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

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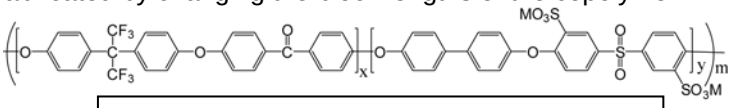
Introduction

A nano-phase separated block copolymer system, 6FK-BPS100, was investigated by solid-state and pulsed-field gradient (PFG) NMR spectroscopy for characterizing the correlations between the chain motions and transport properties of the polymer matrices that are fabricated by changing the block lengths of the copolymer system. This polymer system has been developed for the next-generation of polymeric membrane materials for use in fuel cell and reverse osmosis (RO) applications.



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

Experimental

^{1}H T_1 and $T_{1\rho}$ relaxation of methine protons on the polymer chains were measured indirectly via the directly bonded ^{13}C, utilizing ^{1}H-^{13}C cross-polarization (CP) experiment under the magic-angle spinning (MAS) condition. ^{1}H T_1 and $T_{1\rho}$ experiments were carried out to detect motions of the polymer chains in the nanoseconds and microseconds regime, respectively. The centerband only detection of exchange (CODEX) NMR experiment was performed to detect the slow reorientational motions of polymer chains. 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

Figure 1 shows that the hydrophilic-hydrophobic nanophase separations are increased when the sizes of the x and y blocks increase as confirmed by the TEM images. SAXS data also demonstrate that the extent of domain separations increase as the block sizes increase as can be determined by 1/q. Both the slow and fast water diffusion in the polymer matrices determined by PFG NMR show close correlations in their trends to the ^{1}H T_1 relaxation and CODEX data which determines the fast (nanosecond) and slow (millisecond) motions of molecular segments or chains. Motions in the intermediate time scales in the microsecond regime that governs $T_{1\rho}$ time however do not show any correlations to the diffusion data.

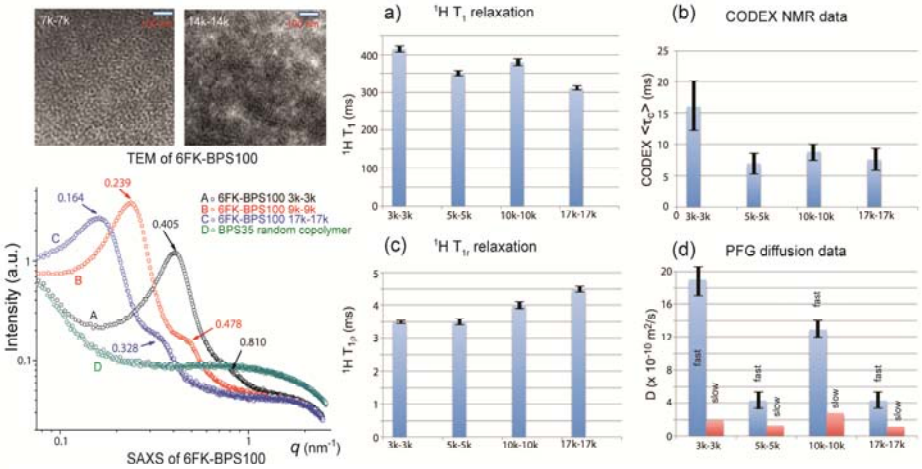


Fig.1 TEM, SAXS, PFG-NMR, and solids' ^{1}H T_1, $T_{1\rho}$, and CODEX NMR data of 6FK-BPS100 polymers with different block lengths obtained at 600 MHz at the NHMFL. Bigger domain size separations are clearly visible in both TEM and SAXS data (by 1/q). Fast motions in the nanoseconds regime as determined by ^{1}H T_1 and slow reorientational motions of the polymer backbone in the milliseconds regime as determined by CODEX[1,2] have close correlations to the water transport property measured by PFG NMR.

Conclusions

The water diffusion coefficients in the block copolymer system, 6FK-BPS1000, have changed by varying the size of the copolymer blocks in the polymer sequence. The mesoscopic water transport property in the polymer matrices has demonstrated correlations to the fast and slow polymer segmental or chain motions as determined by ^{1}H T_1 and CODEX NMR experiments measured in the solid state.

Acknowledgements

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References

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[2] deAzevedo, E. R., *et al.,* J. Chem. Phys., **112**, 8988-9001 (2000).