# Random or Precise? Solid-State NMR Structure and Dynamics Characterization of Zinc Neutralized Polyethylene Acrylic Acid Ionomer

Janelle E. Jenkins[1], Michelle E. Seitz[2], C. Francisco Buitrago[2], Karen I. Winey[2], Kathleen L. Opper[3], Travis W. Baughman[3], Kenneth B. Wagener[3] and Todd M. Alam[1]

[1]Electronic and Nanostructured Materials, Sandia National Laboratories, Albuquerque, NM 87185. [2]Department of Material Science, University of Pennsylvania, Philadelphia, PA 19104. [3]Department of Chemistry, University of Florida, Gainesville, Florida 32611.

Introduction

Ionomers, polymers with ionic groups covalently bonded along the polymer backbone, have unique properties that researchers are hoping to exploit for use as polymeric electrolytes in the development of future fuel cells and battery materials. The mechanical and conductive properties of ionomers vary and change with manipulation of the ionomer morphology.[1] Currently, a more detailed understanding of the correlation between structure and function in ionomers is needed before these polymers can be fine tuned to optimize the coveted ionomer properties for efficient use in new applications. Until recently, limitations in synthetic processes have produced ionomers with randomly placed ionic groups, making it difficult to determine correlations between properties and structure in ionomers. With the development of two new synthetic methods, acyclic diene metathesis (ADMET) and ring-opening metathesis polymerization (ROMP), ionomers with precise ionic group and pseudorandom ionomers with equimolar ionic groups as those present in the precise ionomers can now be synthesized, making direct comparisons between precise and random ionomers possible.[2] These synthesis methods have provided a unique opportunity to characterize the structure and dynamics of ionomers utilizing solid-state NMR methods and to establish correlations between the various morphologies of these materials. The differences between precise and random poly(ethylene-*co*-acrylic acid) (EAA) with various carbonyl spacing are investigated (**Figure 1**).[3] The effect of zinc neutralization at different percentages was also be investigated.[4]
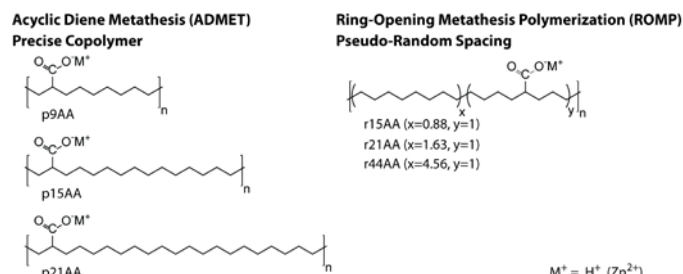
Figure 1. Poly(ethylene-*co*-acrylic acid) with precise and pseudo-random spacing of the carbonyl pendant group synthesized by the ADMET and ROMP methods, respectively.

Experimental

Materials Preparation. The synthesis and characterization of the linear ethylene-*co*-acrylic acid copolymers has been previously described.[3] Polymers with precisely spaced carboxylic acid groups were prepared using the acyclic diene metathesis (ADMET) method. These polymer samples are designated as p9AA, p15AA and p21AA, and reflect samples where the carboxylic acid group precisely (p) located every 9th, 15th and 21th carbon along the backbone, respectively. The relative acid concentrations are 22, 13.3, and 9.5 mol%, respectively. A ring-opening methathesis polymerization (ROMP) procedure was used to produce materials of equivalent acid concentrations, but with the carboxylic acid groups randomly distributed along the polymer backbone. The designation r15AA, r21AA and r44AA reflect the random (r) nature and the average number of carbons between acid groups. The structures of these random and precise materials are shown in Figure 1.

The Zn^{2+} neutralization of the PE-AA copolymers has been previously described.[4] These polymer samples are designated as p21AA-56%Zn, p21AA-116%Zn, p15AA-82%Zn and p9AA-66%Zn to reflect the initial precise copolymer and the extent of neutralization. The extent of Zn^{2+} neutralization achieved was determined using inductively coupled plasma elemental analysis performed by Galbraith Laboratories (Knoxville, TN). The generalized structure for the exchanged PE-AA copolymers is shown in Figure 1. The materials utilized for the NMR studies had previously been hot pressed at 150 °C (~ 0.4 mm film thickness) for X-Ray scattering analysis. These polymer films were used as received unless otherwise noted.

Solid-State NMR Spectroscopy. The solid-state ^{13}C MAS NMR spectra were obtained on a Bruker AVANCE 400 MHZ spectrometer using a 4 mm broadband MAS probe, operating at 100.63 MHz for ^{13}C. All experiments were collected at 10 kHz MAS, with spin regulation maintained at ± 1Hz through the experiments. The temperature was regulated at 298 K for all samples, with the exception of p15AA which was regulated at 248 K to ensure that data was collected below T_g for this sample. The ^{13}C MAS NMR chemical shifts were referenced to the external standard adamantane, $\delta(^{13}C)$ = +38.56 ppm for the downfield peak.

