

Solution-grown crystals of precise acid- and ion-containing polyethylenes

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ABSTRACT

Crystals of precise acid- and ion-containing polyethylenes were prepared from solution. While large pendant groups on polyethylene backbones are typically excluded from the crystalline domain, the precisely-placed acid and ionic functional groups are accommodated into the solution-grown crystals. Polyethylene containing carboxylic acid pendant groups on every 21st carbon atom (p21AA) grows into rectangular shaped crystals with an average thickness of 9 nm, which is 3–4 times the all-*trans* chain length between the functional groups. This thickness indicates that the carboxylic acid groups are incorporated within the crystals. Electron diffraction images and Raman spectra indicate that p21AA backbones are hexagonally packed with more *gauche* chain conformations than the polyethylene orthorhombic phase. The precise polyethylene containing geminal carboxylic acid groups placed every 21 carbon atoms (p21gAA) forms irregular-shaped crystals with an average thickness 8 nm. Similar to p21AA, p21gAA incorporates the geminal acid groups into its solution-grown crystals. Surprisingly, the polymer with imidazolium bromide groups on every 21st carbon (p21ImBr) produces remarkably large crystals with thicknesses of 200–900 nm, and widths of 6–12 μm . Finally, we propose a multi-layer stack of adjacent reentry structures that is consistent with the incorporation of large functional groups into the solution-growth crystals of these precise polyethylenes. Interestingly, this stacked structure is distinct from our recent results in melt-crystallized p21AA, where the layers are nearly transverse to the lamellae.

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1. Introduction

Since the discovery of polymer single crystals and the observation of chain folding phenomenon in the 1960s, characterization of polymer single crystals and investigation of their growth mechanism have been extensively reported, especially for polyethylene (PE) [1–4]. Polyethylene crystallizes from solution in the form of thin lamella on the order of 10 nm in thickness, in which the chains are folded back and forth on themselves at the top and bottom surfaces of the crystal [5]. PE single crystals grown from dilute xylene solution exhibit lozenge shapes with characteristic angles of 67° and 113° at lower crystallization temperature and the

growth front corresponds to the (110) planes of the orthorhombic crystal lattice [6]. Hollow pyramidal shaped PE single crystals were also identified, in which the chains are tilted with respect to the crystal surface by ~30° [7,8]. The hollow pyramids collapse onto the substrates, which tilts the chains at each sector and produces central pleats in the crystal [8]. Truncated-lozenge-shaped PE crystals have also been observed when the concentration or the crystallization temperature is raised [4]. The (110) sectors and (200) sectors in truncated PE single crystals were found to have different chain tilt angles leading to a thickness difference of 1 nm [9]. Understanding the crystalline morphology and chain folding behavior of PE is indispensable for designing PE-based copolymers with broader properties and applications.

In the majority of research on functionalized polyethylene copolymers, pendant groups are randomly placed along the CH₂ backbone [10–13]. The random placement of the functional groups results in disordered morphologies [14,15]. In contrast, nylons,

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which have amide units uniformly separated by CH₂ segments, have a high degree of crystallinity, stiffness, and toughness [16]. Nylons usually crystallize into lathlike single crystals from dilute solutions, e.g. nylon 6, nylon 66, nylon 46, and nylon 68 [17–20]. At low temperature, the chains are found to be either inclined at substantial angles to the lamellar normal with a triclinic unit cell [17] or perpendicular to the lamellar surfaces forming monoclinic unit cell [19–21]. By studying nylon crystalline structures, we know that the unique properties of nylon require both the amide groups and their precise sequence in the polymer microstructure. The amide groups are precisely placed along the backbone and form hydrogen bonds between adjacent chains. Therefore, ordering the functional pendant group sequence in polyethylene copolymers could be a promising and effective strategy to manipulate the morphology and improve physical properties.

Previous studies involving crystallization of precise polyethylenes were mainly focused on polymers with non-associating groups, e.g. alkyl or halide pendants [22]. The precise placement of side groups on the CH₂ backbone (e.g. every 21st carbon) was achieved via acyclic diene metathesis polymerization (ADMET) starting from symmetric diene monomers [23,24]. The ADMET synthesis produces atactic configurations of the pendant groups in the precise polyethylenes. The precisely placed pendant groups facilitate better defined crystalline structure in the polymer, and higher levels of crystallinity compared to polymers with randomly placed pendant groups [14]. An earlier study on the effect of alkyl branch length on the nanoscale morphology of precise PEs demonstrates that larger pendant groups create larger lattice distortions, change the overall lattice structure from orthorhombic to monoclinic, and expel the pendant groups to the surface of solution-grown crystals [25]. The bulky pendant groups are expelled to the crystal surfaces resulting in crystal thicknesses close to the all-*trans* CH₂ length between the pendant groups.

