Equilibrium Aggregation in Perfluorinated Ionomer Solutions

Peter A. Cirkel,* Tatsuhiro Okada, and Shinichi Kinugasa

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan

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I. Introduction. Perfluorinated ionomer membranes have unique properties with respect to stability, solubility and ionic conductivity, which make them suitable for a variety of applications.[1] An important step in the modification of these membranes is the so-called recast process, in which a film is formed after evaporating the solvent from a ionomer solution. For a fundamental understanding of this process, detailed knowledge of the solution properties is a prerequisite. One of the most widely used perfluorated ionomers is called Nafion. This is a commercial name used by DuPont.

Nafion is readily available as membranes, which are insoluble in almost all solvents at room temperature. A standard procedure was developed to dissolve Nafion in ethanol/water mixtures, at relatively high temperatures using an autoclave.[2,3] To get Nafion dissolved in other solvents most of the solvent was evaporated from this solution, after which it was substituted by the solvent of choice.[4] Later on it became custom to evaporate all the solvent to produce a powder, which can be dissolved in a large number of solvents.[5]

From the start it became apparent that Nafion solutions contain large particles.[3] Neutron- and X-ray scattering experiments showed that these particles are (locally) rod like,[6,7] with a cross-sectional radius of about 2 nm, independent of the solvent. This was however contradicted by studies using NMR[8] and ESR[9] spectroscopy, which showed no evidence of aggregation in ethanol and *N*-methylformamide, as opposed to other solvents. A study by viscometry,[4,10] showed a pronounced increase in the reduced viscosity at low concentrations. This behavior was attributed to an increase in the polymer extension due to the lack of screening by other chains at low concentrations. It was noted however that the observed effect occurred at concentrations 10 times lower and its intensity was 10 times higher compared to other ionomer solutions.[10] Moreover for Nafion the effect is unlikely to be observed in view of its relative stiffness.[6,7] In retrospect it seems more likely that this behavior is due to thermodynamically driven side-side aggregation, in which the aggregates break up at low concentration, as is observed in other ionomer solutions.[11] This kind of aggregation involves an equilibrium between aggregates and loose polymers. It could explain contradicting reports about aggregation if one of the techniques used is much more sensitive to the occurrence of aggregates than the other. Observations supporting this interpretation are delayed effects on the viscosity upon dilution[3] and sonication.[4]

Here this hypothesis is tested by dynamic light-scattering. Dynamic light scattering is not only very sensitive in detecting aggregates, it is also one of the few techniques that are able to resolve a possible coexistence between large aggregates and loose polymers, dissolved molecularly.

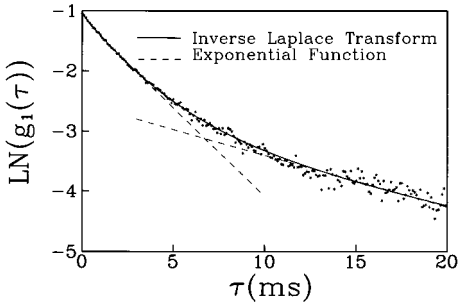

Figure 1. Logarithmic plot of the field time correlation function of the sample taken directly from the autoclave. The drawn line shows the fit to the data. The dotted lines are single-exponential functions. The observation that this correlation function can almost be described by 2 such functions is reflected by two peaks in Figure 2.

II. Experimental Section. 1. Sample Preparation. Nafion 117 membranes from DuPont were cleaned in boiling nitric acid and subsequently dissolved in a 50/50 mixture of ethanol/water, using an autoclave at 230 °C for 4 h. This solution was concentrated in a rotary vacuum evaporator to obtain the other solutions and Nafion powder. The Nafion powder was obtained from this concentrated solution as described in ref 5. All solvents used were of analytical grade and filtered through a fluoropore filter, with pore size 0.5 μm, before use.

