

Morphology of Nafion Membranes Prepared by Solutions Casting

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Nafion, an ionomer composed of perfluorocarbon backbone and vinyl ether side chains terminated with $-\text{SO}_3^-$ groups, has dual solubility parameters, i.e. $\chi_1 = 9.7 \text{ (cal/cm}^3)^{1/2}$ relating to perfluorocarbon backbones and $\chi_2 = 17.3 \text{ (cal/cm}^3)^{1/2}$ relating to sulfonated vinyl ether side chains. In this study, the conformations of Nafion molecules in dilute solutions with solvents of various dielectric constants and solubility parameters, i.e. N,N'-dimethyl acetamide (DMAc, $\chi_1 = 10.8 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 37.8$), N,N'-dimethyl formamide (DMF, $\chi_1 = 12.2 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 36.7$), N-methyl formamide (NMF, $\chi_1 = 16.1 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 182.4$), methanol-water mixture (4/1 g/g, $\chi_1 = 16.3 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 40.3$), ethanol-water mixture (4/1 g/g, $\chi_1 = 16.3 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 40.3$), and propanol-water mixture (4/1 g/g, $\chi_1 = 16.3 \text{ (cal/cm}^3)^{1/2}$, $\chi_2 = 40.3$) were freeze dried and observed by transmission electron microscope (TEM). The Nafion membranes were prepared by solutions casting with these solvents and evaporated the solvents at temperatures below T_G of Nafion, then annealed the membranes at temperatures above T_G of Nafion. The morphology of Nafion membranes were investigated using small angle X-ray scattering (SAXS), differential scanning calorimeter

(DSC), and thermal gravimetric analysis (TGA). These observations showed conformations of Nafion molecules in dilute solutions and membranes morphology were strongly influenced by χ_1 and χ_2 of solvents. The Nafion molecules behaved coiled-like structures and low molecular aggregations in solvents (i.e. DMAc and DMF) with low χ_1 and closing to $\chi_1 = 9.7 \text{ (cal/cm}^3)^{1/2}$ of Nafion perfluorocarbon backbone and thus low ionic $-\text{SO}_3\text{H}$ aggregations in membranes after solvents were evaporated by solutions casting. The Nafion molecules behaved rod-like structures and low molecular aggregations in solvents (i.e. NMF) with high χ_1 and closing to $\chi_2 = 17.3 \text{ (cal/cm}^3)^{1/2}$ of Nafion vinyl ether side chains and thus low degree of perfluorocarbon backbones aggregations and low ionic $-\text{SO}_3\text{H}$ aggregations in membranes after solvents were evaporated by solutions casting. The Nafion molecules showed molecular aggregations in solvents (i.e. alcohol-water mixture solvents) with low χ_1 and closing to $\chi_2 = 17.3 \text{ (cal/cm}^3)^{1/2}$ of Nafion vinyl ether side chains and thus high degree of perfluorocarbon backbones aggregations and high ionic $-\text{SO}_3\text{H}$ aggregations in membranes after solvents were evaporated by solutions casting.

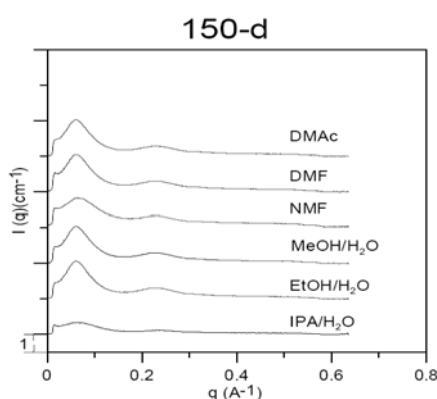


Figure 1. SAXS data of Nafion membranes prepared by solutions casting from various solvents and annealed at 150°C for 90 min. The membranes were stored at 25°C with RH 37% before SAXS study.

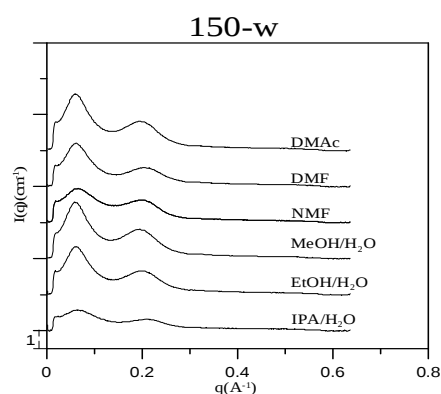


Figure 2. SAXS data of Nafion membranes prepared by solutions casting from various solvents and annealed at 150°C for 90 min. The membranes were stored at 25°C in distilled water before SAXS study.