

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE Feb 27, 2007		3. REPORT TYPE AND DATES COVERED Final Report 6/06-11/06
4. TITLE AND SUBTITLE NMR Studies of Micro-Structured and Nano-Structured Polymeric Membrane Systems			5. FUNDING NUMBERS DAAD19-03-1-0087	
6. AUTHOR(S) Guoxing Lin				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Clark University, 950 Main St, Worcester, MA 01610			8. PERFORMING ORGANIZATION REPORT NUMBER #40403-Ch	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 44931.3-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report describes our achievement in the investigation of the influence of structure on diffusion in styrene-ethylene/butylene-styrene triblock copolymers (SEBS) during the period of June1, 2006 to November 30, 2006. This type of triblock copolymers has the potential for chemical protection and fuel cell application. Our progress is made in the following fields: (I) Pulse-field-gradient (PFG) Nuclear Magnetic Resonance (NMR) study of the translational diffusion; (II) lattice model simulation of diffusion. From the study, it shows that the copolymer structure and the extent of sulfonation of SEBS have significant influence on penetrant diffusion and sulfonated SEBS (sSEBS) may have a good selectivity for water over DMMP depending on the sSEBS structure.				
			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

(1) (a) Papers published in peer-reviewed journals-

Guoxing Lin, Darryl Aucoin, Marcus Giotto, Alana Canfield, Wen-Yang Wen, and Alan A. Jones, "Lattice Model Simulation of Penetrant Diffusion along Hexagonally Packed Rods in a Barrier Matrix As Determined by Pulse-Field-Gradient Nuclear Magnetic Resonance", *Macromolecules*, 2007, 40(5), 1521-1528

(b) Papers published in non-peer-reviewed journals or in conference proceedings

Xueqian Kong, Tabitha Hargrove, Sara Ouellette, Marcus V. Giotto, Darryl Aucoin, Guoxing Lin, and Alan A. Jones, "Penetrant Diffusion in Triblock Polymer by Pulse-field-gradient NMR and Lattice Model Simulation", Accepted for publication on MRS 2006 fall meeting proceeding. Peer reviewed

(c) Papers in preparing

Xueqian Kong, Guoxing Lin, Tabitha Hargrove, Sara Ouellette, Marcus V. Giotto, Seth Drury, Wen-Yang Wen and Alan A. Jones, "Penetrant Diffusion in SEBS Triblock Copolymer by Pulse-field-gradient NMR"

(2) "Scientific Personnel" supported by this project

Marcus Giotto-post-doctoral fellow
Xueqian Kong-graduate student

Master thesis: Xueqian Kong
Title: NMR Study of Structure and Diffusion in Block Copolymer Membranes

(3) report of inventions-none

(4) Scientific progress and accomplishments

NMR Studies of Micro-Structured and Nano-Structured Polymeric Membrane Systems

Guoxing Lin

Chemistry Department

Clark University

950 Main St

Worcester, MA 01610

Email: glin@clarku.edu

This report describes our achievement in the investigation of the influence of structure on diffusion in styrene-ethylene/butylene-styrene triblock copolymers (SEBS) during the period of June 1, 2006 to November 30, 2006. This type of triblock copolymers has the potential for chemical protection and fuel cell application. Our progress is made in the following fields: (I) Pulse-field-gradient (PFG) Nuclear Magnetic Resonance (NMR) study of the translational diffusion; (II) lattice model simulation of diffusion. From the study, it shows that the copolymer structure and the extent of sulfonation of SEBS have significant influence on penetrant diffusion and sulfonated SEBS (sSEBS) may have a good selectivity for water over DMMP depending on the SEBS structure.

(I) PFG NMR diffusion:

PFG NMR has been performed to measure the diffusion of 2,2,4-trimethyl pentane (TMP), dimethyl methylphosphonate (DMMP) and water in different SEBS samples, which mainly include unsulfonated SEBS with a molecular weight of 49 kDalton and styrene endblocks of 16 kDalton (7758 film), 20 % sulfonated 7758 film (20T) and 40 % sulfonated 7758 film (40T).