All $^1H \rightarrow ^{13}C$ cross-polarization (CP) data was matched to the -1 spinning sideband (ssb) of the Hartmann-Hahn (HH) condition. $^1H \rightarrow ^{13}C$ CP conditions consisted of a 3.4μs ^1H pulse, followed by a 1 ms contact pulse with ^1H rf field strength of 70kHz. A recycle delay of 5 s and two-pulse phase-modulated (TPPM) ^1H decoupling with a rf field strength of 70kHz was used. The spin-lock experiment consisted of a ^1H 3.4 μs pulse, followed by a 5ms ^1H spin-lock pulse, followed by a 1 ms CP contact pulse consistent with the CP conditions above. The dipolar filter consisted of a 15 ^1H 90° pulse train separated by a delay τ, where τ = 11 μs. The train of pulses was looped twice prior to a 1ms CP contact pulse consistent with the above CP conditions.

All directly detected ^{13}C data was collected with recycle delays ranging from 60 to 600s depending on the sample, with TPPM ^1H decoupling of rf field strength of 70kHz used. To ensure that the data was quantitative, ^{13}C T_1 values were evaluated for each sample (data not shown) and a recycle delay in excess of 5 times the longest ^{13}C T_1 for an individual sample was utilized. Spectra deconvolutions were performed utilizing the DMFIT software package.[5]

Results and Discussion

Pseudo-Random versus Precise Samples. The solid-state ^{13}C data exhibits the expected large signal from the backbone CH_2 resonances between 28-33ppm, with a small signal for the CH at 44-49ppm (**Figure 2**). ^{13}C CP experiments, in combination with dipolar and spin-lock filtering techniques were utilized to highlight amorphous and crystalline regions of the each sample, respectively. This data was then deconvoluted to extract peak
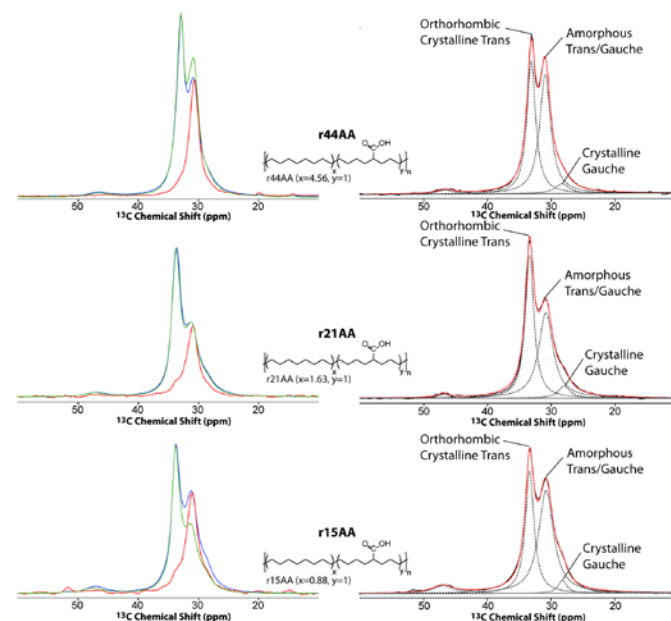
Figure 2. Solid-state ^{13}C NMR data of pseudo-random polymers with stack plot of ^{13}C CP experiments shown on the left with ^{13}C CP (blue), ^{13}C CP with spin-lock (green), and ^{13}C CP with dipolar filter (red). On the right are the corresponding fully relaxed, quantitative ^{13}C direct data with deconvoluted peaks shown in dashed lines.

