# Precise Acid Copolymer Exhibits a Face-Centered Cubic Structure

C. Francisco Buitrago,[†] Kathleen L. Opper,[‡] Kenneth B. Wagener,[‡] and Karen I. Winey*[,†,§]

Departments of [†]Chemical and Biomolecular Engineering and [§]Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, United States

[‡]Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

**ABSTRACT:** A linear polyethylene precisely functionalized with geminal phosphonic acid pendants on every 21st carbon atom exhibits face-centered cubic (FCC) packing of acid aggregates. X-ray scattering from isotropic films result in higher-order scattering peaks used to determine the lattice parameter at room temperature ($a_{FCC}$ = 4.19 nm) and above the melting temperature of the polyethylene matrix ($a_{FCC}$ = 4.06 nm). Upon stretching the precise acid copolymer, an anisotropic scattering pattern featuring two coexisting crystalline orientations results, both having the ⟨110⟩ direction of the FCC lattice along the stretching direction. This is the first report of cubic ordering of aggregates in an acid copolymer and it is the direct consequence of the molecular precision of the polymer.
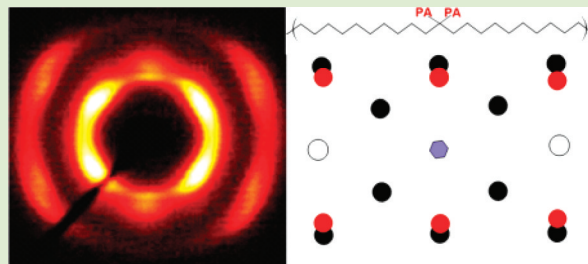
Acyclic diene metathesis (ADMET) polymerization has produced the first family of precise acid copolymers[1,2] and ionomers.[3] These precise materials are linear, high molecular weight polyethylenes featuring acid or ionic pendants separated by a specific and constant number of carbon atoms. Precise acid copolymers and ionomers present researchers with unprecedented control over the molecular structure of polyethylenes functionalized with polar moieties, which in turn allows for a thorough investigation of the factors controlling the resulting morphologies and properties.

Baughman et al.[1] published room temperature X-ray scattering data for linear polyethylene with precisely placed carboxylic acid groups and reported a set of new higher-order scattering peaks corresponding to the separation between carboxylic acid dimers. FT-IR and NMR[4] further confirm the presence of acid—acid dimers at room temperature. The distance between acid dimers in the semicrystalline copolymer with a carboxylic acid group on every 21st carbon is 2.53 nm, which is comparable to the length of 21 carbon—carbon bonds in an all-*trans* conformation (2.7 nm). This correlation distance between acid groups decreases systematically as the number of carbons between acid groups decreases. Moreover, in the semicrystalline acid copolymer, the acid dimers are arranged in layers that are perpendicular to the polymer chain, although Baughman et al. were unable to determine if acid layers are positioned inside or on the surface of the lamellae. The morphologies of these precise acid copolymers were also studied above the melting temperature, where Seitz et al.[3] found a weak X-ray scattering peak, indicating smaller separations between acid dimers, as expected for an amorphous structure.

In precise polyethylene ionomers partially neutralized with Zn, the ionic groups form ionic aggregates.[3] As the content of Zn cations increased due to higher acid content and higher percent of neutralization, the extent of polyethylene crystallinity

at room temperature decreased and the ionic aggregates persisted about the melting temperature. However, the most striking observation was when the ionic aggregates were found to assemble on a cubic lattice. Specifically, the precise ionomer with a carboxylic acid on every ninth carbon and partially neutralized with Zn (66 mol %) has a high temperature (120 °C) X-ray scattering profile that is consistent with a body-centered cubic (BCC) packing of aggregates with a radius of ~0.5 nm.[3] That was the first report of ionic aggregates packing into a periodic structure, and it is a direct result of the precision in the parent acid copolymer.

More recently, precise copolymers with phosphonic acid (PA) pendants have been synthesized.[2] In a previous study[5] of branched, randomly substituted polyethylene with PA groups, microphase separation of PA aggregates was demonstrated by DSC and DMA. Microphase separation driven by hydrogen bonding between the PAs reduces the interfacial area between the PA pendants and the nonpolar polyethylene. While carboxylic acids have two hydrogen bonding sites and therefore prefer to form dimers, PA groups have three hydrogen bonding sites that could lead to larger assemblies. Here we report a face-centered cubic (FCC) morphology of a linear polyethylene precisely substituted on every 21st carbon atom with two PA groups. A combination of room and elevated temperature X-ray scattering from isotropic and stretched polymers were critical in identifying the FCC morphology in this precise geminal PA copolymer.

