

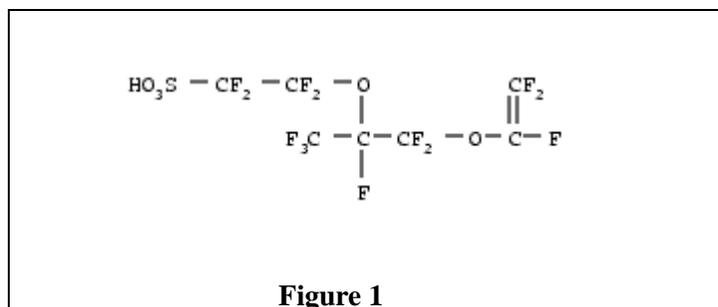
## NAFION<sup>®</sup> PERFLUOROSULFONATE IONOMER MEMBRANES

Although ion-containing polymers have been around for some time, the past fifteen years have been witness to an explosion of information in the literature. Most of the research effort on these **ionomers** have been devoted to only a small number of materials, notably the ethylenes, styrenes, rubbers, and those based on poly(tetrafluoroethylene).<sup>1</sup> **Nafion<sup>®</sup>** is one such example of a poly(tetrafluoroethylene) based ionomer.<sup>2</sup> From its development by DuPont in the 1960s, it has etched applications in liquid and gas separations, fuel cells, and the chlor-alkali industries. Because of its thermal and chemical resistance, ion-exchange properties, selectivity, mechanical strength, and insolubility in water, its application is only limited by imagination and foresight.

### A. Nafion<sup>®</sup>

Nafion<sup>®</sup> DuPont's brand name for a series of fluorinated sulfonic acid copolymers, is the **first synthetic ionic polymer**. The sulfonic acid groups are chemically active, but they are fixed within the Teflon polymer matrix. Thus, Nafion is resistant to chemical breakdown, making it useful for membranes in fuel cells.

Sulfonic Acid – is an organic compound containing the **functional group**  $R\text{SO}_2\text{OH}$ , which consists of a sulfur atom, S, bonded to a carbon atom that may be part of a longer chain of carbon atoms and also bonded to three oxygen atoms, O, one of which has a hydrogen atom, H, attached to it. **The hydrogen atom makes the compound acidic.** In Figure 1 the sulfonic function group is attached to the Teflon type polymer.



Structurally, Nafion<sup>®</sup> is complex. Although the exact structure is not known, several models have been proposed since the early 1970s, to describe the way in which ionic groups aggregate within the Nafion<sup>®</sup> polymer. Recently, Robertson, has summarized many of these such models, to include, The Mauritz-Hopfinger Model, The Yeager Three Phase Model, The Eisenberg Model of Hydrocarbon Ionomers, and The Gierke Cluster Network Model.<sup>3</sup> A common objective of these models is to predict the fundamental feature of unique equilibrium ionic selectivities, as well as, the ionic transport properties of perfluorinated ionomer membranes.<sup>3</sup>

As a result of electrostatic interactions, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters.<sup>1</sup> The presence of these electrostatic interactions between the ions and the ion pairs enhance the intermolecular forces and thereby exert a significant effect on the properties of the parent polymer.

### B. Structural Model

Previous small angle x-ray scattering (SAXS)<sup>4</sup> and neutron scattering experiments clearly indicate that ionic clustering is present in Nafion<sup>®</sup>. However, details on the arrangement of matter within these clusters have not fully been realized. Although no one model has been found to provide a complete explanation of the properties and selectivities found, several, base these properties and selectivities on an extensive micro-phase separated morphology.<sup>1,3-10</sup> A stylized, semi-empirical view of a polar/nonpolar microphase separation in a hydrated ionomer can be seen below in Figure 2.

