

Sulfur Clustering in Copolymer Polyelectrolyte.

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The mechanism of proton conductivity for many polyelectrolyte membranes is based on the presence of sulfuric acid groups attached to polymer chains that assemble together and form highly polar clusters. The sulfur groups create a network of nanosized hydrophilic domains that is responsible for high proton and water permeability, while the rest of the polymer chain forms a hydrophobic phase. The hydrophobic phase provides the required mechanical properties and stability of the material. Phase separation in hydrated ionomers has been demonstrated by numerous scattering experiments, but clustering of sulfur in dry membranes is more difficult to assess. Recently we were able to directly image the network of the hydrophilic sulfur clusters in dry polyelectrolyte membrane by electron microscopy [1].

In this work we continue studying clustering in polyelectrolytes in order to determine the 3-dimensional distribution of clusters and the process of their formation. We use CTEM and HAADF STEM imaging and electron tomography in both CTEM and STEM modes in order to investigate the clustering mechanism. The sample we use is a sulfonated polystyrene-polymethylbutylene (PSS-PMB) diblock copolymer synthesized by anionic polymerization [2]. The volume fraction and sulfonation level of the polystyrene are 25 percent and 40 percent respectively. We prepare the samples by solvent casting from tetrahydrofuran (THF) solution on lacey carbon film.

Our experiments show that sulfur clustering in the cast film starts as a result of the water or water vapor treatment. For example, samples made by solvent casting as well as samples annealed in the organic solvent do not exhibit clustering while morphology changes during annealing are obvious. Films made by solvent casting have a very disordered, wormlike morphology with low level of contrast while films annealed in THF vapor have a very distinguishable lamellar morphology. Figure 1 shows a slice of a CTEM tomographic reconstruction of an annealed sample in a plane perpendicular to the surface of the film, which directly reveals the ordering of the lamellar structure. Annealing the films in water vapor introduces very different changes. Low temperature annealing has little effect on morphology. We conclude that changes are too slow to be recognized. Annealing at 40 °C results in the formation of sulfur clusters. The arrangement of the PSS and PMB phases remains preserved. Increasing temperature to 50 °C transforms the polymer to a honeycomb type morphology with cells containing the PMB phase and the PSS phase enveloping each PMB cell. Figure 2a shows a HAADF projection image collected from such a sample. Sharp bright spots on this image are the clusters of sulfur which scatter electrons to high angles more strongly than the carbon backbone. While clustering is clear in this image the spatial arrangement of the clusters in the two phases is ambiguous. Some of the clusters appear to reside inside of the PMB cells. STEM tomography removes this ambiguity. Figure 2b and 2c show slices of a tomographic reconstruction parallel to the surface near the surface and the center of the film. One can see that the surface is uniformly filled with clusters while in the middle of the film all clusters are concentrated at the boundaries between the cells.

Clusters formed in this material appear to be very stable. Drying of the sample as well as reannealing in organic solvent does not destroy them. Figure 3a shows a slice of a tomographic reconstruction of the reannealed sample. In this case material with a honeycomb like morphology and strong

clustering developed during annealing in water vapor was annealed at low temperature in THF vapor. After annealing the sample shows distinct lamellar morphology and strong clustering. For comparison a slice of a similar reconstruction from the cast material subsequently annealed in THF vapor is shown at Figure 3b. One can see that this reconstruction does not reveal any clustering.

We conclude that the morphology of the polyelectrolyte containing the clusters is thermodynamically stable. Its formation is promoted by water, but organic solvent does not destroy it. Correlation of cluster formation and changes in conductivity observed when polyelectrolyte membranes are treated under different conditions [2] may lead to better understanding of the conductivity mechanism in polyelectrolyte membranes.

References

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- [2] Wang, X., et al., *On the Origin of Slow Changes in Ionic Conductivity of Model Block Copolymer Electrolyte Membranes in Contact with Humid Air*. Macromolecules, 2010. **43**(12): p. 5306-5314.
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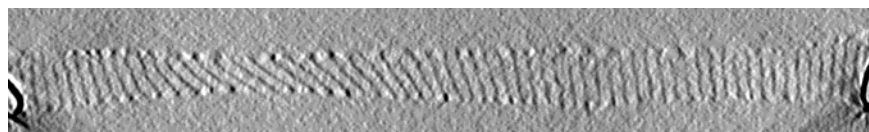


FIG. 1. Slice of TEM tomographic reconstruction in a plane perpendicular to the surface of the film. The sample was cast and annealed at room temperature in THF.

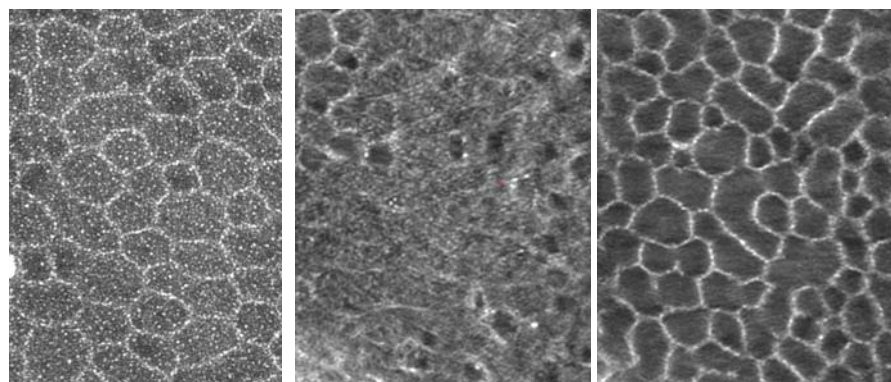


FIG. 2. Film annealed in water vapor at 50 C. a) HAADF image, b and c) slice of tomographic reconstruction (HAADF-STEM) in planes passing through the surface and middle of the film.

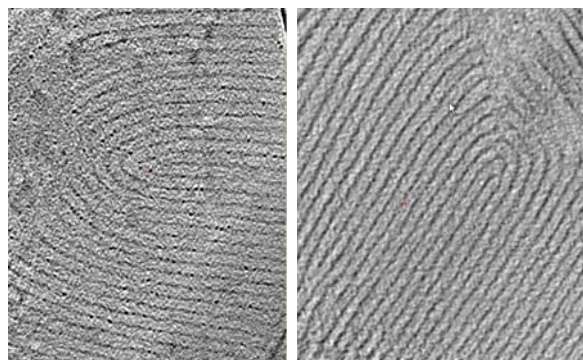


FIG. 3. Slice of TEM tomographic reconstruction in a plane parallel to the surface a) sample annealed in water at 50 C and reannealed in THF, b) sample only annealed in THF