(1) TMP diffusion

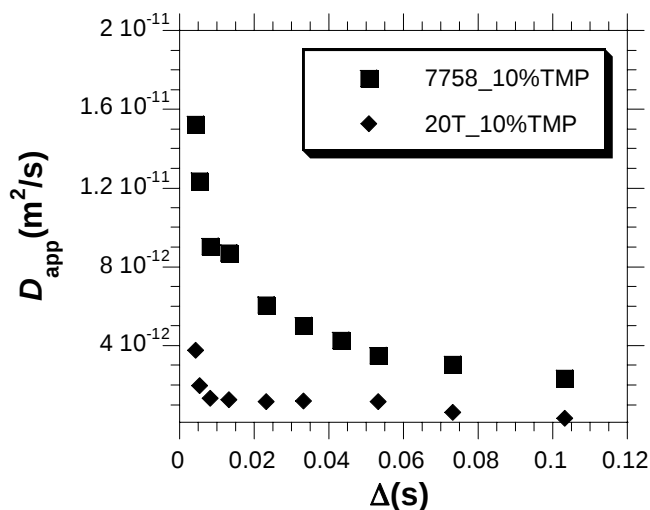


Figure 1. Apparent diffusion coefficient versus Δ for 10 wt % TMP in SEBS 7758 film and 20 % sulfonated 7758 film.

In Figure 1, diffusion results of 10 wt % TMP in unsulfonated and sulfonated 7758 films are presented. The TMP diffusion in sulfonated SEBS film is 4 to 5 times slower than that in unsulfonated SEBS film, which may result from poor phase separation and slower segmental motion of EB chain in sulfonated SEBS.

In order to better understand the morphology influence on penetrant diffusion, we have also measured the TMP diffusion in the following three different unsulfonated SEBS samples: 1657 SEBS film with 13 wt % polystyrene (PS) in endblocks, 1129 SEBS film with 31 wt % PS in endblocks and 7758 film. The expected morphologies for the three samples may be PS sphere in ethylene/butylene (EB) phase (1657), PS cylinder in EB phase (1129) and EB cylinder in PS phase (7758). Figure 2 shows the morphology influence on the diffusion coefficient in those samples. In the three different morphologies, the amplitudes of diffusion coefficient drops are different at the bending points, which should correspond to the grain boundary where EB phase orientation changes. With the EB phase changing from majority phase to minor phase in the copolymer, the diffusion coefficient drop becomes more severe.

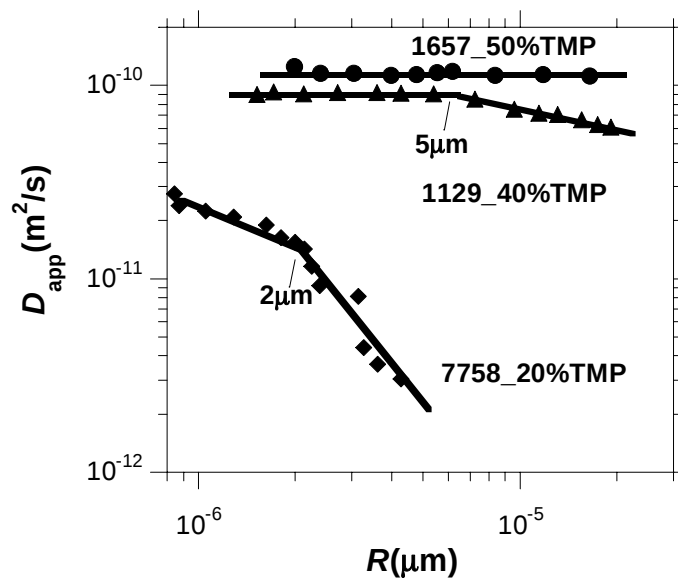


Figure 2. Diffusion coefficient versus displacement in different morphologies.

