Supplementary Information

Microstructure of unmodified membranes by SAXS

2D SAXS scattering images (Figure 1) of Nafion show isotropic scattering for all temperatures. The outer halo ring in SAXS images is related to scattering from ionic clusters and it is observed that the intensity of the ionomer peak decreases in unmodified Nafion with increasing temperature. The inner ring corresponds to scattering from crystalline regions of the membrane and shows an increase in intensity with increasing temperature. The corresponding 1-D SAXS spectra for unmodified Nafion [SI file Figure 1 (bottom)] are shown from 30°C up to 190°C. Both the broad matrix peak and ionomer peak can clearly be distinguished in the 1-D spectrum of unmodified Nafion at 30°C, which indicates that phase separation is present in this sample. The peak at q ~ 0.23 $Å^{-1}$ is the ionomer peak attributed to a scattering maximum from the interparticle interference characteristic of the existence of ionic aggregates that are spatially distributed throughout the sample. Using the Bragg equation $d=2\pi/q$ we can calculate the average spacing between the scattering objects. For unmodified Nafion at 30°C the average spacing between ionic clusters is 27.3 Å and for fully hydrated Nafion it is reported to be 50 Å. The position of the ionomer peak is also strongly dependent on the volume fraction of water within the membrane. In the present case Nafion was in a dry state during SAXS analysis which can account for the difference in intercluster spacing. The position and intensity of the ionomer peak is also influenced by temperature. With increasing temperature there is a decrease in the scattering intensity of the ionomer peak. From this data it is apparent that the morphology of Nafion is highly dependent on temperature. At elevated temperatures, the elastic forces exerted upon the polymer chains emanating from the ionic aggregates tend to increase with temperature, to the point that exceeds the electrostatic attractive forces between ionic groups within the cluster. This results in the destabilization of ionic aggregates where the static electrostatic network (i.e. a network of physically cross linked chains with ion pair junction sites securely connected to stable ionic aggregates) transitions to a dynamic network through the process of ion hopping (i.e. the thermally activated process of ion pairs “hopping” from one aggregate to another in order to relieve local stress. With increasing thermal energy, the mobility of ion pairs in the cluster increases and the distribution of ion pairs becomes more homogeneous and thus the ionomer peak decreases in intensity. There seems to be no significant changes in the broad matrix peak with an increase in temperature and suggests that the crystalline phases of nafion membranes are stable at least up until 190°C. The general trend for unmodified Nafion is that the order of ionic clusters decreases with increasing temperature and results in a decrease in proton conductivity of the membrane as shown by conductivity results.

The 2D SAXS images of unmodified Hyflon (Figure 2) show anisotropic scattering for all temperatures (from 30°C up to 190°C) indicating that these membranes show strong structural orientation. There is no visible cluster peak in 2D images of Hyflon which suggests that the nature of clustering of ionic groups is not the same as it is in Nafion, which is due to the short side chain of Hyflon. Since unmodified Hyflon shows strong structural orientation 2D SAXS images when integrated in both the horizontal and vertical directions, with the top SAXS images corresponding to the vertical direction and the bottom SAXS image is related to the horizontal direction for all cases. The 1-D scattering spectrum for Hyflon shows a broad peak in the range of q = 0.03-0.07 $Å^{-1}$, which is related to the crystallinity present in Hyflon. There are very limited reports on the SAXS of the short side chain perfluorinated ionomer and no high temperature SAXS studies on Hyflon. Kreuer et al. have recently investigated the short side chain (SSC) perfluorinated ionomers with different ion exchange capacities[1]. They also observed a broad peak in the range q=0.03-0.07 $Å^{-1}$, attributed to the crystallinity. At low hydration values an ionomer peak was not observed for the SSC ionomer, however, an ionomer peak was clearly seen at higher degrees of hydration. At higher levels of hydration they observed the ionomer peak for the SSC membrane to be broader than that of Nafion and its position less dependent on the water volume fraction. From SAXS data it is evident that phase separation is more developed in Nafion membranes and also implies that the average width of hydrophilic domains is smaller for SSC ionomers. The Hyflon membrane has a lower equivalent weight than Nafion (890 g/SO_3H for Hyflon and 1100 g/SO_3H for Nafion) due to its short side chain and corresponds to a higher ion exchange capacity. No ionomer peak is observed in Hyflon's scattering profile which is attributed to the short side chain of the Hyflon membrane, and indicates that phase separation is not visible in Hyflon membranes compared with Nafion membranes in the experimental q range. Hyflon membrane forms smaller size clusters in comparison to Nafion membranes which can form larger size clusters due to its longer side chain. The longer side chain of Nafion is flexible and allows more sulfonic acid groups to aggregate together to form larger ionic domains in comparison to Hyflon. The short side chain of Hyflon is less flexible and mobile than its Nafion counterpart which restricts the amount of sulfonic acid groups that can aggregate together to form ionic domains and hence results in smaller size clusters being formed. In Hyflon membranes we observe an increase in intensity of the matrix peak with increasing temperature which indicates strong ordering of crystallites which was not so prominent for Nafion. These results indicate that elevated temperatures increase the density and long range ordering in Hyflon membranes. This is due to Hyflon having a short side than Nafion leading to higher crystallinity. The short side chain length of Hyflon results in a decrease in size and density of clusters which makes it more difficult to achieve percolation. Unmodified Hyflon membranes show a decrease in conductivity with temperature up to 100°C. After 100°C Hyflon became resistive as the percolation threshold could no longer be achieved due to an increased distance between ionic domains.