positions and linewidths for the amorphous and crystalline regions. These linewidths and peak positions could then be utilized as constraints to fit the fully relaxed, quantitative data and extract percentages of amorphous and crystalline regions in each sample (**Figure 2**, right side). The left side of **Figure 2** depicts the CP experiments with the dipolar and spin-lock filters. The signal-to-noise for the CH peak in these filtering experiments is too low to make any concrete conclusions in determination of the inclusion of the CH in the crystalline or amorphous regions; however these filtering experiments can be utilized to investigate the CH_2 peaks. When comparing the red spectra (dipolar filter) to the overlay of the CP spectra (blue) for each sample, it is evident that the higher ppm peak is suppressed, as well as a small shoulder on the lower ppm side. This indicates that the higher ppm peak and low ppm shoulder are crystalline for all three pseudo-random samples, with the remaining signal indicative of a disordered, amorphous region.
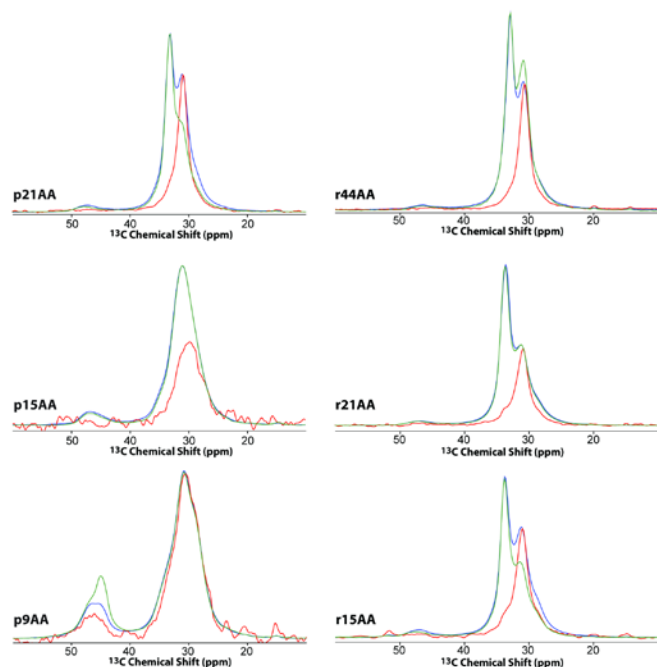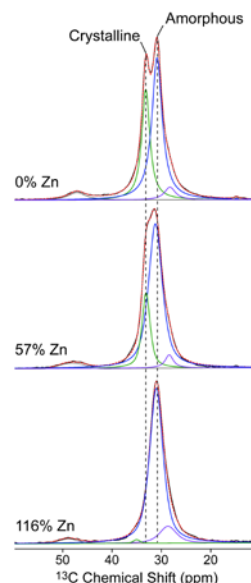

Figure 3. Solid-state ^{13}C NMR data of the precise (left) compared to the pseudo-random (right) polymers with stack plot of ^{13}C CP (blue), ^{13}C CP with spin-lock (green), and ^{13}C CP with dipolar filter (red).

A comparison of the ^{13}C CP data for the precisely spaced pendant groups and pseudo-random samples is depicted in **Figure 3**. It is evident from the filtering experiments, as well as the lack of distinct crystalline chemical shifts for the p15AA and p9AA that unlike the pseudo-random samples, every precise sample does not contain a large crystalline component. These differences are also observed in the ^1H CH_2 lineshape.[6] In the pseudo-random samples, where there are possibilities of long CH_2 runs before a pendant group, there is a larger percentage of the sample that is able to form crystalline regions. A distinct crystalline peak is observed in the p21AA, were the pendant groups are the farthest apart. However, as the distance between the pendant groups decreases for p15AA and p9AA, a crystalline peak is not present indicating that theses samples are more disordered. This is most likely the inherent nature of an increase in defects that are caused by the closer spaced pendant groups.

Zinc Neutralization of Precise Ionomer. Fully relaxed, quantitative direct ^{13}C NMR data of p21AA with increasing amount of zinc neutralization is seen in **Figure 4**. As mentioned above, this is the only precise sample that exhibits a distinct crystalline region. Following this crystalline resonance in **Figure 4**, the peak decreases with increasing Zn neutralization. At 57% Zn neutralization, the crystalline peak has decreased by approximately half its size and at 116% Zn, the crystalline peak is arguably gone. This decrease in crystallinity is attributed to pendant groups aggregating around the Zn, increasing the degree of disorder with increasing Zn neutralization. It should

also be mentioned that the amorphous peak shifts to a slightly higher ppm with increasing Zn neutralization.

Figure 4. Solid-state fully relaxed, quantitative direct ^{13}C NMR data of p21AA with increasing amount of zinc neutralization.

Conclusions

All three pseudo-random samples exhibit a percentage of crystallinity, while only the precise sample with the largest spaces between pendant groups (p21AA) is partially crystalline. This indicates that as pendant group spacing decrease and molar percent of the pendant group increases, a larger number of defects are present that prevent cryallization. Additionally, an increase in Zn neutralization causes a decrease in crystallinity. Again this is most likely due to the pendant groups aggregating around the Zn ions, increasing the degree of disorder and preventing crystallization. It is also shown that ^{13}C CP experiments with dipolar and spin-lock filters can be utilized to obtain constraints, such as peak position and linewidths, which can them, be applied to fit fully relaxed, quantitative direct ^{13}C data. This method is applied to both the pseudo-random and precise samples (data not shown here).

References
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