear Physics Institute, National Research Centre "Kurchatov Institute", Gatchina, Russia. E-mail: kulvelis@pnpi.spb.ru
[b.] St. Petersburg Department of Boreskov Institute of Catalysis, Siberian branch of Russian Academy of Sciences, St. Petersburg, Russia
[c.] Research Institute for Solid State Physics and Optics, Wigner Research Centre for Physics Hungarian Academy of Sciences, Budapest, Hungary
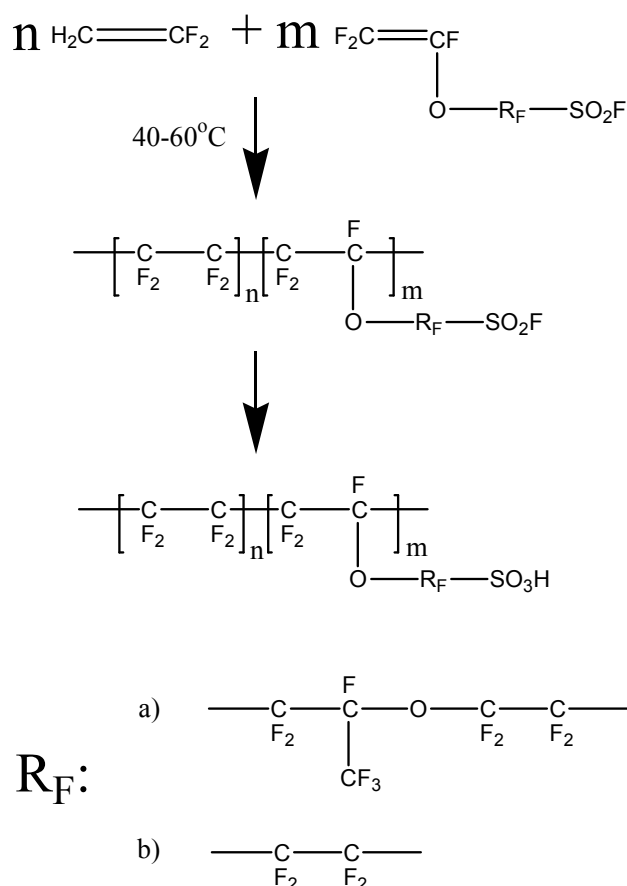
Fig. 1. Synthesis route for LSC (a) and SSC (b) perfluorinated polymers. n and m varies membrane composition (equivalent weight). SSC membranes in the present work have n = 4.7-7.4, m = 1.

During selection the copolymerization conditions we were guided by the results obtained in terms of developing an aqueous emulsion copolymerization of TFE with perfluoro (3,6-dioxa-4-methyl-7-octene) sulfonylfluoride (FS-141 monomer)[8]. Specific features of this method relate to the fact that a stable emulsion may be formed in the aqueous emulsion system containing a surfactant (emulsifier), depending on the method of acting on the system (mixer, ultrasound, etc.). Thus ultrasonic treatment may lead to formation of dispersed microdroplets of perfluoro (3,6-dioxa-4-methyl-7-octene) sulfonylfluoride. TFE is injected to this emulsion from outside under pressure. When TFE is injected, a certain ratio of concentrations of TFE and perfluorinated monomer is formed, depending on temperature, TFE pressure and solubility of TFE in the monomer. These conditions make possible to create certain ratios of molar concentrations of TFE and monomer, compensating their difference in reactivity during copolymerization. The resulting microdroplets of perfluorinated monomer containing the correct ratio TFE/monomer lead to form the copolymer with constant composition, corresponding to concentration ratio of initial monomers. The resulting copolymer, due to its limited solubility in the monomer and insolubility in water, is released from

microdroplets forming copolymer latex particles. The ratio of components in microdroplet is kept constant during copolymerization. TFE is consumed during the process but permanently restore to equilibrium level, while perfluorinated monomer, being in excess, is consumed gradually. Advantages of aqueous emulsion copolymerization technique compared with traditional solution method are providing constant composition of copolymer and therefore time constant equivalent weight to high degrees of conversion. Thus it is possible to regulate equivalent weight by addition of modifier that changes the viscosity of emulsion microdroplets. The aqueous emulsion nature of polymerization system also enables full safety compared with Freon used in a solution method[8].

Fig. 2 shows the transformation of the initial emulsion droplets of functionalized monomer. The particle sizes were determined by dynamic light scattering (Malvern Zetasizer Nano-ZS with He-Ne laser). In case of FS-141 monomer the initial emulsion droplets are ~ 2.5 times larger and less stable, than for PFEVE monomer at the same concentration of emulsifier and standard procedures for obtaining emulsion of monomers. SSC latexes do not show residual monomer droplets around 1000 nm at high PFEVE monomer conversion degree, but SSC latex particle size is significantly larger than observed for latex particles of TFE-FS-141 copolymer. It is worth to mention that two copolymerizable systems differ on the velocities of transformation into latex.

