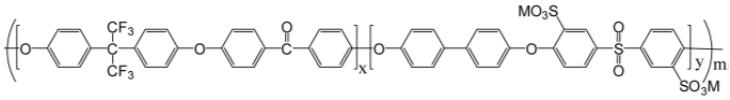
Investigation of Dynamics-Transport Correlations in Polymeric Membranes of Fuel Cell and Reverse Osmosis Applications

S. Wi (NHMFL); B. Freeman (U. of Texas, Austin); J.E. McGrath (Virginia Tech)

Introduction

We have investigated a nano-phase separated block copolymer system, 6FK-BPS100, by solid-state NMR spectroscopy that has been developed for the next-generation polymeric membrane materials for use in fuel cell and reverse osmosis (RO) applications. The purpose of this study is to understand the basic structural and morphological features as well as the dynamics of the polymer matrix to understand the molecular transport properties of the polymeric membranes that are fabricated by these block copolymers.



6FK(x)-BPS100(y); x = y = 3k, 5k, 10k, and 17k.

Experimental

^{1}H T_1 relaxation of methine protons on the polymer backbone chains were measured indirectly via the directly bonded ^{13}C in the solid state for understanding the dynamic features of the polymer chain molecules, utilizing ^{1}H-^{13}C cross-polarization (CP) experiment under the magic-angle spinning (MAS) condition. The ordering or aggregation of the sodium sulfonate side-chains in the hydrophilic domains were investigated by ^{23}Na NMR under the static condition. The diffusion of water molecules in the polymer matrices was examined by the pulsed field gradient (PFG) NMR on the mesoscopic level.

Results and Discussion

Table I and Fig. 1 show NMR and various macroscopic experimental data of 6FK(x)-BPS100(y) block copolymers of varying x and y values. The membrane sample made of x = y = 17k, which provides the highest water uptake, IEC values, and water permeabilty with the lowest NACl rejection, provides the fastest water diffusion in the polymer matrix with the shortest 1H T1 value.

	3k-3k	5k-5k	10k-10k	17k-17k
^{1}H T_1 (ms)	393	344	323	291
PFG NMR water diffusion (m^2/s)	1.4×10^{-10}	1.4×10^{-10}	2.0×10^{-10}	6.3×10^{-10}
Water uptake (wt %)[a]	40	60	60	65
Water permeability (L μm/m^2 h bar)	0.48	0.66	0.84	1.87
Ion exchange capacity (meq/g)[b]	1.50	1.50	1.55	1.55
NaCl rejection (%)	96.9	96.1	96.4	90.8

a: Measured in ACID form; b: Measured from ^{1}H NMR

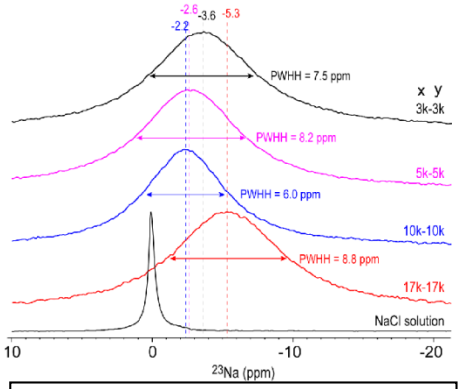


Fig. 1. ^{23}Na solid-state NMR spectra of 6FK(x)-BPS100(y).

The ^{23}Na NMR spectrum of this sample also exhibits the most upfield chemical shift value (-5.3 ppm), with the broadest peak width (PWHH = 8.8 ppm). The nature of the anisotropic frequency dispersion of ^{23}Na NMR spectrum would be originated from the extent of molecular disordering of sodium sulfonate side-chains that are aggregated in the hydrophilic domains of the polymer matrix. The presence of highly disordered hydrophilic domains of 17k-17k would exhibit highest water diffusion, permeability, and uptake, while demonstrating lower salt rejection. We are currently undergoing additional experiments to further differentiate 3k-3k, 5k-5k, and 10k-10k samples.

Conclusions

The membrane properties of the block copolymer system, 6FK-BPS1000, changed greatly according to the variation in the size of the copolymer block in the polymer sequence. Solid-state and PFG NMR data have demonstrated close correlations to the macroscopic properties, such as water uptake, permeability, and NaCl rejection measurements.

Acknowledgements

This experiment was supported by the NHMFL user services via the National Science Foundation Cooperative Agreement No. DMR-1157490 and, the State of Florida.