(2) DMMP diffusion

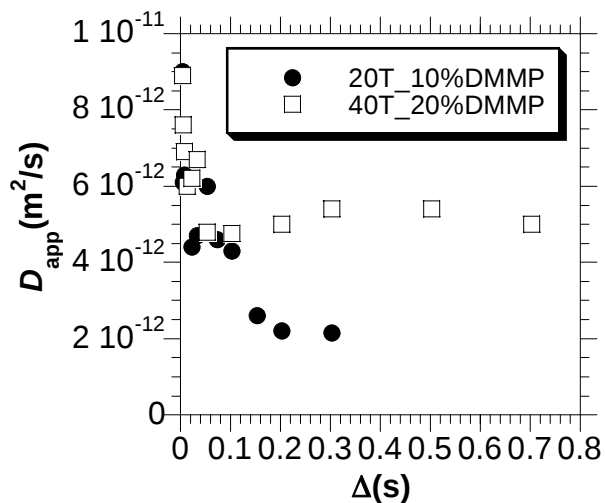


Figure 3. The apparent diffusion coefficients of DMMP in sSEBS 7758 samples.

From Figure 3, the DMMP diffusion is at the order of $10^{-8} \text{ cm}^2/\text{s}$, which is at about the same scale for DMMP diffusion in Nafion. Contrast to TMP, DMMP is a strong Lewis base; therefore, the DMMP molecules may prefer to stay near the ionic clusters in sSEBS sample. At short time, the DMMP diffusions in the two samples are at similar rates because the ratios of DMMP to sulfonic group are the same. At long time, the DMMP diffusion coefficients are approximately doubled for the 40T_20%DMMP sample, which may be due to the better connection between ionic clusters with higher degree of sulfonation.

(3) Water diffusion

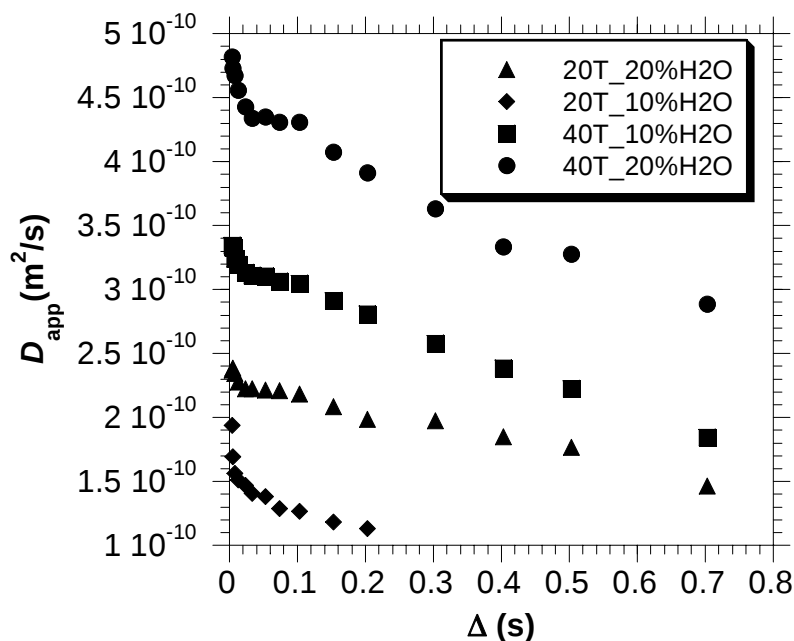


Figure 4. The plot of apparent diffusion coefficient of water through sulfonated 7758 membranes.

At short time, the water diffusion is of the order of 10^{-6} cm²/s, two orders faster than that of the DMMP, which is comparable with what has been measured in Nafion. Unfortunately it is difficult for PFG NMR to measure the long time diffusion coefficient in this system. The ionic channels greatly assist water transport through polar interaction. From Figure 4, it is clear that the water diffusion is controlled by two factors. One is the degree of sulfonation; the higher sulfonation resulting in a fast diffusion rate. The other is the concentration of the water; the higher concentration of water the faster the diffusion is.

