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Polyethylene Functionalized with Precisely Spaced Phosphonic Acid Groups

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Introduction

Incorporating polar functionality into polyolefins, particularly in polyethylene (PE), broadens the possibilities of altering both microstructure and morphology, thus targeting properties for specific applications.[1,2] Phosphonic acid-based functionalization in polyolefins has gained increasing attention due to the range of properties attainable, rendering these materials useful for applications such as chemical separation, ion exchange, and ion conductive membranes,[3,4] flame retardants,[5] and biomaterials suitable for cell adhesion,[6] bone integration,[7] and dental cements.[8−10] Specifically, because of its importance in a number of these applications, poly(vinylphosphonic acid), PVPA, has been the focus of detailed investigations of homopolymerization mechanisms and resulting microstructures.[11−15] While vinylphosphonic acid polymers have been examined rather extensively, copolymers of ethylene and vinylphosphonic acid have received less attention: they have proven to be difficult to make.

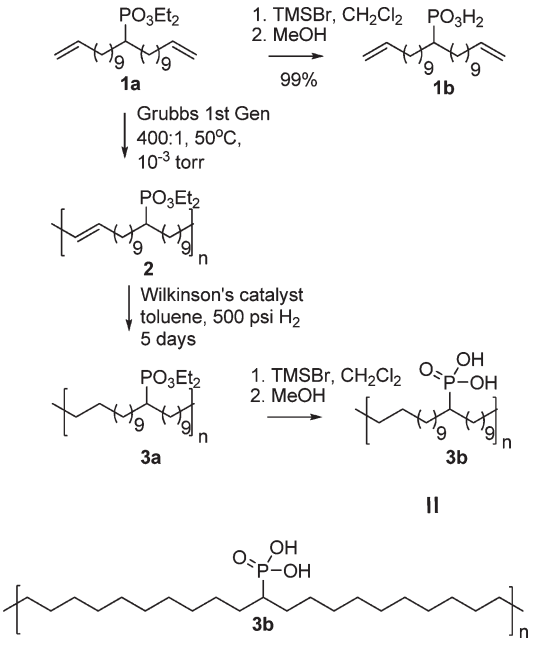
Ethylene-based copolymers containing a variety of functional groups can be made via metathesis polymerization,[16−18] and recently we have begun to examine ethylene-based polymers containing precisely placed acid groups. For example, we reported the preparation of a series of precision ethylene/acrylic acid copolymers, where for the first time structural precision changed the typical morphology for such polymers from clusters of acid groups to a layered morphology.[19]

We now report the preparation of a precision phosphonic acid copolymer, an analogue of the carboxylic acid materials mentioned above, placing the phosphonic acid functional group on each and every 21st carbon of a strictly linear polyethylene backbone. The copolymer was synthesized by metathesis polycondensation chemistry of an appropriately protected α,ω-diene monomer, followed by complete saturation and quantitative deprotection (Scheme 1). *Compared to the typical oxidative phosphorylation reactions on polyethylene,[20−22] this method offers complete control of the microstructure, which will lead to a systematic understanding of how microstructure and resulting morphology dictate particular properties.*

Results and Discussion

Key to success in this synthetic strategy is the preparation of a diene monomer with the functional group of interest (in this case, the phosphonic acid) symmetrically disposed within. This symmetry is carried into the repeat unit, thereby leading to unequivocal structural precision. Also key to success is devising suitable protection chemistry, sufficient to avoid poisoning of the rhuthenium catalysts yet capable of being completely removed after the polymer chemistry is done. This chemical balancing act is a major challenge, one that has been met in the case of these polymers.

