

Supporting Information

Nanoscale Morphology in Precisely Sequenced Poly(ethylene-*co*-acrylic acid) Zinc Ionomers

Michelle E. Seitz, Christopher D. Chan, Kathleen L. Oppen, Travis W. Baughman, Kenneth B. Wagener, Karen I. Winey

Experimental Details

Materials. A branched poly(ethylene-*ran*-methacrylic acid) copolymer (Nucrel[®] 699) with randomly spaced acid groups was obtained from Dr. John Paul of DuPont and was used as received (see **Figure 1**). It contains ~4 mol% (11 wt%) methacrylic acid and is denoted BPERMAA₄. Using ZnO in a melt extrusion process, it was neutralized to 29, 55 and 78 mol% (see **Table 1**). The neutralized form is denoted BPERMAA₄-ZnY where Y is the neutralization extent. Earlier reports on these melt-neutralized materials include work by Welty, Ooi, and Grady¹ as well as Winey *et al.*² Neutralizing BPERMAA₄ from solution rather than in the melt does not affect the size or morphology of the ionic aggregates as evaluated by STEM and X-ray scattering.³

Linear poly(ethylene-*co*-acrylic acid) copolymers with either precise or pseudo-random acid spacing were synthesized via ADMET and ROMP techniques, respectively. Details of their synthesis and characterization have been previously described.⁴ They are shown schematically in **Figure 1** and denoted, respectively, as PEpAA_x and PErAA_x where x is the mol% acid. For neutralization of the ADMET and ROMP materials, the acid copolymers were dissolved at a concentration of 10% w/w in a 75/25 v/v solvent mixture of 1,4 dioxane and 1-butanol at 50 °C. A stoichiometric amount of dried zinc acetate was dissolved in 75/25 dioxane/butanol at less than 0.1% w/w concentration. The zinc acetate solution was added drop wise into the polymer solution. The solution was stirred for 3 h and then precipitated in methanol. The precipitate was

recovered via filtration and then dried under vacuum at 80 °C for 5 days. The extent of neutralization achieved from the solution neutralization procedure was determined by inductively coupled plasma elemental analysis performed by Galbraith Laboratories (Knoxville, TN) on samples with masses ranging from 6 – 28 mg. The error is estimated at ± 0.5 wt% which corresponds to approximately ± 5 % in the reported mol % neutralization. The neutralized samples are denoted with ZnY where Y is the mol% neutralization determined from the elemental analysis. The materials studied are summarized in **Table 1**.

Sample Preparation. The samples were melt-pressed at 150 °C between sheets of polytetrafluoroethylene in a Carver 4122 hot press to form X-ray samples of approximately 30 x 10 x 0.4 mm. Pressing resulted in the formation of uniform films for all samples. All samples were subjected to rapid cooling (~ 8 °C/min) in the press by flowing tap water. The drawn samples are produced by cutting 10 x 1 x 0.4 mm pieces from the X-ray samples, heating them with a hot air gun, elongating while soft, and allowing them to cool very rapidly in air (~ 200 °C/min). For X-ray scattering studies at elevated temperatures, samples were loaded into 1.0 mm diameter glass capillaries (Charles Supper Co. Special Glass 10-SG) which were then flame sealed.

Characterization. Scanning transmission electron microscopy (STEM) specimens were sectioned from the X-ray films using a Reichert-Jung ultra-microtome equipped with a diamond knife. Specimen preparation was performed at -120 °C with a cutting speed of 0.4 mm/s and nominal section thickness of 50 nm. STEM experiments were performed on a JEOL 2010F field emission scanning transmission electron microscope equipped. The instrument was operated at 197 kV with either a 0.3 nm or 0.7 nm STEM probe and 70 mm condenser aperture. Images were acquired using a high-angle annular dark field (HAADF) scintillating detector with linear

intensity response. The collection angles were 50-110 mrad. Feature sizes were determined using the protocol described by Benetatos *et al.*⁵

Differential scanning calorimetry (DSC) was performed using a TA instruments Q2000. Calibrations were made using a sapphire standard for peak temperature transition and enthalpy. The samples were 5 mm diameter discs of approximately 6 - 9 mg cut from the X-ray samples and then hermetically sealed into aluminum pans. They were then heated to 150 °C to erase thermal history, cooled to 35 °C at a rate of 10 °C and isothermally recrystallized for 1 hour. Samples were then measured at a heating rate of 10 °C/min under a helium purge.