Poly(ethylene-*co*-vinylidene phosphonic acid) was polymerized by ADMET chemistry, and its synthesis, molecular characterization, and thermal properties are described elsewhere.[2] The result is a linear, high molecular weight

polyethylene ($M_n$ = 19.5 kg/mol, PDI = 1.71) precisely functionalized with geminal phosphonic acid groups on every 21st carbon atom. This acid copolymer is shown in Scheme 1 and is denoted as p21gPA, where p and g indicate a precise copolymer with geminal substitution.

**Scheme 1. Linear Poly(ethylene-*co*-vinylidene phosphonic acid) with Geminal Phosphonic Acid Groups on Every 21st Carbon Atom, p21gPA**
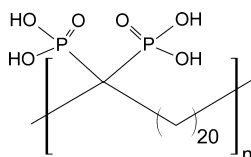
The one-dimensional X-ray scattering profile of p21gPA at room temperature shows several intense peaks between scattering vectors ($q$) of 1.5 and 8.0 nm$^{-1}$, Figure 1a. The observed peak breadth in Figure 1a for p21gPA is ~0.2 nm$^{-1}$, as given by the half-width-at-half-maximum. This is comparable to the peak breadth measured for highly crystalline silver behenate over the same $q$ range. Thus, the instrument resolution, rather than the finite crystal size, dominates the observed peak breadth. The first peak at $q$ = 2.6 nm$^{-1}$ has a shoulder at ~3.1 nm$^{-1}$. Moreover, there are two peaks at 4.8 and 5.1 nm$^{-1}$ that overlap. The $q$ values of these four peaks can be converted to Bragg distances ($d$) in real space by $d = 2\pi/q$. These peak positions deviate significantly from the two previous cases discussed in the introduction, namely, a layered morphology and a BCC lattice of aggregates in precise acid copolymers[1] and ionomers,[3] respectively. In addition, this scattering profile is not consistent with the modified liquid-like scattering model of monodisperse spheres that is widely applied to acid-containing polymers and ionomers.[6]

The multiple scattering peaks for p21gPA agree exceptionally well with the expected reflections from a FCC ordering when the 2.6 nm$^{-1}$ peak is taken as the first allowed reflection. The allowed reflections for a FCC lattice are indicated by their {$h\ k\ l$} Miller indices in Figure 1a. The expected {2 2 0} reflection for FCC is not observed. If, as a first approximation, we assume that the PA aggregates form spheres, the aggregate size can be determined by form factor scattering. An aggregate radius ($R_{agg}$) of 1.1 nm produces a minimum in the spherical form factor scattering that coincides with the missing {2 2 0} reflection, Figure 1a. One can certainly imagine other ionic aggregate shapes from ellipsoids to strings to 3D continuous periodic structures that might minimize chain stretching. In fact, recent simulated bead−spring polymers with precisely spaced ionic groups have found both discrete, globular aggregates and percolated, string-like aggregates, depending on the details of the molecular architectures.[7] For the remainder of this letter, we will maintain the underlying assumption of spherical aggregates.

Using the experimentally observed Bragg distances ($d$) and the Miller indices, the FCC lattice parameter ($a_{FCC}$) was determined using

$$d = \frac{a_{FCC}}{\sqrt{h^2 + l^2 + k^2}} \tag{1}$$

The data in Figure 1b corresponds to a FCC lattice with $a_{FCC}$ = 4.19 ± 0.03 nm. Given this lattice parameter, the center-to-center distance between aggregates is 2.96 nm, which is larger than the aggregate diameter (2.2 nm), as expected. The data presented in Figure 1 demonstrates that at room temperature, phosphonic acid groups in p21gPA microphase separate and assemble on a FCC lattice in a polyethylene matrix.