Four samples with different characteristics were studied (table 1). It was varied the number of –SO_3H groups per weight unit (resulting in different equivalent weight and other characteristics) and amount of modifying additive used during polymerization (two samples were synthesized with additive, and another two samples – without additive). The preliminary studies have shown that using additive changes (reduces) the molecular weight of copolymers, evaluated in terms of melt flow index (MFI) measured at a capillary viscometer with constant pressure (load 2.16 kg, diameter of the die 2.095 mm, and at temperature close to 270°C). MFI values for the studied samples were in the range 0.1-1.0 g/10 min for copolymers in SO_2F-form. Larger MFI corresponds to lower molecular weight (1920±170 kDa for SSC-1 sample with MFI = 0.8 g/10 min), determined by static light scattering (Malvern Zetasizer Nano-ZS with He-Ne laser)[11] for synthesized copolymer in SO_3H-form in solution.
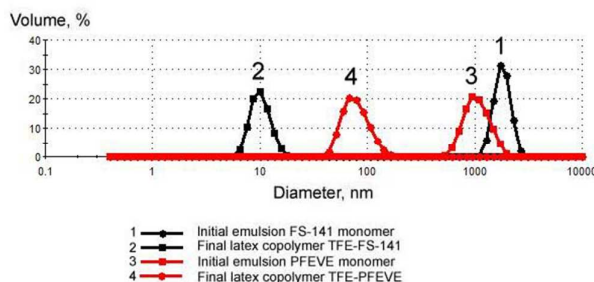
Fig. 2. Size distribution by volume of initial emulsion particles of monomers FS-141 and PFEVE and resulting copolymer latexes of these monomers with TFE obtained by dynamic light scattering.

Table 1. Physicomechanical and electrochemical characteristics of samples.

Sample	Equivalent weight, g/mol SO_3H	Water uptake, wt %	Proton conductivity, S/cm (20°C)	Ion-exchange capacity (IOC), mg-equiv/g	Modifying additive
SSC-1	752±12	72.3	0.158±0.009	1.33±0.02	-
SSC-2	804±23	50.1	0.148±0.005	1.25±0.03	+
SSC-3	807±7	50.8	0.146±0.001	1.24±0.01	-
SSC-4	1021±21	35.7	0.073±0.003	0.98±0.02	+

Water uptake was defined after heating of membrane in $-SO_3H$ form at 100°C in distilled water for 2 h. Wet membrane with weight W_w was dried in vacuum at 70°C to a constant weight W_d. Water uptake C_w was calculated as follows: $C_w = (W_w - W_d) / W_w \cdot 100\%$.

Proton conductivity in the equilibrium state of saturation with water at 20°C was measured by impedance spectroscopy on Z-3000X impedance meter (Elins, Russia) using cell with stainless steel electrodes at four-electrode scheme in the frequency range 10-150000 Hz.

The ion-exchange capacity (IOC) for the determination of sulfonic acid groups content was measured by titration method[12]. Equivalent weight of the copolymer, was calculated in terms of IOC (EW = 1 / IOC).

The proton conductivity of the resulting membranes in the range of 0.16-0.05 S/cm is linearly dependent on copolymer EW within range of EW 750-1200 g/mol SO_3H. This allows to select the optimum compositions of membranes for their use in fuel cells.

The studies of relation between the structured (associated with ionic groups) and unstructured (free) water contained in membranes, measured by differential scanning calorimetry, allowed to establish the relationship of the proton conductivity, EW and the amounts of structured and unstructured membrane water[13].

Experiments on small-angle neutron scattering (SANS) were carried out at the facilities "Yellow submarine" (Budapest Neutron Center, BNC, Hungary) in the range of momentum transfer $q = (4\pi/\lambda)\sin(\theta/2) = 0.2$-7 nm^{-1} where θ is the scattering angle, neutron wavelength $\lambda = 0.3$ nm, $\Delta\lambda/\lambda \sim 0.1$) and "Membrana" (Petersburg Nuclear Physics Institute, PNPI, Russia) at $q = 0.04$-0.8 nm^{-1} ($\lambda = 0.3$ nm, $\Delta\lambda/\lambda \sim 0.3$). The method involves measuring and analyzing scattering curves – the relations of neutron scattering cross section $d\Sigma/d\Omega$ vs. momentum transfer q. All scattering curves were reduced to absolute values (including normalizing them to the samples thicknesses, scattering intensity for the H_2O-standard), that makes it possible to compare the results obtained for different samples and at different facilities, complementary to each other by q range.