Scheme 1. Synthetic Scheme of Precisely Functionalized Polyethylene with Phosphonic Acid on Every 21st Carbon



Scheme 1 provides a view of the protection and polymer chemistry we have used to synthesize the first precision ethylene/vinylphosphonic acid copolymers reported to date. The monomer was synthesized using the alpha dialkylation approach described previously,[23] incorporating the polymer repeat unit into the single symmetrical α,ω-diene **1a**. The ethyl groups present in the starting material served as protecting groups throughout monomer synthesis, purification, and metathesis polycondensation chemistry. Complete deprotection was first demonstrated on the monomer (prior to polymerization) as a model study of this chemistry. Quantitative deprotection was observed using the bromotrimethylsilane approach to form a silated ester in situ, which was then cleaved in aqueous methanol to the free acid **1b** with no further purification necessary after removal of residual reactants.[24] There is no question that the protection group can be removed quantitatively using this approach.

Copolymer **2** was obtained after polymerization of protected monomer **1a** using Grubbs' first-generation catalyst under the mild conditions of 50 °C and high vacuum. Exhaustive catalytic hydrogenation using Wilkinson's catalyst and 500 psi hydrogen gas yielded the linear ethylene-*co*-vinylphosphonic acid diethyl ester copolymer **3a** with a phosphonic acid ester on every 21st PE backbone carbon. The relative M_n of 19 500 and PDI of 1.7 (determined by GPC vs polystyrene standards) indicate a successful strategy in forming the protected version of the target precision copolymer.

The ^{1}H, ^{13}C, and ^{31}P solution NMR of **3a** (the protected version of the target copolymer) clearly demonstrate the pristine chemical microstructure (Figure 1). The ^{1}H NMR spectrum shown on top contains the methyl end group at 0.88 ppm;

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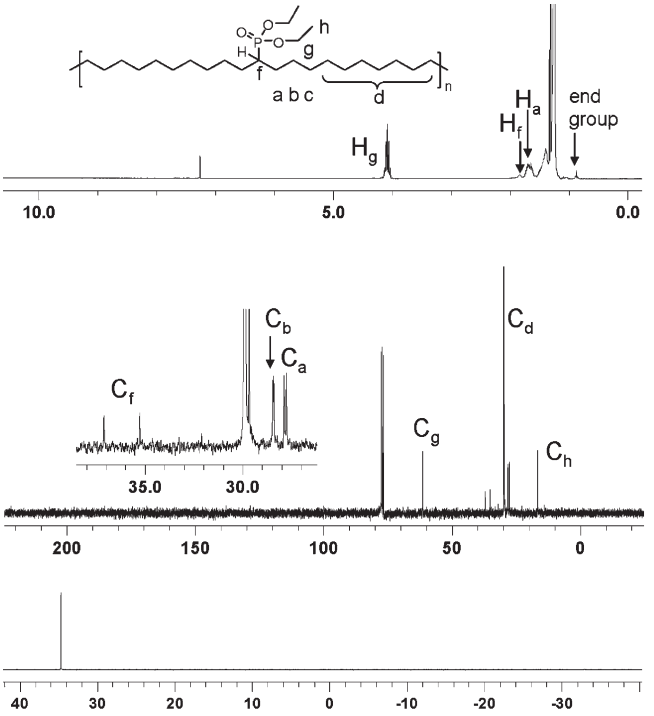

Figure 1. Solution NMR in $CDCl_3$ of ester copolymer **3a**; from the top ^1H, ^{13}C, and ^{31}P spectra.