The 1.1 nm aggregate radius, which was approximated by matching a spherical form factor minimum with the missing peak in the scattering data, can be evaluated by comparing the volume fraction of acid aggregates based on the FCC structure ($\phi_{FCC}$) and the volume fraction of acid groups calculated based on stiochiometry ($\phi_{stoi}$).

$$\phi_{FCC} \equiv \frac{4 \cdot \left(\frac{4}{3} \cdot \pi \cdot R_{agg}^3\right)}{a_{FCC}^3} \tag{2}$$

$$\phi_{stoi} = \frac{2 V_{PA}}{V_{p21gPA}} \tag{3}$$

In eq 3, $V_{PA}$ is the volume of a PA pendant, $V_{p21gPA}$ is the volume per repeating unit of p21gPA, and the factor of 2 reflects the geminal functionalization. These volumes were
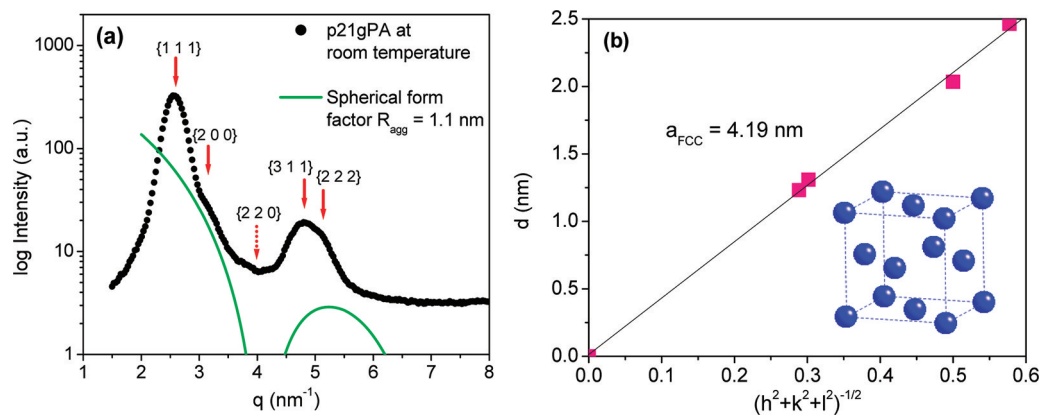
**Figure 1.** (a) X-ray scattering intensity as a function of $q$ for p21gPA at room temperature. The arrows indicate the peak positions corresponding to the allowed reflections from a FCC lattice with a lattice parameter of $a_{FCC}$ = 4.19 nm. The green line is the spherical form factor for acid aggregates of radius $R_{agg}$ = 1.1 nm. (b) The measured Bragg distances from X-ray scattering as a function of the assigned Miller indices. The best-fit line uses eq 1 to determine $a_{FCC}$. The inset shows a FCC lattice, but note that the acid aggregates in blue are shown smaller than experimentally determined for clarity.
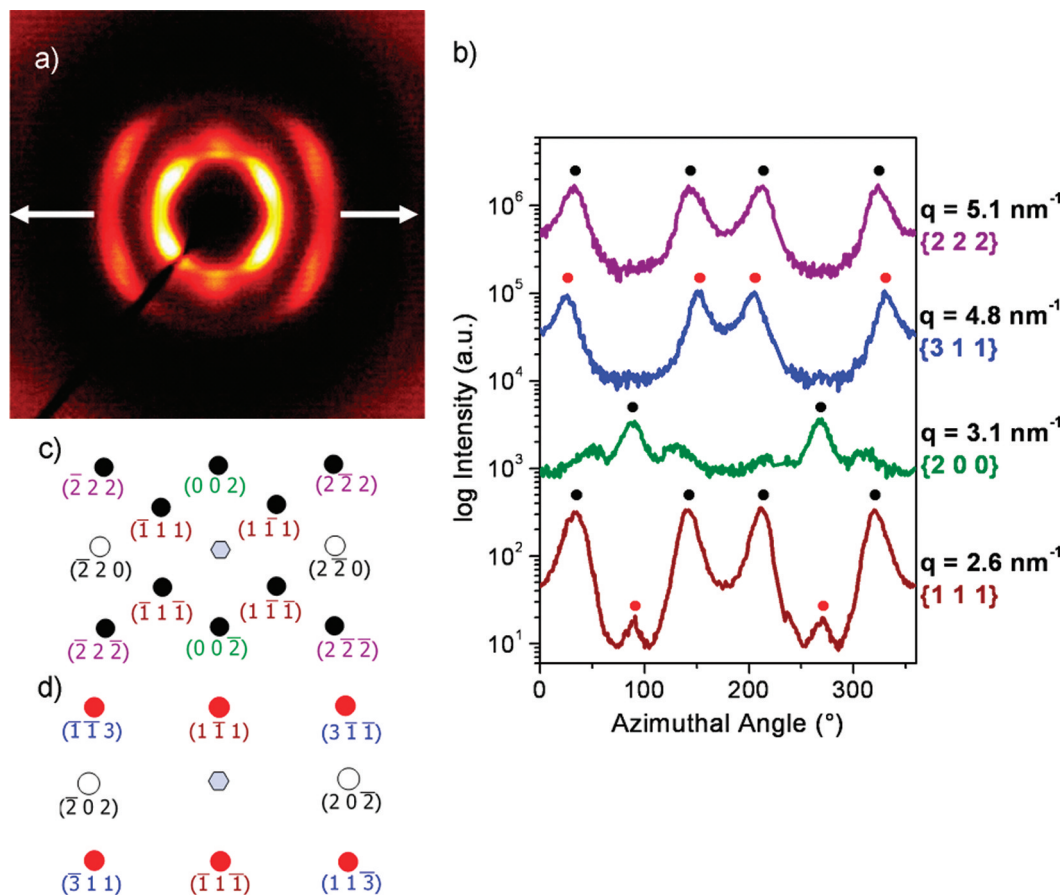
**Figure 2.** (a) Room temperature X-ray scattering data from a stretched film of p21gPA, where the arrows indicate the stretch direction and correspond to the ⟨1 1 0⟩ direction. (b) X-ray scattering intensity as a function of azimuthal angle extracted from (a) and the specified $q$ values. Simulated diffraction patterns for single crystal FCC lattices when the beam is along the [1 1 0] direction (c) and along the [1 2 1] direction (d). The expected {2 2 0} points, which are not observed in the data due to a minimal in the form factor scattering, are represented as open circles. Black and red dots in (b) indicate whether the observed diffraction peak corresponds to the crystal orientation in (c) or (d), respectively.

