

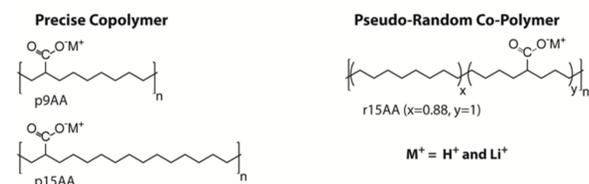
Todd M. Alam^{1,*}, Janelle E. Jenkins¹, Dan S. Bolintineanu¹, Mark J. Stevens¹, Amalie L. Frischknecht¹, C. Francisco Buitrago², Karen I. Winey², Kathleen L. Opper³, and Kenneth B. Wagener⁴

¹Sandia National Laboratories, Albuquerque, NM ; ²University of Pennsylvania, Philadelphia, PA; ³DuPont Central Research and Development, Wilmington, DE; ⁴University of Florida, Gainesville, FL.

ABSTRACT

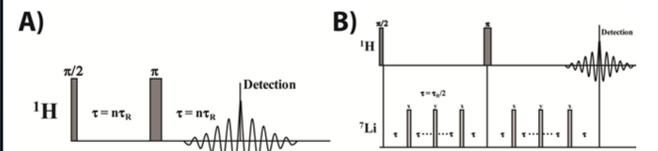
The carboxylic acid proton and the lithium coordination environments for precise and random Li-neutralized polyethylene acrylic acid p(E-AA) ionomers were explored using high speed solid state ^1H and ^7Li MAS NMR. While the ^7Li NMR revealed only a single Li environment, the chemical shift temperature variation was dependent on the precise or random nature of the p(E-AA) ionomer. The ^1H MAS NMR revealed two different carboxylic acid proton environments in these materials. By utilizing ^1H - ^7Li rotational echo double resonance (REDOR) MAS NMR experiments, it was demonstrated that the proton environments correspond to different ^1H - ^7Li distances, with the majority of the protonated carboxylic acids having a close through space contact with the Li. Molecular dynamics simulations suggest that the shortest ^1H - ^7Li distance corresponds to un-neutralized carboxylic acids involved in the coordination environment of Li clusters. These solid state NMR results show that heterogeneous structural motifs will need to be included when developing descriptions of these ionomer materials.

Methods: NMR & Calculations



Polymers with precisely spaced carboxylic acid groups were prepared using the ADMET chemistry, and polymers with randomly spaced carboxylic acid groups were obtained with the ROMP synthetic method. The unneutralized polymer materials are designated as p9AA, p15AA and r15AA, and correspond to samples with the carboxylic acid groups either precisely (p) located every 9th and 15th carbon along the backbone, or to samples where the acid groups are randomly (r) located on the polymer backbone, but with the average number of 15 carbons between the acid groups.

The Li^+ neutralized ionomers were prepared by dissolving the acid copolymer in a 1:4 mixture of 1,4-dioxane and 1-butanol at 90 °C, adding the appropriate amount of lithium acetate salt, followed by filtration of the resultant precipitant. These Li-neutralized materials are designated as p22AA-43%Li, p15AA-45%Li and r15AA-31%Li.



The solid-state 1D ^1H magic angle spinning (MAS) NMR spectra were obtained on a Bruker AVANCE-III spectrometer operating at 600.13 MHz using a 2.5 mm broadband MAS probe, with a 30 kHz spinning speed. The ^1H - ^7Li REDOR experiments were obtained using the XY8 sequence (B). The REDOR buildup curve simulations were performed using the SIMPSON software package. A series of different ^1H - ^7Li dipolar coupling were analyzed to produce the different buildup curves shown in Figures 2 and 3. Fully atomistic molecular dynamics simulations were carried out using the LAMMPS software, and the OPLS-aa force field. Simulations were carried out at a constant density and a constant temperature of 150 °C, well above the glass transition temperature of these materials. The number of polymer chains in the simulations varied between 80 and 200 depending on the spacer length, with each chain containing four repeat units (i.e. four acid groups). The small $\text{Li}^+(\text{CH}_3\text{COOH})_4$ clusters were optimized in the gas phase using the Gaussian 09 software (Gaussian Inc., Wallingford CT) using the 6-311++G(2d,2p) basis set, and density functional theory (DFT) utilizing Becke's three parameter exchange functional, and the LYP correlation function (B3LYP). To evaluate the variation in the chemical shield as a function of Li-O distance, structures were re-optimized assuming a fixed and equal bond distance (symmetric cluster). The chemical shielding tensors, σ , were calculated using the Gaussian 09 program utilizing the gauge-including atomic orbital (GIAO) method at the DFT level.