All samples were studied by SANS at 20°C in two conditions – dry and swollen in H_2O (**dry** and **H** states). Saturation in H_2O was produced by keeping samples submerged at least 30 minutes (enough for full saturation). All samples were measured wrapped in aluminum foil (transparent for neutrons), preventing wet samples from drying during measurement. Empty foil was used in background measurements.
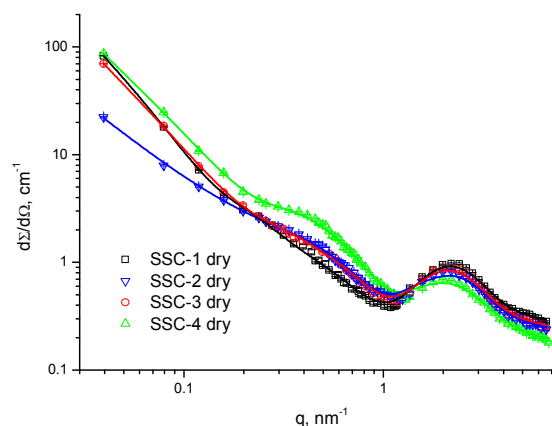

Fig. 3. Scattering cross sections of dry samples vs. momentum transfer: experimental data (points), and the fitting curves for the model (1).

Results and discussion

The SANS curves for dry and wet samples are shown in fig. 3 and 4. They are well approximated by the model scattering function (1), being the asymptotic approach for the description of scattering on the system of fine but long cylindrical objects (straight, curved or branched). It is similar to the formula already applied earlier for fitting long side chain Nafion-type perfluorinated membranes[9]:

$$\frac{d\Sigma}{d\Omega} = \frac{I_0 R_g^3}{(qR_g)^n} e^{-(qR_g)^2/2}(1 + \sum_{i=1}^{4} C_i \frac{\sin qR_i}{qR_i}) + B \qquad (1).$$

The squared form factor of scattering objects in this model $\frac{1}{(qR_g)^n} e^{-(qR_g)^2/2}$ is a modified form factor of long cylindrical objects $\frac{1}{q} e^{-(qR_g)^2/2}$ with radius R and length L ($1/L << q \leq 1/R$) (see [14]).
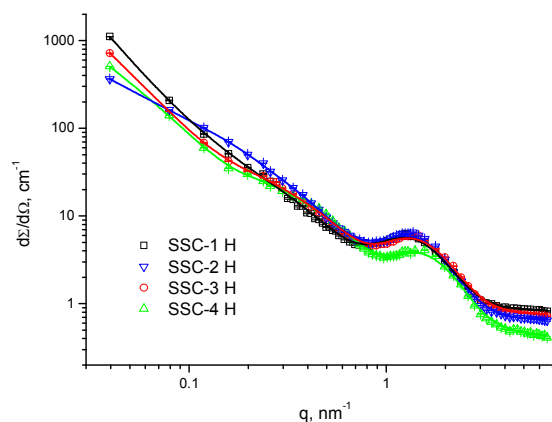

Fig. 4. Scattering cross sections of samples saturated with H_2O vs. momentum transfer: experimental data (points), and the fitting curves for the model (1).

The parameter R_g is a gyration radius of cylinders with diameter = $2R = 2\sqrt{2}\,R_g$ (see [15]). We have introduced the exponent n into the formula, characterizing the geometry of cylindrical channels. The value of $n = 1$ corresponds to straight cylinders, $1 < n < 2$ means bent channels, $n = 2$ should mean statistically bent tube, similar to Gaussian polymer chain, and at $2 < n < 3$ it is an object of a kind of branched (entangled) chain. So the applied squared form factor describes scattering objects in polymer matrix as long cylindrical channels with length exceeding the value of the minimum reciprocal momentum transfer, $L \gg 1/q_{min} \sim 25$ nm. The parameter I_0 characterizes the intensity of forward scattering, the scattering ability of the structural elements, and depends on the squared nuclear contrast for neutrons (density difference) of our objects (channels) and the surrounding polymer, and on the volume fraction of channels. All curves profiles have well-defined ionomer peaks, corresponding to highly-organized structure, strong regularity in channels arrangement, which also observed for Nafion and described in numerous papers [16-19].

Therefore the structure factor $1 + \sum_{i=1}^{4} C_i \dfrac{\sin qR_i}{qR_i}$ is introduced which

describes pair spatial correlations of channels at several characteristic distances R_i. The coefficient C_i is the average number of channels correlating with the selected channel at the distance R_i (negative values of C_i mean inability of channels to settle at a

certain distance – a sort of excluded volume). The constant B is a level of incoherent background scattering. Fitting parameters are listed in table 2.