Author	Model	Description	Type	Comment
Gierke et al.[2]	Cluster Network	Hydrated nafion	Spherical ionic clusters with an inverted micelle structure (3-5nm in diameter) interconnected by narrow water channels (1nm in width).	Too simplistic because of the assumption of periodic distribution of spherical clusters.
Fujimura et al.[3, 4]	Core-Shell	Dry	Clusters surrounded by a fluorocarbon phase, embedded in an intermediate ionic phase consisting of both fluorocarbon polymer and non clustered ionic sites.	Poor fit to experimental data, dimensional and contrast values extracted from best fits were determined to be unrealistic.
Dreyfus et al.[5]	Local Order	Dry	spherically shaped ionic clusters with a tetrahedral like packing arrangement but with short range order	Better fit to SAXS and SANS profiles of hydrated Nafion than those of the core-shell model
Gebel/Lambard.[6]	Demonstrate the feasibility of local order		As above	As above
Litt et al.[7]	Lamellar	Hydrated	lamellar organization of planar clusters, Hydrophilic ionic micelles separated by thin, lamellar PTFE-like crystallites	A convenient and simple explanation for the swelling behavior of Nafion however, ignores the low angle maximum attributed to the crystalline, interlamellar long range spacing.
Haubold et al.[8]	Sandwich-like model		Core region sandwiched between shells made of hydrophilic groups and polymer side chains. The lateral dimensions are between 1.5 and 4.5 nm with a total thickness of 6 nm.	Gives information on the basic structural unit while ignoring the mesoscale structure
Gebel et al.[9]	polymer rod-like aggregates, these elongated polymeric aggregates are surrounded with ionic groups	Dry hydrated	Cylindrical polymer aggregates have a diameter ~4 nm and length > 100 nm randomly distributed at the mesoscale	
Schmidt-Rohr.[10]	parallel cylindrical water channels	Hydrated	parallel cylindrical water channels having diameters between 1.8 and 3.5 nm	This model incorporates 10 vol % of Nafion crystallites which form physical crosslinks and are elongated and parallel to water channels, can explain fast diffusion of water and protons through Nafion and its persistence at low temperatures.

Table 1. Summary of models used to describe structure of Nafion.