^1H - ^7Li REDOR MAS NMR

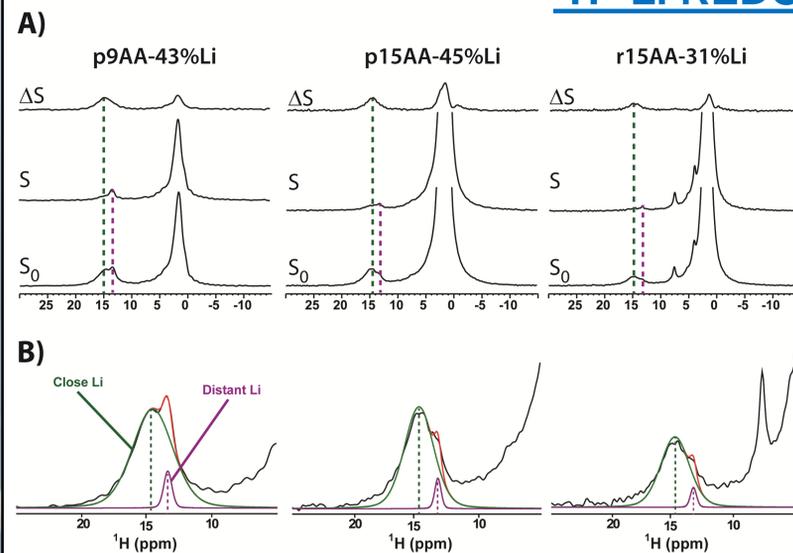


Figure 1: A) The solid state ^1H MAS REDOR NMR of the partially Li-neutralized precise and pseudo-random p(E-AA) ionomers for $\tau = 1.8$ ms. The reference spectra are denoted by S_0 , while the ^1H - ^7Li -dipolar coupled dephased spectra are labeled S , and the differences spectra by ΔS . B) The spectral expansion of the reference spectra for carboxylic acid region showing the deconvolutions of the acrylic acid proton region into two different environments corresponding to a "close" and "distant" ^1H - ^7Li distances.

Table 1: ^1H and ^7Li MAS NMR chemical shifts, line widths, and relative fractions of the acid proton and lithium environments in the random and precise Li-neutralized p(E-AA) ionomers.

Sample	T_g (K)	$\delta(^1\text{H})$ (ppm) ^a	FWHM (^1H) (Hz) ^a	Fraction (%) ^a	$\delta(^7\text{Li})$ (ppm) ^b	FWHM (^7Li) (Hz) ^b
p9AA-43%Li	346	+14.7 +13.4	2050 520	89% 11%	0.20	280
p15AA-45%Li	347	+14.8 +13.3	1680 360	94 6	0.21	290
r15AA-31%Li	313	+14.9 +13.3	1790 360	94 6	0.35	265

^a ^1H MAS NMR results obtained at 294 K, at 30 kHz spinning speed. ^b The ^7Li MAS NMR chemical shift reported for 315 K.

What is the Structural Motif?

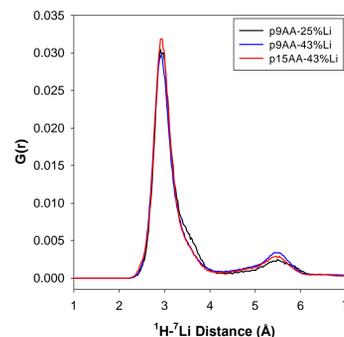


Figure 7: ^1H - ^7Li pair correlation functions for different p(E-AA) ionomers predicted from MD simulations (150 °C).

Table 2: Position of the maximum, relative fraction and average distance for the different ^1H - ^7Li environments predicted from MD simulations.

Sample	^1H - ^7Li (Å)	Major Fraction (%) ^a	^1H - ^7Li (Å)	Minor Fraction (%) ^a	$\langle ^1\text{H}$ - $^7\text{Li} \rangle$ (Å)
p9AA-25%Li	2.91	84	5.49	16	3.43
p9AA-43%Li	2.93	80	5.43	20	3.49
p15AA-43%Li	2.95	83	5.53	17	3.42

^a $G(r)$ integration regions were between 0 and 4 Å, and 4 and 7 Å.

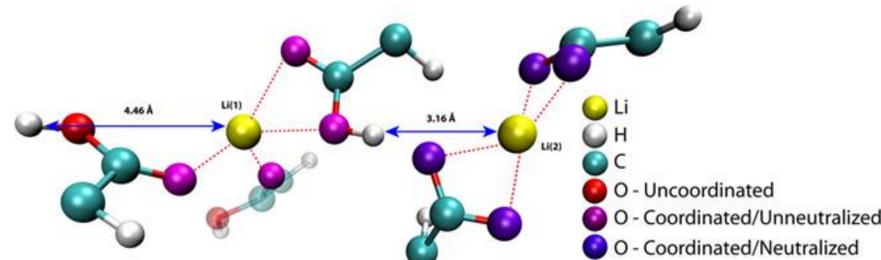


Figure 8: Extracted MD snap shot showing the two different ^1H - ^7Li bonding environments.