Earlier Nafion-115 and two its Russian analogues (MF-4SK and PFM-E, synthesized by different methods, were studied using SANS method and obtaining the similar number of parameters [9], therefore special interest arises to compare the structure of LSC and SSC membranes.

The data fitting for **dry samples** demonstrates that all SSC membranes contain channels with $R_g = 0.23-0.26$ nm, (diameter 0.7 nm), that is 1.5-2 times less than that in LSC membranes [9]. In addition, the channels are bent ($n = 1.4 – 1.9$). The exponent n rises for samples in the row SSC-2, -4, -3, -1 from 1.4 (curved channels, like in MF-4SK sample, analogue of Nafion, produced by traditional solution method) to 1.9 (low dense structure, close to polymer coil, like in PFM-E sample, analogue of Nafion, produced by new aqueous-emulsion method). The original commercial Nafion-115 has $n = 1$, indicating straight channels in all observable range of distances, up to 20-30 nm, that is consistent very well with the structure described in other papers [17-19]. The error in defining R_g is quite large, 40-90%, indicating difficulties in pointing the precise diameter values in dry samples. Probably, the surface of channels in dry state is so diffuse and the channels are so bent that there are no sharp borders between empty channels and polymer matrix. Similar situation was observed in the case of PFM-E, when we needed to fix R_g for fitting.

Correlations between dry channels are observed at the distance R_2 = 2.8-3.0 nm, corresponding to ionomer peaks on scattering curves, that is less than was for Nafion-115, MF-4SK and PFM-E (~ 4 nm). So, the neighbour channels in SSC samples are less in diameter and located closer, than in LSC membranes. The coefficient $C_2 = 0.6-0.9$ indicates the average number of correlating objects (channels) at a distance R_2 from any channel. The C_2 is less than 1, so the "bundle" of channels consists in average from $(C_2 + 1) < 2$ channels. So, in average channels partially have one neighboring channel and for some part of their length they are aside of any other channels. This partial "isolation" of channels arises with the reduction of C_2 value, in the row SSC-1, -3, -2, -4.

There is also ordering at larger distances $R_4 = 18-30$ nm. The most ordered sample at such distances is SSC-4, resulting in clearly seen matrix knee on scattering curve in the range of $q = 0.2-0.8$ nm^{-1}. Samples SSC-1 and -3 also have correlations at R_4, but less ordered than SSC-4 (value of C_4 is lower and the matrix knee is less expressed). SSC-2 does not have such peculiarities, it is more homogeneous at large distances.

Parameters for **the samples saturated with H$_2$O** show that the channel diameter rises about twice upon saturation, $R_g = 0.4-0.7$ nm, (diameter 1.2-1.9 nm), that is also less than in wet LSC samples (2.4 nm). Samples SSC-2 and SSC-4 (obtained with the presence of modifying additive) show reduction of parameter n upon swelling in H$_2$O meaning straightening of channels. Similar fact was observed for LSC PFM-E sample, and it is an expected result, as membranes are elongating as soon as they absorb water. It should be mentioned that SSC-2 H has $n = 1.25$, close to 1, meaning almost straight channels. But SSC-1 and SSC-3 samples (synthesized without additive, meaning higher molecular weight according to preliminary data) demonstrate an opposite behaviour – n rises from

Table 2. Parameters of fitting SANS-curves by the model (1).

	SSC-1 dry	SSC-2 dry	SSC-3 dry	SSC-4 dry
I_0, cm^{-1}nm^{-3}	16±12	15±8	14±9	12±9
n	**1.917**±0.036	**1.463**±0.023	**1.886**±0.034	**1.744**±0.019
R_g, nm	**0.23**±0.21	**0.26**±0.11	**0.24**±0.19	**0.24**±0.17
C_1	-1.682±0.031	-1.49±0.07	-1.550±0.031	-1.247±0.031
R_1, nm	1.57±0.09	1.62±0.06	1.56±0.11	1.51±0.13
C_2	0.89±0.04	0.77±0.05	0.79±0.06	0.62±0.06
R_2, nm	**2.88**±0.13	**2.82**±0.11	**2.97**±0.11	**3.00**±0.10
C_3	-0.168±0.024	-0.172±0.021	-0.203±0.033	-0.29±0.06
R_3, nm	5.03±0.19	7.15±0.10	5.28±0.16	6.49±0.08
C_4	0.021±0.007	-	0.018±0.006	0.074±0.016
R_4, nm	**30.1**±0.6	**-**	**20.6**±0.7	**18.11**±0.32
B, cm^{-1}	0.26±0.06	0.22±0.04	0.24±0.05	0.18±0.04