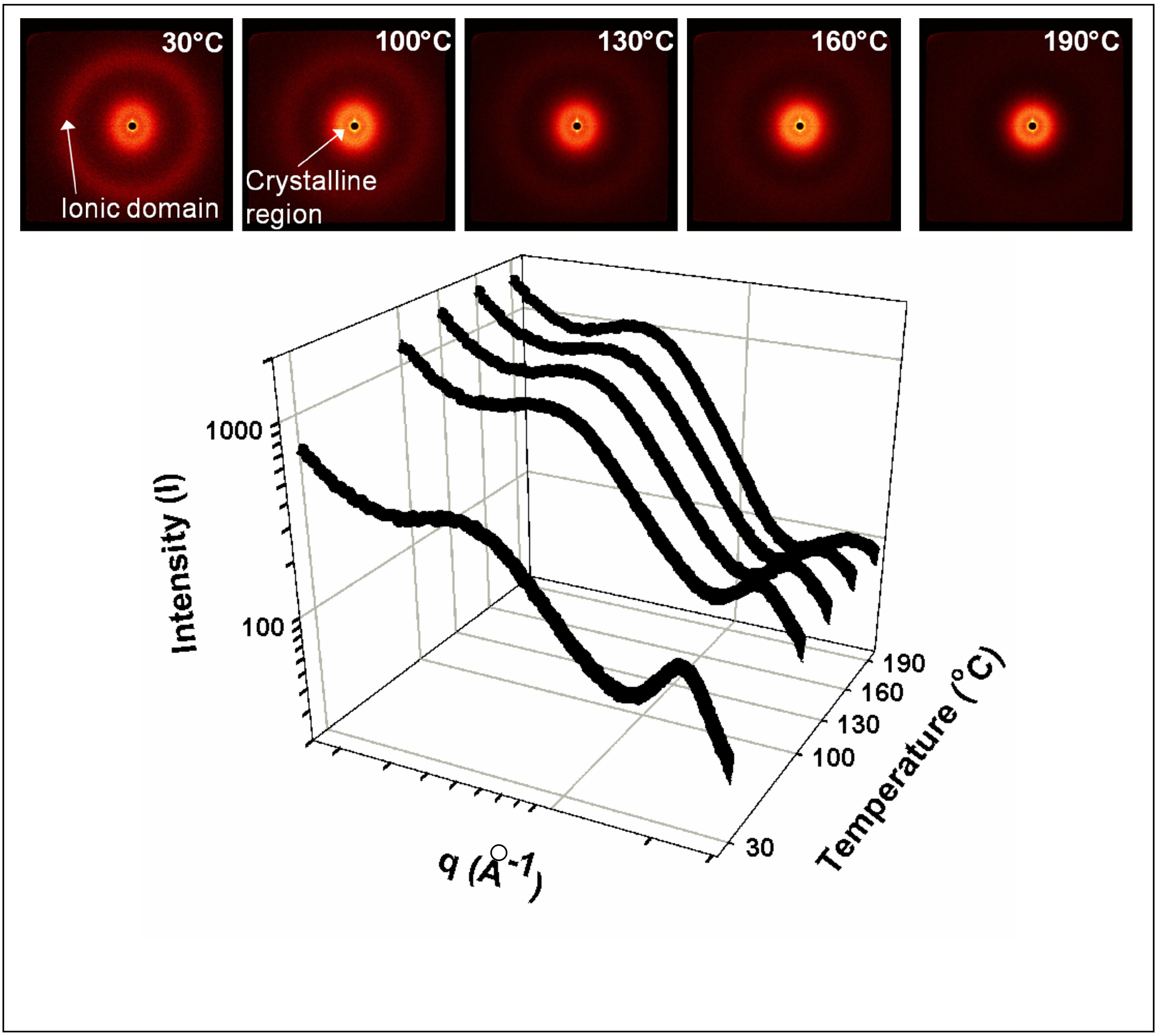

Figure 1. 2D images and 1D SAXS spectra for unmodified Nafion.