2. Experimental Setup and Data Analysis. Dynamic light scattering experiments were done at 25 ± 0.1 °C, using a standard setup consisting of a 10 mW helium neon laser (λ = 632.8 nm) and a goniometer−correlator combination from Otsuka Instruments, type DLS 7000. The intensity time correlation functions $g_2(\tau)$, were converted to the field time correlation functions, $g_1(\tau)$, via the Siegert relation[12] and were fitted using an inverse Laplace procedure (Figure 1). Comparing the fit results for different scattering angles (40, 90, and 150°) showed that the peak positions in the correlation time distributions thus obtained were proportional to the inverse scattering vector squared and thus could be used to calculate the corresponding collective diffusion coefficients. Because of the high dilution these were assumed to be equal to the self-diffusion coefficient of particles with a hydrodynamic radius, R_h, which was calculated using the Stokes−Einstein equation. This leads to the black bars in Figures 2 and 3, showing the size distribution multiplied by the structure factor of the corresponding particles. For a spherical shape of the particles the molecular mass scales with the third power of the hydrodynamic radius and the radius of gyration equals $\sqrt{3/5}$ times the hydrodynamic radius. This has been used to calculate the number distribution functions displayed as gray bars.[12,13] It is assumed in this calculation that the particles are sufficiently small so that the angular dependence of the scattered light intensity is in the Guinier regime.[12]

III. Results and Discussion. 1. Nafion Membranes Dissolved in Autoclave. Figure 2 shows the distribution function of a 10 mg/mL Nafion solution in an ethanol/water mixture (50/50). This sample shows two peaks in its distribution function, one peak around

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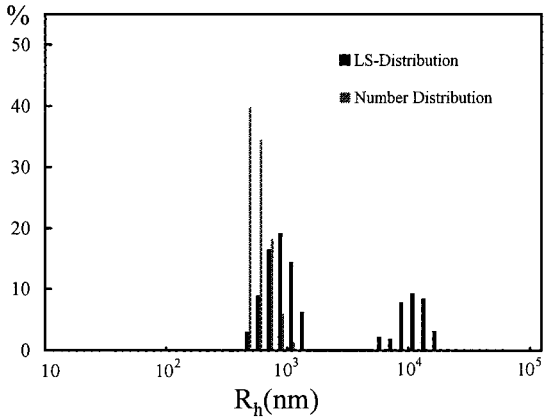

Figure 2. Black bars: Distribution function from an inverse Laplace transformation of the field time correlation function in Figure 1. Gray bars: This distribution function converted to a number distribution. Sample taken directly from the autoclave (Nafion concentration 10 mg/mL). Detection angle = 40°.

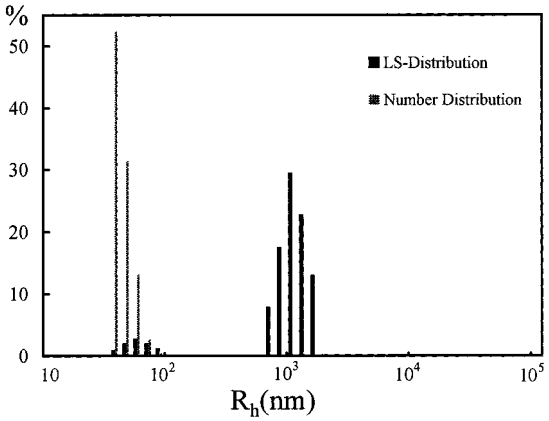

Figure 3. As in Figure 2, with the sample diluted by ethanol, filtered, and concentrated again (Nafion concentration 10 mg/mL). Detection angle = 90°.

10^3 nm and another one around 10^4 nm. This sample itself could not be flown through a filter with pore size 0.5 μm, but a sample 10 times diluted with ethanol could. A filtered sample thus obtained only showed a small upturn in its correlation function at short times, corresponding to an R_h between 50 and 100 nm. Static light-scattering on this sample showed an average particle radius of gyration, R_g, of 160 nm. These radii are a little large to be accounted for by loose polymers, for which the molecular weight is between 10^5-10^6 g/mol[1], corresponding to a hydrodynamic radius of typically several tens of nm. However this type of ionomers is rather stiff,[6,7] and the value of R_h is an average in which larger particles have a high weight (see differences in LS and number distribution in the figures). It is thus conceivable that these signals correspond to loose polymers. The difference between R_h and R_g is an indication for an anisotropical shape of these particles, which can be related to the stiffness of the polymer. It seems obvious that no big aggregates were present after, as opposed to before, dilution and filtration. The filtered sample was concentrated by slow evaporation. To the sample thus obtained ethanol was added in such a way that the Nafion concentration became similar to the sample directly taken from the autoclave. The distribution function from a dynamic light scattering experiment on this sample is shown in Figure 3. This distribution function shows the same peak at 10^3 nm as the sample, taken directly from the autoclave. The peak corresponding to very large particles of about 10^4 nm has disappeared and a peak corresponding to small sized particles ($R_h \approx 50$ nm), which seems to be associated with loose Nafion polymers is observed. This appearance of loose polymers is most likely related to the difference in solvent between an ethanol/water (50/50) mixture and pure ethanol. Diluting this sample 2 times with ethanol had no major effect on the peak positions.