|	SSC-1 H	SSC-2 H	SSC-3 H	SSC-4 H
I_0, cm^{-1}nm^{-3}	19.4±0.6	23.13±0.15	25.32±0.32	21.47±0.15
n	**2.731**±0.023	**1.249**±0.006	**2.158**±0.025	**1.685**±0.014
R_g, nm	**0.445**±0.020	**0.689**±0.009	**0.519**±0.014	**0.543**±0.010
C_1	-1.478±0.028	-1.209±0.018	-1.412±0.025	-1.349±0.031
R_1, nm	2.214±0.038	2.429±0.033	2.195±0.034	2.205±0.031
C_2	0.630±0.028	0.815±0.025	0.617±0.026	0.754±0.033
R_2, nm	**4.32**±0.06	**4.574**±0.031	**4.19**±0.05	**3.83**±0.05
C_3	-0.142±0.009	-0.079±0.005	-0.172±0.007	-0.257±0.008
R_3, nm	7.32±0.09	26.5±0.4	7.75±0.07	7.60±0.06
C_4	-	-	0.0144±0.0019	0.094±0.007
R_4, nm	**-**	**-**	**28.2**±0.7	**26.09**±0.24
B, cm^{-1}	0.840±0.005	0.675±0.003	0.764±0.004	0.442±0.003
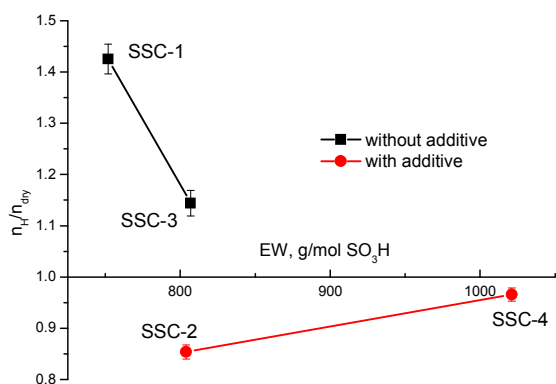
Fig. 5. Changing of relative channel curvature n_H/n_{dry} upon saturation by water for membranes synthesized without modifying additive (higher molecular weight) and with additive (lower molecular weight) vs. equivalent weight.

1.9 to 2.1 (for SSC-3) and to 2.7 (for SSC-1), indicating more complicated geometry, more bent and branched channels. This fact means that SSC membranes obtained without additive (SSC-1 and SSC-3) possess more complicated structure. They have some hidden (squished) channels in dry state, invisible for neutrons, but these channels become observable in saturated state. Larger effect observed for SSC-3 correlates with its lower equivalent weight and larger water uptake. This is also valid for comparing SSC samples obtained with additive (SSC-2 and SSC-4). Lower equivalent weight (more SO_3-groups per weight unit) and larger water uptake lead to more significant changes of parameter n upon swelling in water, as demonstrated in fig. 5. The difference in using additive in synthesis is that for samples synthesized with additive (lower molecular weight) the parameter n reduces showing the structure simplification, and in the case of synthesis without additive (higher molecular weight) the parameter n rises and the structure becomes more complicated. It is clear if compared fitting parameters for samples SSC-2 and SSC-3 as the samples with the same equivalent weight (and the same water uptake) and different molecular weights. Hence it is evident that molecular weight of the polymer affects the structure – hidden channels in dry state, observed for high molecular weight membranes SSC-1 and SSC-3 do not exist in low molecular weight samples SSC-2 and SSC-4.

The radius R_2 of the correlation of a channel with the neighbouring channels increases by swelling in water to 3.8 – 4.6 nm. The lowest value 3.8 nm is for SSC-4 – sample with the lowest water uptake. The radius R_2 for other samples varies in the range 4.2-4.6 nm that is a little less than for LSC membranes (4.7 – 5.4 nm). Ordering at larger distances remains for SSC-4 (R_4 = 26 nm) and to a less degree for SSC-3 (R_4 = 28 nm). Fig. 6 shows schematic structures of studied SSC samples.

A special interest is to compare scattering curve profiles of SSC membranes, studied now, and LSC membranes, investigated recently (fig. 7 and 8). They show that the cross-sections of
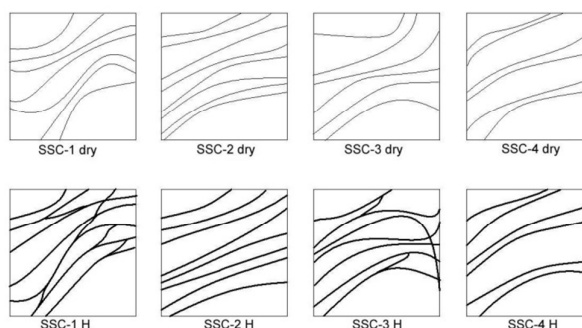

Fig. 6. Schemes of the channels arrangement according to SANS experiment in dry and wet SSC membranes.

different samples are generally close to each other. The main difference is in the position of ionomer peak (SSC samples perform larger q for peak as the correlation distance R_2 for the neighbouring channels is lower) and in the range of q = 0.2 – 0.8 nm^{-1}, where the matrix knee is well performed for Nafion-115, indicating Nafion as the most ordered sample.