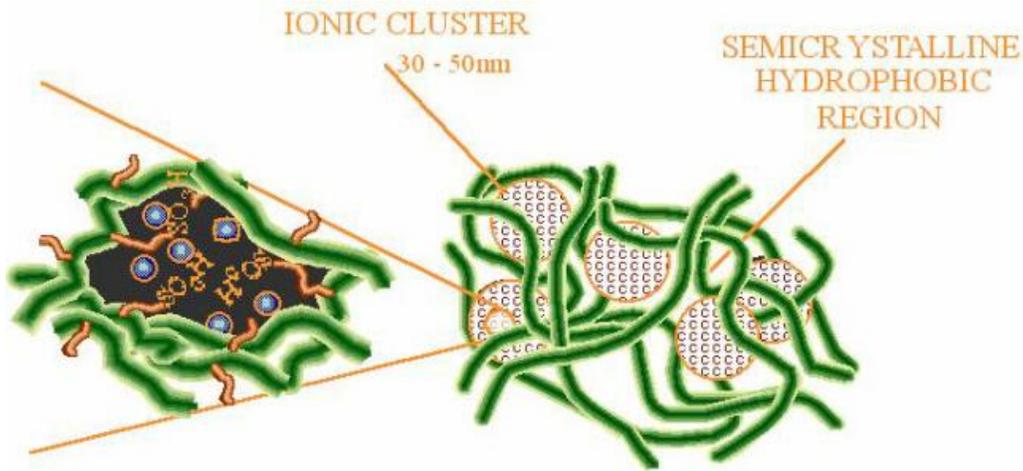


Figure 2. Stylized view of polar/nonpolar microphase separation in a hydrated ionomer.

This over-simplification shows a phase separated morphology of discrete hydrophobic and hydrophilic regions. The hydrophobic region is composed of the polymer fluorocarbon backbone. Conversely, the hydrophilic region contains the ionic groups and their counter ions.

As seen in Figure 3, the Yeager Three Phase Model is a phenomenological based model. This model is based on a three-phase clustered system with interconnecting channels within the polymer. The three regions consist of (A) a fluorocarbon backbone, some of which is microcrystalline, (B) an interfacial region of relatively large fractional void volume containing some pendant side chains, some water, and those sulfate or carboxylic groups and counter ions which are not in clusters, and (C) the clustered regions where the majority of the ionic exchange sites, counter ions, and sorbed water exists.<sup>4,10</sup>

From experimental means, such as, small-angle x-ray scattering (SAXS) it has been determined that the phase-separated morphology is on the order of 30-50Å Bragg spacing.<sup>10</sup> However, upon hydration, Nafion<sup>®</sup> with its unique ability to sorb relatively large amounts of water, can increase its dry weight by as much as 50 percent or more depending upon equivalent weight, counter ion, and temperature. Upon hydration, however, cluster diameter and the number of exchange sites are thought to increase, leading to fewer, larger clusters.<sup>10</sup>

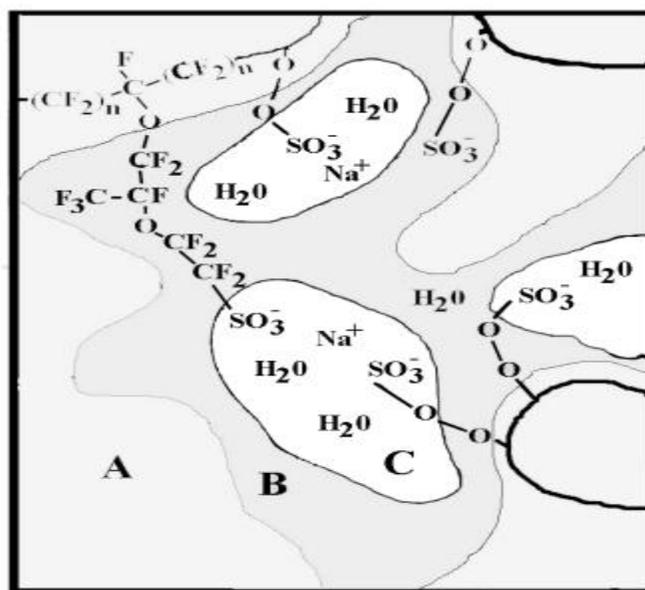


Figure 3. The Yeager 3 Phase Model of Nafion<sup>®</sup> Clusters

Nafion<sup>®</sup>, with its existing ionic clusters and postulated inter-cluster channels, serves not only as a stable platform or template, but also as a catalyst. The sulfonate exchange sites in the ionomer are extremely acidic. Therefore, the clusters in Nafion<sup>®</sup> serve as reaction vessels in which future polymerizations can occur without addition of an external catalyst. The pre-existing morphology of Nafion<sup>®</sup>, as discussed above, has a direct influence on the in situ grown morphology of any inorganic phase in view of the fact that the clusters are only 30-50Å in size. Therefore, one can generate distinct ordered structures in the clusters and form a network between clusters using the short channels that connect the aggregates. Upon doing so, the original ionomer properties can be altered and tailored to specific uses and needs, such as, specific gas and liquid separations and fuel cell operations.