The materials investigated in this paper contain associating pendant groups: carboxylic acid groups, geminal carboxylic acid groups, and 1-methylimidazolium bromide groups on every 21st carbon atom, named p21AA, p21gAA, and p21ImBr, respectively (Fig. 1). The morphologies of these precise acid- and ion-containing polymers have been studied in the bulk via DSC, solid-state NMR, X-ray scattering [26–28], broadband dielectric spectroscopy [29,30], and quasi-elastic neutron scattering (QENS) [31], as well as by atomic molecular dynamic (MD) simulation [32–34]. All three of these polymers exhibit a melting temperature in DSC. Upon cooling from the melt, these polymers exhibit layered morphologies and a hexagonal crystal structure according to X-ray scattering, and the acid- and ion-rich layers are embedded within the crystallites [28]. Note that both layered morphologies and the hexagonal structure are absent above the melting temperatures [27]. The alkyl segments provide the structure with mechanical strength, while the acid- or ion-rich layers might serve as channels for ion or small molecule conductivity. These precise acid- and ion-containing

precise polymers provide an alternative chance for designing new solid polymer electrolyte with both good conductivity and mechanical properties [28]. In the present work, we prepare crystals of these precise PEs from dilute solution and investigate their crystal motifs, unit cell structures, and chain conformations.

2. Experiment

2.1. Materials

The synthesis methods and morphological studies of the three precise materials were published previously [26–28,35]. Symmetric diene monomers were polymerized via acyclic diene metathesis (ADMET) using Grubb's 1st generation catalyst, and the unsaturated polymers were hydrogenated in a high pressure H₂ environment at elevated temperature. The nomenclature of these precise polymers uses “p” to indicate precise and a number indicating the number of carbons in the monomeric repeat unit, Fig. 1. For example, p21AA contains acrylic acid (AA) on exactly every 21st carbons; p21gAA contains geminal acrylic acid (gAA) groups on every 21st carbon; and p21ImBr has 1-methylimidazolium bromide (ImBr) groups on every 21st carbon. The details of the materials are described in Table 1. For comparison, HDPE purchased from Sigma Aldrich was also studied.

2.2. Sample preparation

As shown in Table 1, four types of polymer crystals were grown from dilute solution via a self-seeding method [36] at appropriate crystallization temperature (T_c). To prepare the solution-grown polymer crystals, the polymer was dissolved in solution at a concentration of 0.01 wt% or 0.05 wt%, and was heated to the melting temperature (T_m). The solution was held at the T_m isothermally for 1 h to fully dissolve the polymer. Then the solution was slowly cooled to T_c and held for at least 30 min to induce initial crystallization. After crystallizing for at least 30 min, the polymer solution was heated to the self-seeding temperature (T_s), and held for 10 min. This step is aimed at melting the majority of non-uniform crystals, while the small unmelted nuclei are kept as the crystal seeds for crystal growth in the following step. The solution was then quenched to the T_c and held overnight. This self-seeding method produces crystallites of uniform size, because the large number of seeds in the solution promote rapid nucleation and steady crystal growth. The detailed experiment conditions for each polymer are provided in Table 1.

2.3. Atomic force microscopy (AFM)

The morphology and lamellar thickness of solution-grown crystals were investigated via AFM. A drop of the crystal suspension was deposited on the silicon wafer, and the solvent was allowed to evaporate completely before characterization. A Bruker Icon AFM was used in tapping mode with a silicon cantilever from MIKROMASCH with 325 kHz resonant frequency, 40 N/m force constant, and aluminum coating. All measurements were carried out under ambient conditions. An amplitude setpoint between 400 and 500 mV and scan rate of 1.02 Hz were used to maximize the scanning quality for polymer crystals. Using Nanoscope Analysis software, the resulting images were flattened by 1st order plane-fit before thickness measurements.

2.4. Electron diffraction (ED)

Polymer crystals suspended in solution were deposited onto ultrathin carbon-coated transmission electron microscope (TEM)

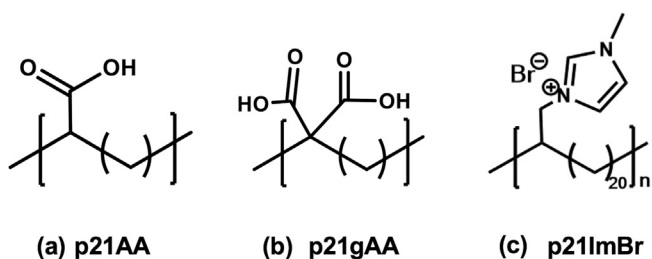


Fig. 1. Chemical structure of three precise polymers: (a) p21AA, (b) p21gAA, and (c) p21ImBr.

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