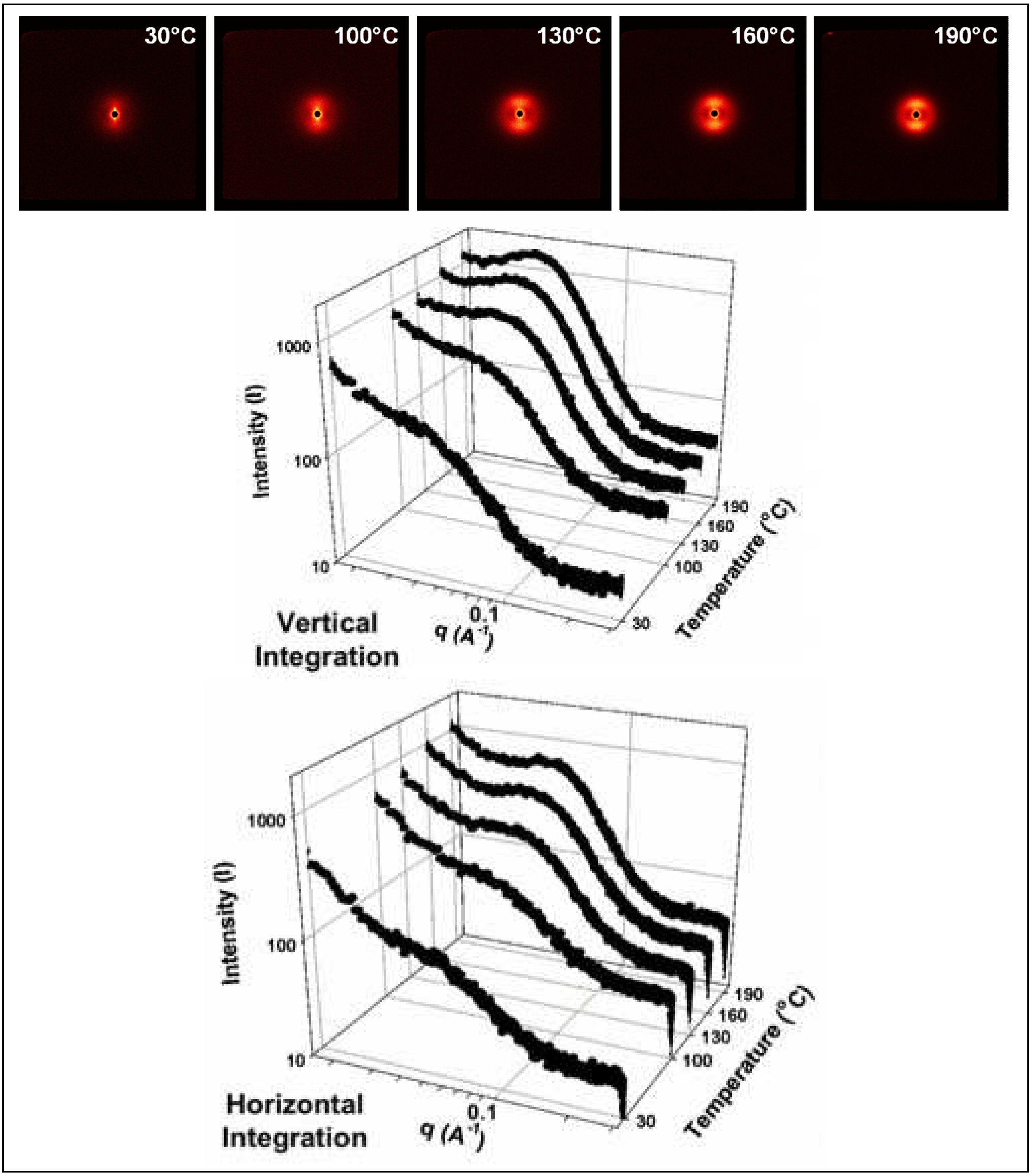

Figure 2. 2D images and 1D SAXS spectra of Hyflon Blank

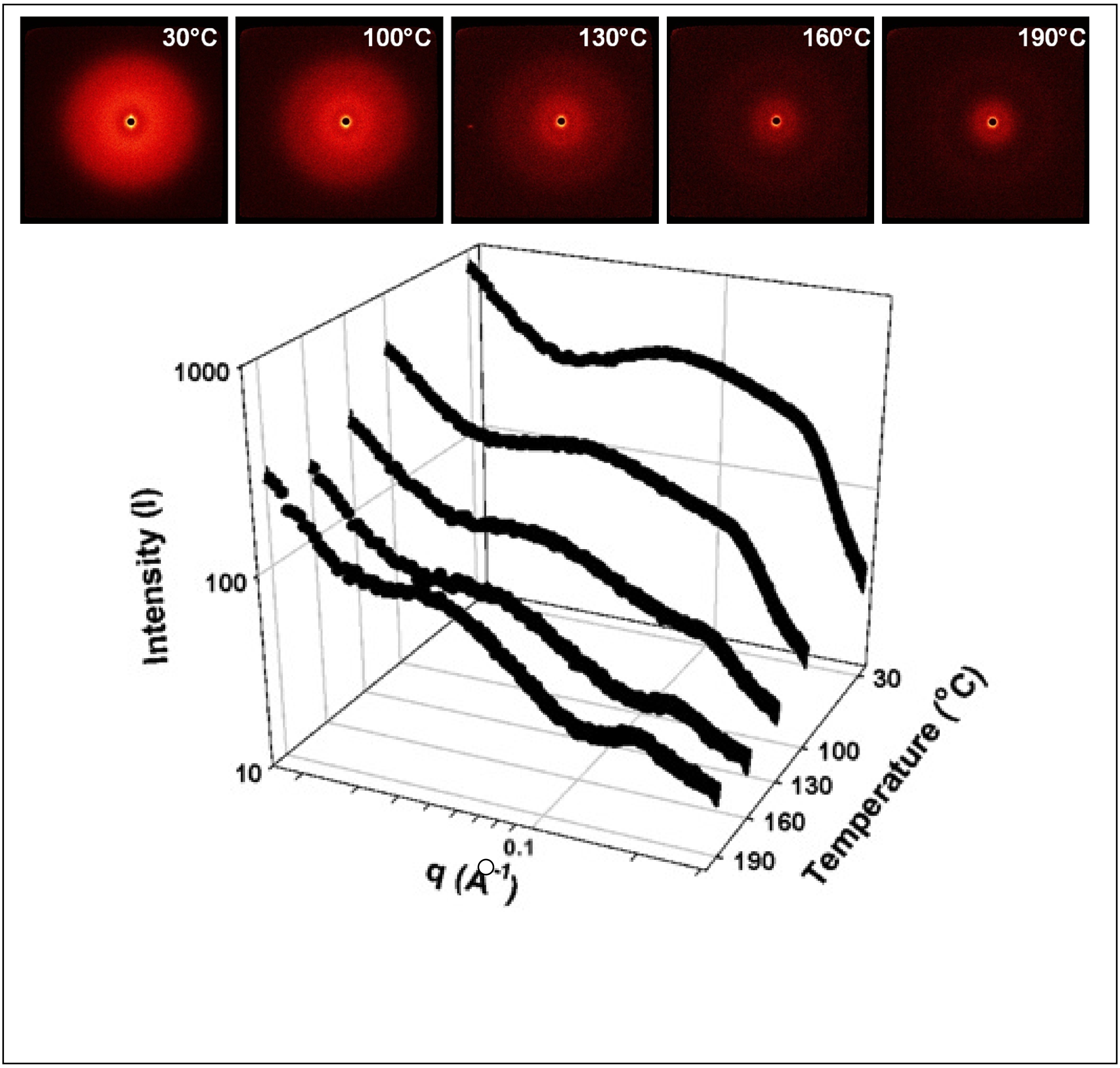

Figure 3. 2D images and 1D SAXS spectra of Nafion SLM

References

1. Kreuer, K. D.; Schuster, M.; Obliers, B.; Diat, O.; Traub, U.; Fuchs, A.; Klock, U.; Paddison, S. J.; Maier, J., *J. Power Sources* **2008,** 178, (2), 499-509.
2. Gierke, T. D.; Munn, G. E.; Wilson, F. C., *J. Polym. Sci., Polym. Phys. Ed.* **1981,** 19, (11), 1687-704.
3. Fujimura, M.; Hashimoto, T.; Kawai, H., *Macromolecules* **1981,** 14, (5), 1309-15.
4. Fujimura, M.; Hashimoto, T.; Kawai, H., *Macromolecules* **1982,** 15, (1), 136-44.
5. Dreyfus, B.; Gebel, G.; Aldebert, P.; Pineri, M.; Escoubes, M.; Thomas, M., *J. Phys. (Paris)* **1990,** 51, (12), 1341-54.
6. Gebel, G.; Lambard, J., *Macromolecules* **1997,** 30, (25), 7914-7920.
7. Litt, M. H., *Polym. Prepr.* **1997,** 38, (1), 80-81.
8. Haubold, H. G.; Vad, T.; Jungbluth, H.; Hiller, P., *Electrochim. Acta* **2001,** 46, (10-11), 1559-1563.
9. Gebel, G., *Polymer* **2000,** 41, (15), 5829-5838.
10. Schmidt-Rohr, K.; Chen, Q., *Nat. Mater.* **2008,** 7, (1), 75-83.