The X-ray scattering apparatus consists of a Nonius FR591 rotating-anode generator operated at 40 kV \times 85 mA, mirror-monochromator or pin-hole focusing optics, an evacuated flight path, and a Bruker HiSTAR multiwire two-dimensional detector. Data were acquired at sample-detector distances of 124, 54, or 11 cm, corresponding to a q ($q=(4\pi/\lambda) \sin\theta$) range of ~ 0.1 -16 nm⁻¹. 2D data reduction, analysis, and curve fitting were performed using Datasqueeze software.⁶ For temperature studies, sample-filled capillaries were loaded into a Linkham oven and temperature was controlled via a Linkham TMS 94 temperature controller. Samples were held at temperature for at least 5 minutes prior to data collection to ensure thermal equilibrium was achieved. Typical data collection times were 120 minutes for distances of 124 and 54 cm, 60 minutes for distances of 11 cm, and 20 minutes for all data take at temperatures higher than room temperature.

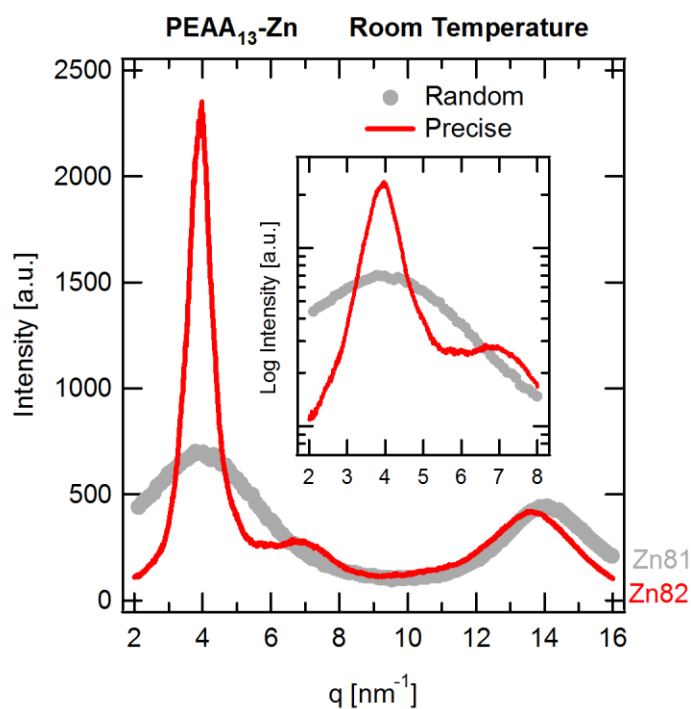


Figure S1. Room temperature scattering curves for PErAA₁₃-Zn82 and PErAA₁₃-Zn81 plotted on a linear scale with the inset showing just the feature associated with interaggregate interference on a log scale.

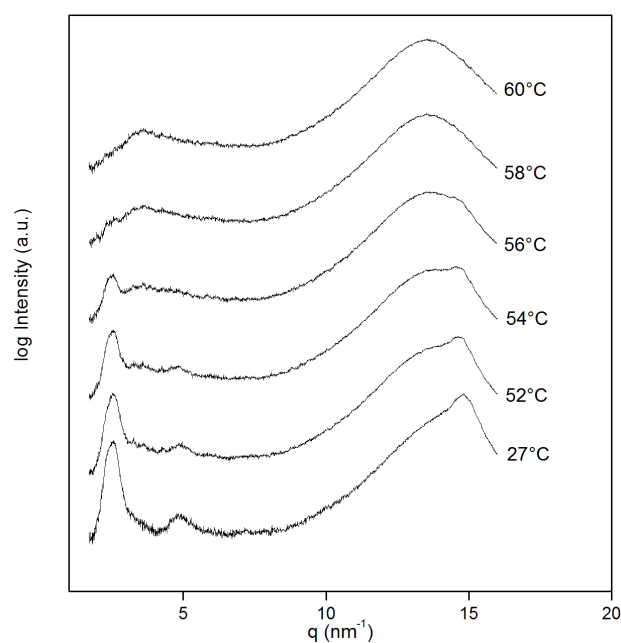


Figure S2. X-ray scattering intensity vs q for PEPAA_{9.5}-ZnO as a function of temperature showing that the transition is complete by 58 °C. Samples were held isothermally for 5 minutes before collecting data for 20 minutes.