Table 1. Mean Hydrodynamic Radii Corresponding to Peaks in the Light-Scattering Distribution Functions (Nafion Concentration 10 mg/mL). Samples Directly Taken from the Autoclave Were Dissolved in Ethanol/Water, 50/50 (v/v)

solvent	$R_{h,1}$ (nm)	$R_{h,2}$ (nm)	$R_{h,3}$ (nm)
ethanol	$>10^4$	880	56
2-propanol	$>10^4$	586	49
N-methylformamide	$>10^4$	759	
water	[a]	395	
autoclave (direct)	10152	799	
autoclave (dilution/filtration/concentration)		1082	51

[a] In water the powder did not dissolve completely even after 1 week. The residue was then filtered off.

2. Nafion Powder Dissolved in Different Solvents (See Table 1). The findings in ethanol are almost the same as the ones displayed in Figure 3, that is, from a sample obtained after dilution with ethanol of a concentrated sample from the autoclave. The main peak is observed at about 10^3 nm and a smaller peak at 50 nm. The relative peak heights are similar as well. Again a peak appears at very large sizes, which can be removed by a dilution filtration concentration sequence. The similarity of these results with Figure 3 indicates that it is justified to compare older experimental results in the literature obtained after solvent substitution with more recent results obtained with Nafion powder. The result in 2-propanol is qualitatively the same. The height of the peak at about 50 nm is however significantly smaller and the size corresponding to the main peak is smaller than in ethanol (Table 1). In *N*-methylformamide and water only one peak was observed.

3. Aggregation in Nafion Solutions. There seem to be two types of aggregates in the Nafion solutions studied. One very large type ($R_h \geq 10^4$ nm), which can be filtered out and seems to be connected with Nafion, which is not properly dissolved possibly due to cross-linking.[5] Although the peak corresponding to these aggregates in the LS-distribution is rather high, the actual abundance is negligible. The other type of aggregates with a hydrodynamic radius of about 10^3 nm reappears after concentrating a filtered solution. This type of aggregation must be thermodynamically driven. It is interesting that dilution of the samples does not significantly change the size of the aggregates. This can be explained if the size of the aggregates is constraint by packing requirements, as is the case in for instance spherical micelles. It has been suggested that this is indeed the case and that the aggregates are pointing their charged sulfonate groups outward[6] (like the surfactant heads in micelles). In this case dilution would only affect the ratio of aggregates and loose polymers. For the data presented here it could also be possible that the supposedly rodlike aggregates change only their radius, keeping their length constant. This would hardly

influence the hydrodynamic radius. Neutron and X-ray scattering data however suggest that this is not the case.[6,7] The hydrodynamic radius is slightly dependent on the solvent. For rod like aggregates this could be due to a change in length or flexibility.

If the results described here are combined with the data in the literature, it seems that there is no qualitative difference in the way Nafion dissolves in different solvents. The study by NMR[8] indicates a combined signal of loose polymers and aggregates in formamide solutions. Other solvents are only used to swell membranes. The signals for these swollen membranes are however very similar to the signals in solution and show a combined signal for formamide and methanol. For water a combined signal is observed at high temperatures. In all cases the thermodynamic conditions such as temperature, solvent content, and the kind of solvent determine the relative amount of both signals. In ethanol and *N*-methylformamide aggregates are undetectable by ESR[9] and NMR[8] spectroscopy. The results in this article show that this can be explained by a small number of aggregates which is negligible in the number distribution, but still detectable by scattering techniques. It seems that in water the opposite is true. At room temperature, only aggregates can be observed, irrespective of the technique used. At higher temperatures the NMR signal from the membranes suggests that parts of the polymer become more mobile due to a better dissolution.[8] It is well conceivable that in solution state this results in molecularly dissolved Nafion. It would be interesting to study this further and see whether indeed all data can be explained by thermodynamic equilibrium between loose polymers and aggregates.

References and Notes

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(13) We performed similar analyses assuming a rodlike or Gaussian chain type of shape. This did change the shape of the individual peaks in Figures 2 and 3 rather drastically. It did however not change the fact that, in the number distributions, the peaks at high hydrodynamic radius were negligible.

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