Conclusions

SANS-experiment on new original short side chain perfluorinated membranes has discovered the parameters of their internal structure, dependent on polymer characteristics. The general structure elements are similar to those observed for LSC samples – cylindrical channels with diameter ~ 1 nm, regularly arranged and forming ordered structure – short-range order for neighbouring channels combined into bundles with gyration radius R_g ~ 3-5 nm and long-range order – correlations between different bundles at the distances > 20 nm.
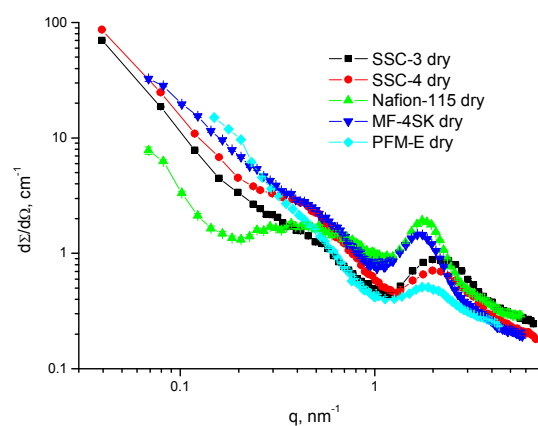

Fig. 7. SANS on dry samples: SSC (SSC-3 and SSC-4) and LSC (Nafion-115, MF-4SK, PFM-E).
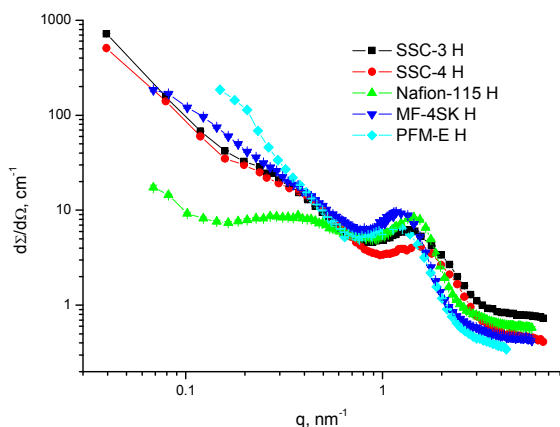
Fig. 8. SANS on wet samples: SSC (SSC-3 and SSC-4) and LSC (Nafion-115, MF-4SK, PFM-E).

The difference of SSC and LSC membranes appears in thinner channels for SSC samples with diameter 20-50% less than for LSC. Neighbour channels are also closer to each other in SSC membranes.

The geometry of channels varies significantly from slightly curved to branched one. In particular, it becomes more simple (channels become more straight) upon saturating with water for samples with lower molecular weight (obtained with the presence of additive), while samples with higher molecular weight (synthesized without additive) perform complication of the structure (channels become more bent and branched) due to "hidden" channels not observable in dry state.

Long-range order is better revealed in SSC-4 sample and to a less degree in SSC-3, i.e. in the samples with larger equivalent weight and less water uptake. So, the larger number of SO_3-groups (lower equivalent weight) makes the structure more uniform at large distances.

Since SSC membranes have thinner and closer to each other channels, and the scattering abilities for SSC and LSC membranes are near the same (the volume fractions of channels in polymer matrix are similar), it follows by the fact that SSC membranes have larger channel density than LSC membranes.

Another interesting experimental result should be discussed, mentioned also in [9], but did not followed by explanation and relevance for practice. Like present work, [9] also performs data to determine the sizes (radii) of channels in perfluorinated membranes – LSC membranes such as commercial Nafion® and its analogues, synthesized using traditional solution method (MF-4SK sample) and aqueous emulsion method (PFM-E sample). The structure of membranes was investigated in dry and wet form. Comparison of the sizes of channels in different samples indicates that channels for dry copolymers obtained by solution method, have diameters of 1.3-1.4 nm (radii of gyration 4.6-5Å), while that for the emulsion method is ~ 0.85 nm (radius of gyration 3Å). When moistening sizes of channels increase for solution polymerization samples in 1.5-2 times, and for emulsion copolymerization membrane – in 2.5 times.