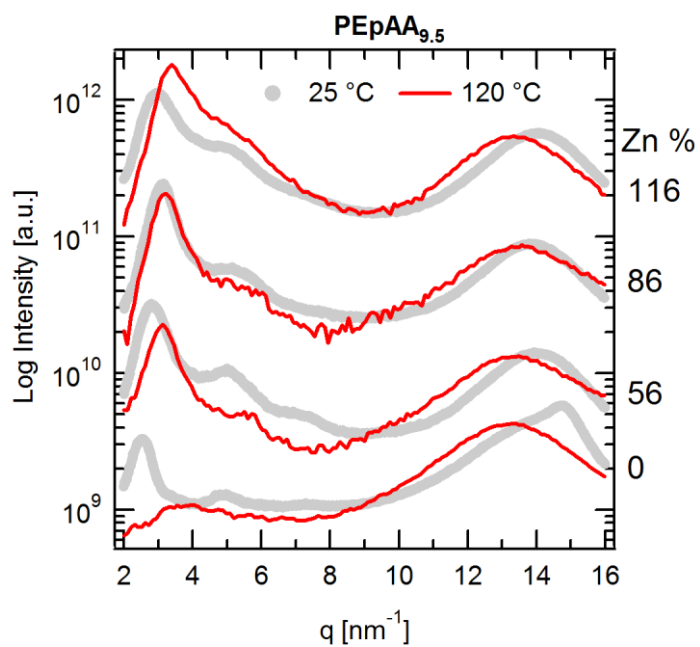


Figure S3. Comparison between X-ray scattering at room temperature (circles) and 120 °C (lines) for PEPAA_{9.5}-Zn ionomers clearly showing the shift in peak locations as the materials become amorphous.

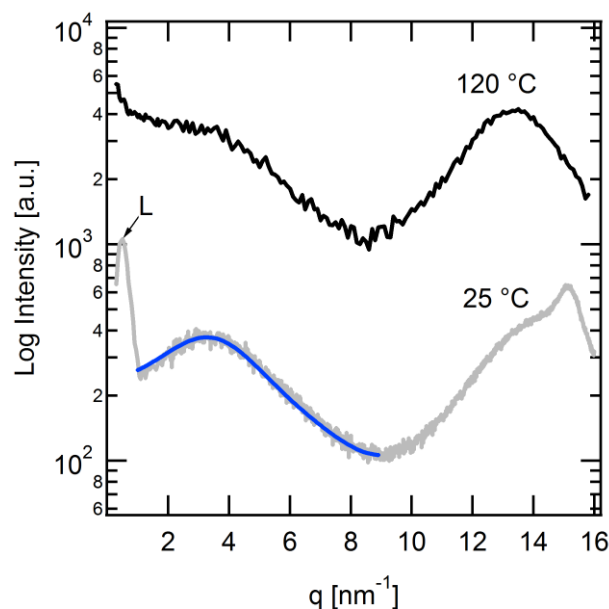


Figure S4 Scattering curves showing expanded q range for BPERMAA₄-Zn78 at room temperature and 120 °C. The peak due to interlamellae scattering is clearly present in the room temperature curve and is marked with an L. The KT fit to the room temperature ionomer peak with $R_I = 0.35$ nm, $R_{CA} = 0.72$ nm, and $N_p = 0.05$ nm⁻³ is shown in blue. The high temperature ionomer peak cannot be fit with confidence.

References

- (1) Welty, A.; Ooi, S.; Grady, B. P. *Macromolecules* **1999**, *32*, 2989.
- (2) Winey, K. I.; Laurer, J. H.; Kirkmeyer, B. P. *Macromolecules* **2000**, *33*, 507.
- (3) Chan, C. D., University of Pennsylvania, 2008.
- (4) Baughman, T. W.; Chan, C. D.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2007**, *40*, 6564.
- (5) Benetatos, N. M.; Smith, B. W.; Heiney, P. A.; Winey, K. I. *Macromolecules* **2005**, *38*, 9251.
- (6) Heiney, P. A. *Commission on Powder Diffraction Newsletter* **2005**, *32*, 9.