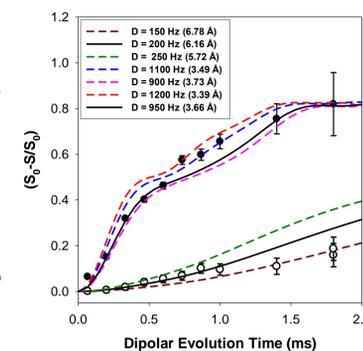


Figure 2: ^1H - ^7Li REDOR MAS NMR buildup curves for the carboxylic acid proton environments at $\delta = +14.7$ ppm (\bullet) and $\delta = +13.4$ ppm (\circ) in the p9AA-43%Li ionomer material.

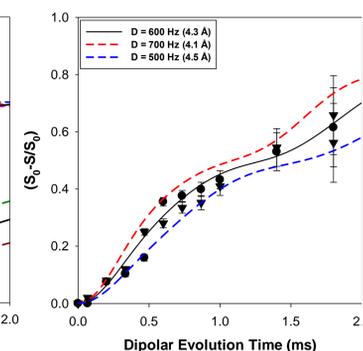


Figure 3: ^1H - ^7Li REDOR MAS NMR buildup curves for the average carboxylic acid proton environments in the p15AA-45%Li (\bullet) and r15AA-31% (\blacktriangledown) ionomer material.

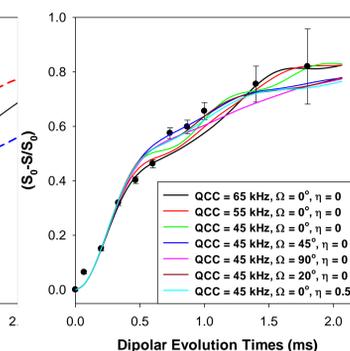


Figure 4: Predicted ^1H - ^7Li REDOR buildup curves as a function of the quadrupolar coupling constant (QCC) and the relative orientation of the EFG and ^1H - ^7Li dipolar tensors (Ω). The experimental REDOR response for the p9AA-43%Li ionomer is also shown (\bullet). The ^1H - ^7Li dipolar coupling constant was 1100 Hz for all simulations.

^7Li MAS NMR

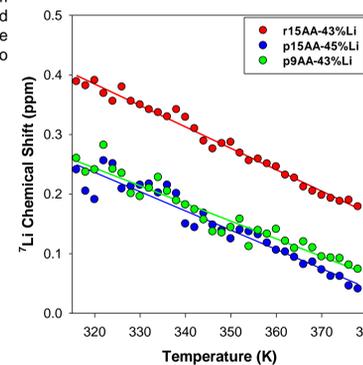


Figure 5: Temperature variation of the ^7Li MAS NMR chemical shifts for different partially Li-neutralized p(E-AA) ionomers.

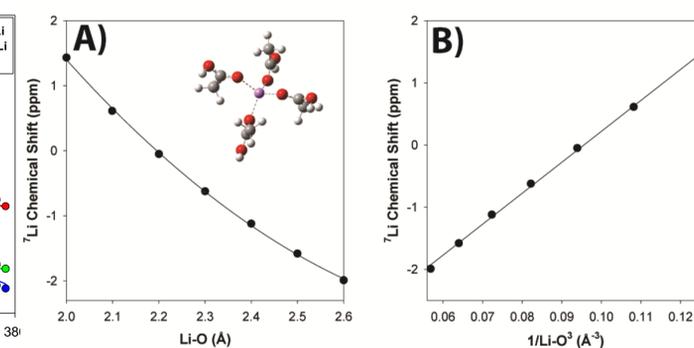


Figure 6: *Ab initio* calculations of the ^7Li NMR chemical shift variation with Li-O distances in the tetra-acetic acid-Li cluster.

Conclusions

- Solid state MAS NMR reveals that distinct heterogeneous carboxylic acid structural motifs exist within the materials, while only a single Li environment was observed.
- Using REDOR NMR it was shown that the two different carboxylic acid proton environments result from different ^1H - ^7Li coordination distances, and reflect the different acid coordination environments.
- These environments do not change significantly with spacing between acid groups or the degree of Li neutralization.
- MD simulations allowed the development of a structural motif that can explain these observations.
- The structure involves acid coordinated Li atoms that are in extended clusters. The majority of the unneutralized carboxylic acids are directly involved in the local Li coordination sphere, with both oxygen atoms coordinating to the Li, and the acid proton forming an additional hydrogen bond to another oxygen coordinated to Li.
- The NMR results also show that isolated, unneutralized, acid-acid dimer formation is not significant in these materials.
- The Li environment is very consistent, and shows only a small variation with temperature.