This fact indicates a significant increase of channel dynamicity in the sample obtained by emulsion copolymerization.

Herewith the proton conductivity is significantly higher (10-15 %) for the sample prepared by aqueous emulsion polymerization compared to membranes prepared in solution[9].

For proper comparison of the properties of LSC and SSC membranes, obtained by aqueous emulsion method, it is necessary to select samples with optimal EW: ~ 1100 g/mol SO_3H for LSC (PFM-E sample [9]) and ~ 800 g/mol SO_3H for SSC (samples SSC-2 and SSC-3). The value of the proton conductivity for SSC samples is 1.7 times greater than that for PFM-E (0.147 S/cm vs. 0.085 S/cm), while channels in wet form for SSC membranes are 1.6 times thinner (gyration radius 0.45 nm vs. 0.72 nm).

Thus it follows, that larger channel distribution density, lower thickness and larger dynamicity of channels when moistening are characterized by larger values of proton conductivity as it was shown experimentally twice: 1) comparing LSC Nafion-type membranes synthesized by different methods[9] and 2) comparing properties of LSC membrane, obtained by aqueous emulsion method[9] with SSC membranes in the current article. Increased water retention properties and the ability to operate at higher temperatures make SSC membranes prepared by aqueous emulsion method the most promising for practical purposes.

The above data appears to be related to the different conditions of formation of physical state (conformation, molecular packing) of hydrophobic and hydrophilic parts of membranes. Method of synthesis affects on the internal packaging of membrane and thus can influence on the proton conductivity and membrane performance. These problems require further research of nanostructural features of polymer membrane materials.

Acknowledgements

Notes and references

1   A. Stassi, I. Gatto, E. Passalacqula, V. Antonucci, A.C. Arico, L. Merlo, C. Oldani and E. Pagano, *Journal of Power Sources*, 2011, **196**, 8925.
2   K.D. Kreuer, M. Schuster, B. Obliers, O. Diat, U. Traub, A. Fuchs, U. Klock, S.J. Paddison and J. Maier, *Journal of Power Sources*, 2008, **178**, 499.
3   D. Wu, S.J. Paddison and J.A. Elliott, *Macromolecules*, 2009, **42**, 3358.
4   J. Liu, R. Suraweera, D.J. Keffer, S. Cui and S.J. Paddison, *The Journal of Physical Chemistry C*, 2010, **114**, 11279.
5   M. Marrony, D. Beretta, S. Ginochcio, Y. Nedellec, S. Subianto and D.J. Jones, *Fuel Cells*, 2013, **13**, 1146.
6   Y. Jeon, H.-K. Hwang, J. Park, H. Hwang and Y.-G. Shul, *Journal of Hydrogen Energy*, 2014, **39**, 11690.

RSC Advances Accepted Manuscript

7   S.S. Ivanchev, O.N. Primachenko, S.Ja. Khajkin, V.S. Likhomanov, V.G. Barabanov and A.S. Odinokov, RU Patent 2545182, 27.03.2015.
8   S.S. Ivanchev, V.S. Likhomanov, O.N. Primachenko, S.Ya. Khaikin, V.G. Barabanov, V.V. Kornilov, A.S. Odinokov, Yu.V. Kulvelis and V.T. Lebedev, *Petroleum Chemistry*, 2012, **52**, 453.
9   Yu.V. Kulvelis, V.T. Lebedev, V.A. Trunov, O.N. Primachenko, S.Ya. Khaikin, D. Torok and S.S. Ivanchev, *Petroleum Chemistry*, 2012, **52**, 565.
10 G.A. Emel'janov, V.M. Rodin, V.I. Purtseladze, S.A. Kulachenkov, G.G. Chernjavskij, G.V. Grigorjan, S.S. Ivanchev and D.P. Blinov, RU Patent 2546109, 10.04.2015.
11 W.-H. Liu, T.-Y. Yu, T.L. Yu, H.-L. Lin, *e-Polymers*, 2007, **109**, 1.
12 T.J. Peckham, J. Schmeisser, M. Rodgers and S. Holdcroft, *Journal of Materials Chemistry*, 2007, **17**, 3255.
13 V.S. Likhomanov, O.N. Primachenko and S.S. Ivanchev, *Russian Journal of Applied Chemistry*, 2014, **87**, 1217.
14 F. Nallet, *Journal de Physique IV Proceedings*, 1999, **9**, pr1-95.
15 D.I. Svergun and L.A. Feigin, Structure Analysis by Small-Angle X-Ray and Neutron Scattering, (Nauka, Moscow, 1986; Plenum, New York, 1987), 81.
16 W.Y. Hsu and T.J. Gierke, *Journal of Membrane Science*, 1983, **13**, 307.
17 L. Rubatat, G. Gebel and O. Diat, *Macromolecules*, 2004, **37**, 7772.
18 G. Gebel and O. Diat, *Fuel Cells*, 2005, **5**, 261.
19 K. Schmidt-Rohr and Q. Chen, *Nature Materials*, 2008, **7**, 75.

