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Solid-State NMR Investigations of a Perfluorinated Ionomer (Nafion) QIANG CHEN, KLAUS SCHMIDT-ROHR, Ames Laboratory and Department of Chemistry, Iowa State University — The chain dynamics and supramolecular structure of Nafion®, a perfluorinated ionomer which is widely used as a hydrophilic permselective membrane in fuel cells and chloralkali electrolysis, have been studied by solid-state NMR. With 1D and 2D NMR under 30-kHz magic-angle spinning (MAS), the ^{19}F and ^{13}C NMR peak widths and positions are determined, which corrects several previous assignments. The peak widths reveal static disorder around the branch point, increasing mobility towards the side group end, and a conformationally ordered backbone, which is essentially polytetrafluoroethylene (PTFE). Fast rotations of the helical backbone segments around their axis are confirmed in PTFE and observed similar in Nafion. The equal ^{19}F chemical shifts within parallel packed rotating chains in PTFE crystals result in slow ^{19}F spin diffusion between differently oriented chains. This spin diffusion is observed very fast for a majority of backbone segments in Nafion and the orientational correlations of the remainder backbones are weak. The typical diameter of backbone "clusters" in Nafion was 1 - 3 nm estimated by ^{19}F spin diffusion. Relatively fast ^{19}F spin exchange from any site in the side group to the backbone is observed. Absorbed water increases the side-group dynamics and conformational averaging, but not the segments near the branch point.

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