calculated from the molecular weight of the monomeric unit and the densities of amorphous polyethylene ($\rho_{\text{PE,amorphous}}$ = 0.855 g/cm$^3$)[8] and pure phosphonic acid ($\rho_{\text{PA}}$ = 1.23 g/cm$^3$).[9] The volume fractions calculated from the proposed morphology and the chemical stoichiometry are in good agreement: $\phi_{\text{FCC}}$ = 0.30 and $\phi_{\text{stoi}}$ = 0.28. This analysis further supports the FCC unit cell. However, an aggregate of $R_{\text{agg}}$ = 1.1 nm contains 25 geminal PA groups, as found by dividing the volume of one aggregate by $V_{\text{PA}}$. This aggregation number appears to be inconsistent with our assumption of spherical aggregates and thereby suggests an alternative aggregate shape with form factor scattering similar to a sphere. Regardless of the aggregate shape, the lattice symmetry is FCC.

The one-dimensional scattering data in Figure 1a was obtained from an isotropic p21gPA film that gave uniform scattering rings at the two-dimensional X-ray scattering detector. Figure 2a is the two-dimensional X-ray scattering profile of a p21gPA sample stretched in the direction of the arrows. This anisotropic scattering pattern is analyzed in Figure 2b by plotting the intensity as a function of azimuthal angle at the four $q$ positions corresponding to FCC peak positions. At the lowest $q$ (2.6 nm$^{-1}$) corresponding to the {1 1 1} family of planes, four strong peaks are evident at azimuthal angles of 36, 144, 215, and 322°. In addition, two weaker {1 1 1} scattering points are detected at 90 and 270°. At $q$ = 3.1 nm$^{-1}$, only two {2 0 0} peaks are observed at 90 and 270°. Both the {3 1 1}

and {2 2 2} families of planes at 4.8 and 5.1 nm$^{-1}$, respectively, have four peaks the maxima of which are slightly different. The {2 2 2} family has peaks at the same angles as the {1 1 1}, while the {3 1 1} are at 27, 153, 206, and 331°.

These experimental results are compared to single crystal scattering patterns for a FCC lattice with $a_{\text{FCC}}$ = 4.19 nm simulated using CrystalMaker. Figure 2c and d show the expected calculated patterns when the X-ray beam is along the [1 1 0] and the [1 2 1] crystallographic directions, respectively. Note that the reflections corresponding to the diffraction patterns in Figure 2c and d are indicated in Figure 2b with black and red dots, respectively. The four {1 1 1} peaks with 2-fold symmetry in Figure 2c correspond to the strongest peaks in the experimental data. The two meridional {1 1 1} peaks in Figure 2d are consistent with the weaker {1 1 1} peaks in Figure 2b. The observed {2 0 0} and {2 2 2} peaks correspond to the single crystal scattering position in Figure 2c, while the experimental {3 1 1} peaks match the pattern in Figure 2d. The allowed {2 2 0} reflections in the single crystal diffraction patterns are shown in Figure 2c and d, but are missing in Figure 2a, because as discussed for the isotropic scattering data the {2 2 0} reflections coincide with a minimum in the spherical form factor.