### C. Summary

Clearly, the basis for the unusual properties exhibited in Nafion<sup>®</sup> arises from the extensive microphase separation morphology as seen from numerous researchers.<sup>1,3-9</sup> Moreover, the way in which the phase separated regions interact and act upon other substances is of great interest, not only in the scientific world, but in industry, as well. Because of this ionic morphology and the inherent ionomer properties of Nafion<sup>®</sup>, its interest scientifically and usefulness technologically should continue well into the future.

### References

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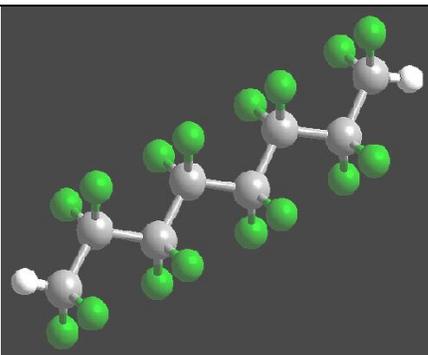
Written by: John Payne (Partially From His Master's Research) <http://www.psrc.usm.edu/mauritz/nafion.html>

Sulfonic Acid –An organic compound containing the functional group  $R SO_2 OH$ , which consists of a sulfur atom, S, bonded to a carbon atom that may be part of a longer chain of carbon atoms and also bonded to three oxygen atoms, O, one of which has a hydrogen atom, H, attached to it. **The hydrogen atom makes the compound acidic**

## Teflon

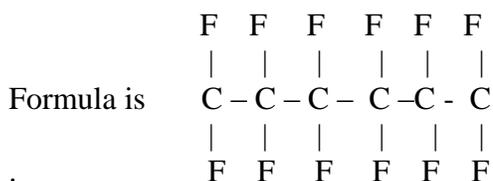
“Teflon PTFE resins have a continuous service temperature of 260°C (500°F),” which means that it can stand exceedingly high temperatures, but only for a short period of time. Teflon is capable of continuous service at 500°F, toughness and flexibility, chemical inertness, low coefficient of friction, zero moisture absorption, and weather resistance [5].

Teflon" is an extremely inert, organic, crystalline white polymer produced by free radical polymerization of the tetrafluoroethylene monomer (a colorless gas)" [15]. Teflon is made of a carbon backbone chain with each carbon having two fluorine atoms attached to it [24]. Fluorine acts as a very strange element when part of a molecule, because when it is part of a molecule fluorine does not like to combine with other elements, even its self, and so it repels anything that tries to attach to it, which is what is responsible for Teflon's nonstick characteristic [24]. Usually found in long chains, Teflon is an ionically bonded set of two carbons and four fluorine elements that result in five single bonds, which about 24 percent is carbon and about 76 percent is fluorine, by mass, in each particular piece [8].



Teflon is a polymer but differs from hydrocarbons in that no H atoms are attached to the C atoms.

The C atoms form the **backbone** of the chain.



Despite its unique properties, if it had not been for World War II, research on Teflon would not have expanded as fast as it did [19]. In World War II, “scientists involved in creating the first atomic bomb needed a material for gaskets that would resist the viciously corrosive gas, uranium hexafluoride, one of the materials used to produce the U-235 for the bomb”. [19] To meet this critical property, Army General Leslie R. Groves ordered DuPont to produce Teflon for bomb production during the war [19]. Due to its use in secret projects, the public knew little of Teflon until it started to appear in the market in 1960.

From <http://www.wfu.edu/users/strack4/serendipitouscience/project4.htm>

## FUNCTIONAL GROUPS CARBON CHEMISTRY

Organic chemists are very interested in groups of atoms attached to carbon atoms or a chain of carbon atoms. These atoms are known as **functional groups** and they provide information about how they will chemically react.

$\text{—OH}$ Alcohol Functional Group	$\begin{array}{c} \text{—C—H} \\    \\ \text{O} \end{array}$ Aldehyde Functional Group	$\begin{array}{c}   \\ \text{—C—N—} \\    \\ \text{O} \end{array}$ Amide Functional Group	$\begin{array}{c} \text{—C—OH} \\    \\ \text{O} \end{array}$ Carboxylic Acid Functional Group
$\begin{array}{c} \text{—C—O—} \\    \\ \text{O} \end{array}$ Ester Functional Group	$\text{—O—}$ Ether Functional Group	$\begin{array}{c} \text{—C—} \\    \\ \text{O} \end{array}$ Ketone Functional Group	$\begin{array}{c}   \\ \text{—N—} \end{array}$ Amine Functional Group