(4) Acid Proton diffusion

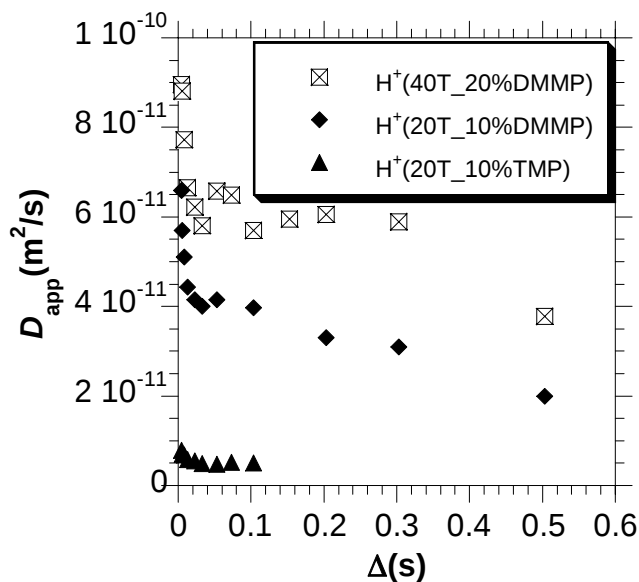


Figure 5. Apparent diffusion coefficient of acid proton in sSEBS 7758 membranes.

In addition, in the sulfonated SEBS film, in addition to the penetrant diffusion process, there is another diffusion process taking place simultaneously. Originally, it was thought that the other diffusion process was that of the penetrant (TMP, DMMP) in another phase in the sulfonated SEBS block copolymer in our interim report in Aug. 2006, however, from our analysis of all the NMR spectra from TMP, DMMP and water in sulfonated SEBS films, it should be the diffusion of the acid proton coming from sulfonation for all the acid protons appear on same position in those NMR spectra. Figure 5 shows the diffusion of acid proton in 10 wt % TMP in 20 % sulfonated 7758 film, 10 wt % DMMP in 20 % sulfonated 7758 film and 20 wt % DMMP in 20 % sulfonated 7758 film.

In sample of 10 wt % TMP in sSEBS film, the acid protons should be bonded to the sulfonic groups for most time and diffuse slowly at the order of 10^{-8} cm²/s. The TMP molecules diffuse through EB phase and do not disturb the acid protons. However, the diffusion rate is increased significantly to the order of 10^{-7} cm²/s with the presence of DMMP. The interaction between DMMP molecules and acid proton could lead to the dissociation of acid protons from sulfonic group. The acid proton diffusion in the sample of water in sSEBS is very close to the water diffusion and is hard to distinguish them.

(II) Lattice Model simulation

In order to understand the structure influence on the diffusion, the lattice model simulation is performed to simulate the apparent diffusion coefficient depending on the diffusion time (equivalently the diffusion length scale) and the NMR signal attenuation induced by diffusion in PFG experiment. The lattice with randomly oriented and randomly sized, hexagonally packed cylinder grains, is built and shown in Figure 6.

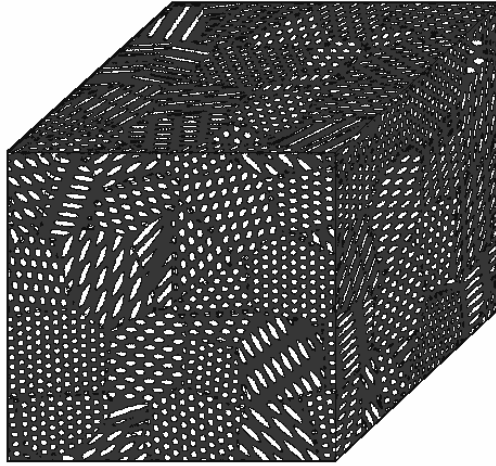


Figure 6. Three dimensional hexagonally packed cylinders lattice with randomly oriented and randomly sized polygonal grain.

The lattice model simulation of diffusion of 20 wt % TMP diffusion in 7758 film is compared with experimental results, shown in Figure 7. The simulation is the average of over 3000 random walks. TMP diffusion is affected by two morphology characteristics including the cylinder diameter and the grain boundary. The former is too short to be detected by current PFG techniques. The latter is determined by grain size in the range of microns. In the unsulfonated 7758 film, the grain size varies from 2 to 5 μm , in which the apparent diffusion constant has an order of magnitude decrease. The big drop is beyond that predicted by the effective medium theory (EMT). From the lattice simulation, to attain such a big diffusion drop, the diameter of the cylinder at the interface must be reduced by a factor of about 0.7, which is related with another parameter used in the simulation, the grain interface thickness (a few nanometer thickness is arbitrary assigned in the simulation), which indicates that EB cylinder phase in one grain is not well connected to the EB in another grain. This is in agreement with the reported dislocations between the cylinders at grain boundary. The short time D_{app} is about one third of the TMP diffusion coefficient in the pure EB phase, which is reasonable that the spatially averaged one dimensional diffusion constant is one third of the three dimensional diffusion constant in pure EB phase. If the morphology is lamella, the short time D_{app} of TMP should be about two third of that in pure EB phase and the drop in diffusion constant at the grain boundary will not be big, which is quite different from the observed PFG diffusion results.