Supplementary information

Table 3 performs some additional parameters used to process the data comparing the samples.

The coefficients C_i (i = 1 … 4) in the structure factor of the model function (1), as it was mentioned above, are the values of correlations of scattering objects (channels) at several distances. 3-4 distances are needed to fit the scattering curves. The coefficient C_2 has positive values and indicates the average number of channels correlating with the selected channel at the distance R_2. C_1 (negative values) shows inability of individual channels to settle at a distance R_1. Neighbour channels are separated by the polymer matrix, they cannot be situated too close to each other. C_3, also negative, demonstrates existing of negative correlations of channels at larger distance R_3 due to longer-range order in membranes. In some cases 3 terms in structure factor were enough, but generally we needed to introduce the 4th term with positive coefficient C_4 showing correlations of channel positions at the distance R_4. In the

Table 3. Parameters of samples measured by SANS.

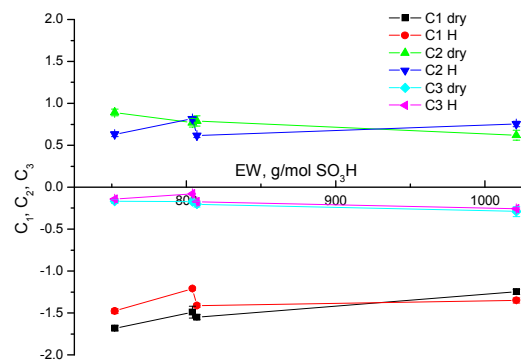| Sample	Number of layers		Total thickness, mm		Neutron transmission	
	BNC	PNPI	BNC	PNPI	BNC	PNPI
SSC-1 dry	8	14	1.56	2.56	0.803	0.717
SSC-2 dry	12	24	1.26	3.19	0.855	0.649
SSC-3 dry	8	7	1.66	1.64	0.806	0.818
SSC-4 dry	10	20	1.28	2.95	0.875	0.745
SSC-1 H	8	14	2.06	3.18	0.497	0.354
SSC-2 H	12	24	1.48	3.85	0.634	0.342
SSC-3 H	8	7	1.82	1.99	0.552	0.566
SSC-4 H	10	20	1.44	3.25	0.727	0.508

Fig. 9. Correlation coefficients C_1, C_2, C_3 for dry and wet samples vs. equivalent weight. C_1 – repulsive correlation, C_2 – attractive correlation, C_3 – weak/no correlation.

case this 4th term was used in fitting, it means correlations of individual channels at larger distances, or correlations of bundles (pairs) of channel.

The number of fitting parameters is too large, making the mathematical solution not evident. But we used some restrictive rules for the parameters to get the unique solution of physical task: $1 \leq n < 3$; C_1, $C_3 < 0$; C_2, $C_4 > 0$; 1 nm $< R_1 < R_2 < R_3 < R_4 < 100$ nm. These numbers of parameters and conditions allowed us to achieve the perfect fitting of the complicated curve profiles.

The values of C_1 … C_3 vs. the equivalent weight of samples are shown in fig. 9.

SANS measurements of SSC samples saturated in D_2O have also been carried out to perform the contrast variation. All samples demonstrated rather low contrast to be compared with dry and H_2O-saturated samples, as it was expected for perfluorinated membranes – scattering cross-section is much lower and ionomer peak is poorly performed, not quite enough for correct fitting. As an example, experimental data points for sample SSC-1 in three conditions are shown in fig. 10.
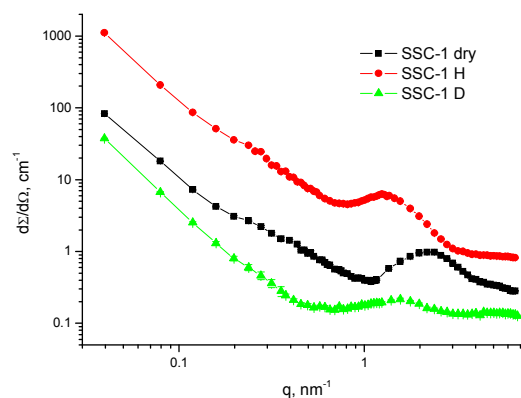

Fig. 10. Scattering cross sections of dry, H_2O-saturated (H) and D_2O-saturated (D) sample SSC-1 vs. momentum transfer.