In summary, the experimental X-ray scattering pattern from a stretched film of p21gPA is consistent with two coexisting FCC crystal orientations. These two crystal orientations have a

common direction, namely the ⟨1 1 0⟩ direction, that is parallel to the stretch direction. These two crystal orientations were found to coexist across the stretched film and were found repeatedly when new films were stretched.

Finally, X-ray scattering on isotropic p21gPA was performed at 155 °C, a temperature well above the reported $T_m$ of this acid copolymer.[2] Figure 3 shows the one-dimensional X-ray
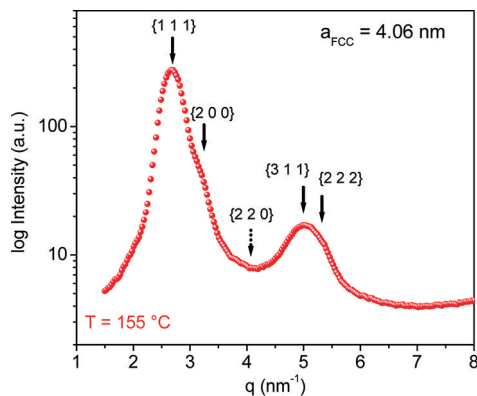


**Figure 3.** (a) X-ray scattering intensity as a function of $q$ for p21gPA at 155 °C. Arrows indicate the allowed reflections for an FCC lattice with $a_{FCC} = 4.06$ nm. The {2 2 0} reflection is absent due to a minimum in the form factor for a sphere with $R_{agg} = 1.1$ nm.

scattering profile. X-ray scattering data at elevated temperature and room temperature are comparable with peak assignments consistent with a FCC lattice. The lattice parameter at 155 °C as determined using eq 1 is 4.06 ± 0.03 nm, just 3% smaller than the room temperature lattice parameter. The cubic ordering of the PA aggregates in p21gPA clearly persists at elevated temperature, which confirms that the reported $T_m$ corresponds to crystallization in the polyethylene matrix rather than ordering of the FCC lattice of aggregates. This observation is in marked contrast to the precise monosubstituted carboxylic acid copolymers wherein the hierarchical structure of layered acid dimers deteriorates significantly when the temperature was raised from room temperature to 120 °C.[3]

The synthesis of linear polyethylene with pendant acid or ionic groups precisely spaced along the polymer chain has resulted in materials with hierarchichal morphologies.[1,3] In this instance, X-ray scattering shows that geminal phosphonic acid substitution on the 21st carbon produces microphase separation with acid aggregates on a FCC lattice. This morphology persists at elevated temperature and the ⟨1 1 0⟩ crystal direction aligns with the stretch direction. This marks the first report of cubic packing in precise polyethylene-based acid copolymers.

## EXPERIMENTAL METHODS

A p21gPA film for room temperature X-ray scattering was hot-pressed at 150 °C and cooled to room temperature in ambient air. An oriented sample was obtained by drawing a hot-pressed film in hot air and then cooling to room temperature under tension. Both films were aged at room temperature for 3 days before X-ray scattering experiments at room temperature. For X-ray scattering at 155 °C, a sample was loaded into a sample cell with mica windows.
X-ray scattering was performed using a Nonius FR 591 rotating-anode generator operated at 40 kV and 85 mA. A bright, highly collimated beam was obtained via Osmic Max-Flux optics and triple pinhole collimation under vacuum. The scattering data were collected using a Bruker Hi-Star multiwire two-dimensional detector with an 11 cm

sample-to-detector distance, corresponding to a scattering vector between 1.5 and 8.0 nm⁻¹. The 2-D data reduction and analysis were performed using the Datasqueeze software.[10] For temperature studies, a Linkham oven controlled via a Linkham TMS 94 temperature controller was used. The sample was held at elevated temperatures for at least 1 h prior to data collection to ensure thermal equilibrium. At both thermal conditions, X-ray scattering data were collected for 45 min.

## AUTHOR INFORMATION

**Corresponding Author**

*Phone: (215) 898-0593. Fax: (215) 573-2128. E-mail: winey@seas.upenn.edu.

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