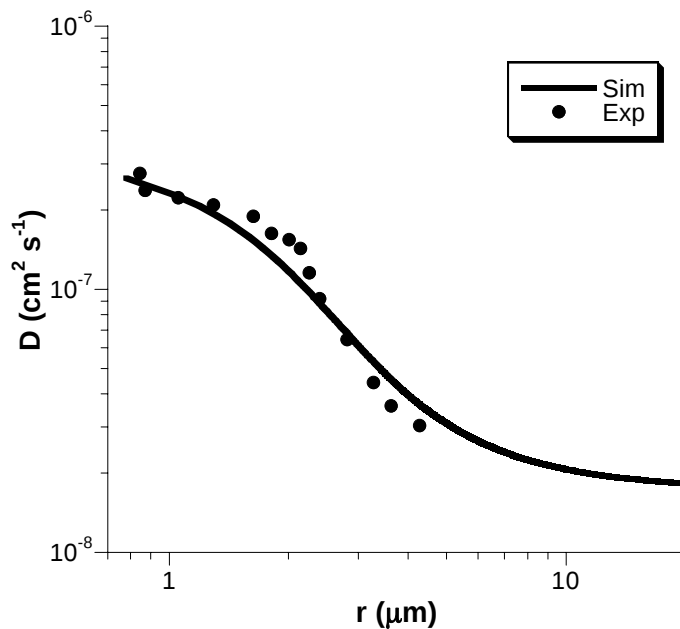


Figure 7. Comparison of apparent diffusion constant as a function of root mean square displacement from lattice model simulation of diffusion and the experimental results. Grain size from the simulation is 2.5 microns.

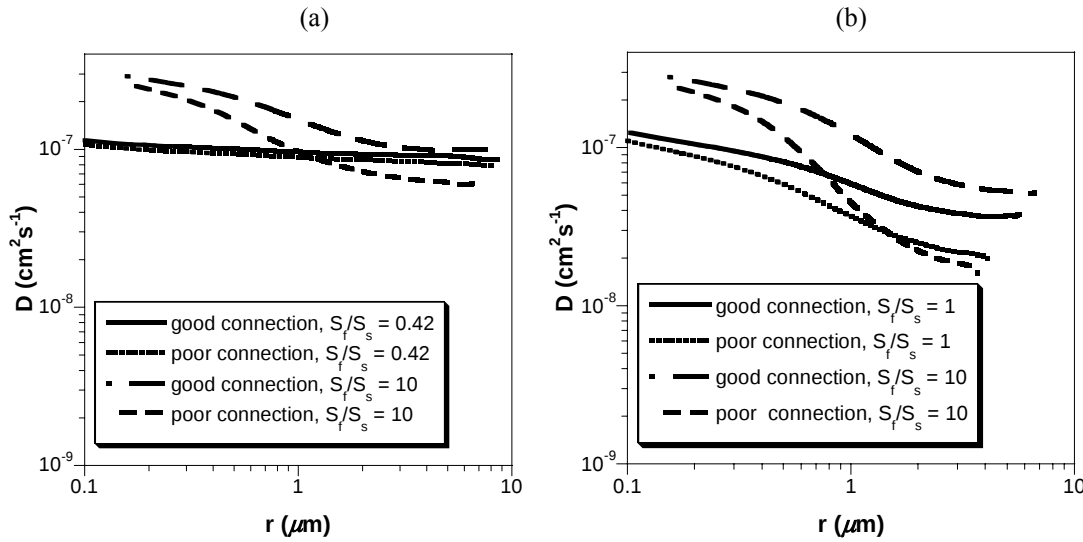


Figure 8. Diffusion constant versus the length scale with different diffusion constant and solubility ratios between the fast and slow phases: (a) $D_f/D_s = 63$; (b) $D_f/D_s = 1000$. The grain size used in the simulation is 1 micron.

When the diffusive phase is not the majority phase, the influence of grain boundary on diffusion is closely related to the difference in solubility and diffusion constant between the two components of the block copolymer. When the solubility difference and difference in diffusion constant are small, the penetrant can diffuse in both phases, so the penetrant diffusion will average over the copolymer structure at short length scale and the connection of the rubbery phase at grain boundary has no significant influence on the diffusion. The situation is similar to the reported gas permeability investigation, which can be described by EMT. With the increase in difference of the solubility and diffusion constant difference, the grain boundary influence becomes more and more significant, the penetrant can not find an alternative path to diffuse if the conductive rubbery phase is not well connected, which leads to a big decrease in the diffusion constant as observed in the PFG TMP diffusion. EMT can not describe this drop because it neglects the grain boundary connection.

The PFG NMR signal attenuation simulation and theoretical fitting are shown in Figure 9. Two extreme connection situations, poor and good connections, are analyzed with theoretical fitting. The poor connection can be treated as diffusion in randomly oriented cylinder, while the good connection can be treated by one dimensional Fickian like diffusion with random direction. The real connection is different from the above two extreme connection situations for the experimental results are away from both fitting curves. The lattice model simulation and the fitting show again that the EB phase connection is not good at grain boundary.

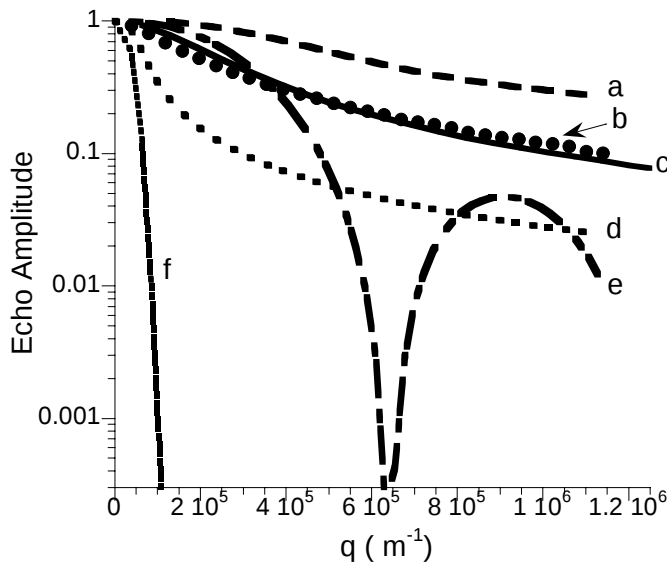


Figure 9. Echo amplitude versus q : (a) spatial averaging over randomly oriented cylinders with $R \rightarrow 0$ and $L = 1.6 \mu\text{m}$; (b) PFG experiment; (c) lattice model simulation; (d) Fickian-like diffusion, spatial averaging over randomly oriented cylinder with $R \rightarrow 0$ and $L \rightarrow \text{infinite}$; (e) cylinder with symmetric axis angle $\theta = 0$, $R \rightarrow 0$ and $L = 1.6 \mu\text{m}$; (f) Fickian diffusion in homogeneous medium.

In summary, from PFG NMR and lattice model simulation, grain boundaries and grain boundary morphology could play important roles in potential applications of block copolymers as membranes. The morphology controlled by relative block size in the triblock copolymer only partially determines transport in an actual membrane. The partially sulfonated SEBS copolymer may have good selectivity for water over DMMP. PFG NMR can directly assess the effects of grain boundaries. The lattice model simulation provides a quantitative interpretation of the PFG NMR experiment and improves our understanding of the diffusion process. In addition, our extension of the lattice model to simulate the diffusion induced PFG NMR signal attenuation leads to a new way to interpret the PFG NMR experiment.

Technology transfer

The results of our measurements and interpretation are shared on an on going basis with our collaborators at the Natick Army Research Laboratory.

Copies of technical reports-none