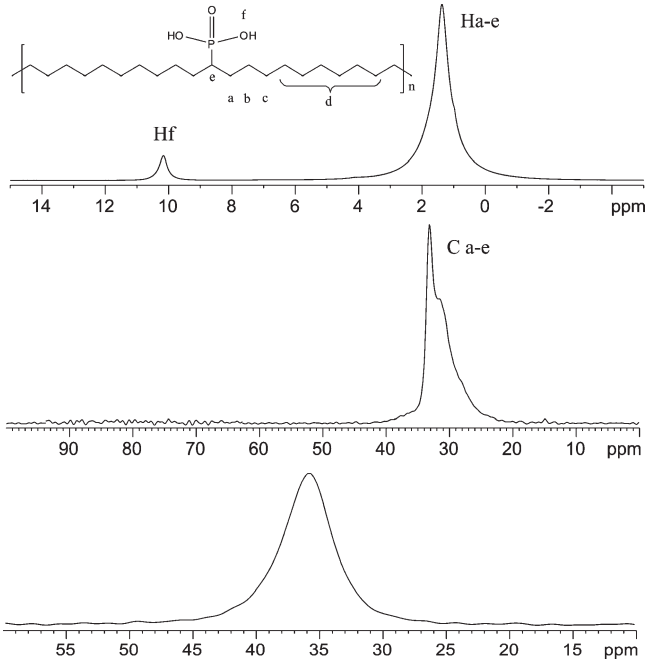

Figure 2. Solid-state NMR of the phosphonic acid copolymer **3b**; from the top ^1H, ^{13}C, and ^{31}P spectra.

incident backbone olefin (d), γ-methylene (c), and methyl groups (h) centered at a broad 1.25 ppm; α-protons (a) centered at 1.69 ppm; methine protons (f) at 1.96 ppm; and downfield-shifted ethyl ester methylene (g) broadened pentet resonance centered at 4.08 ppm. Selected proton integration, specifically ester methylene and the methyl end group, are comparable to the GPC M_n measurement. In addition, the controlled precise microstructure is directly transferred from the symmetrical monomer to the saturated copolymer repeat unit with seven distinct ^{13}C NMR resonances additionally showing coupling to ^{31}P. The ^{13}C NMR spectrum of **3a**, shown in the middle, contains major resonances include the ethyl group CH_2 doublet at 62.45 ppm, $^2J_{CP}$ 6.9 Hz (g), CH_3 doublet at 16.73 ppm, $^3J_{CP}$ 5.9 Hz (h), methine (f), α- (a), β- (b), and γ-methylenes (c), and the remaining unresolved backbone carbons (centered at 29.84 ppm). Coupling between phosphorus and the methine (doublet at 36.20 ppm, $^1J_{CP}$ 137 Hz), α-methylene (doublet at 27.83 ppm, $^2J_{CP}$ 9.2 Hz), and β-methylene (doublet at 28.44 ppm, $^3J_{CP}$ 3.5 Hz) carbon atoms splits the resonances into doublets as shown in the inset, while the γ-methylene remains uncoupled on the shoulder of the unresolved backbone carbons at 29.68 ppm. Additionally, the 100% naturally abundant ester ^{31}P is shown as a sharp singlet at 34.81 ppm in the bottom spectrum.

Deprotection is the final step in the synthesis scheme, and though such chemistry would appear to be a facile part of the general scheme, it can be quite challenging. In this case, deprotection using the conditions applied to the monomer (as a model study) is highly effective: as noted below, deprotection of copolymer **3a** is quantitative to yield the precision phosphonic acid copolymer **3b**.

Copolymer **3b** is an extremely tough material, with interchain interaction between the precisely placed phosphonic acid groups apparently being highly effective. It also is quite insoluble in a variety of typical polar organic solvents and solvent mixtures. Consequently, solid-state proton, carbon, and phosphorus NMR was used to firmly delineate the repeat unit structure (Figure 2).

The ^1H MAS NMR spectrum of **3b** exhibits two peaks at 10.2 and 1.4 ppm corresponding to acidic protons and aliphatic protons, respectively. Similarly to PVPA, the latter resonance is attributed to the polymer backbone while the peak at 10.2 ppm clearly reflects partially immobilized hydrogen-bonded protons of the $PO(OH)_2$ unit.[14] Notably, the corresponding ^{13}C-CP MAS NMR spectrum is rather complex. The sharp peak at 33.2 ppm corresponds to the all-trans conformation in the crystalline regions of PE,[25] which is also present in the corresponding precise polymer with CH_3 groups on every 21st carbon.[26] Broadened resonances around 37, 31.7, and 28.8 ppm are assigned to the CH group and the CH_2 groups of the polymer backbone adjacent to the phosphonic acid group, respectively. Moreover, the CH_2 units in the noncrystalline regions of the system will give rise to a broad peak around 29−32 ppm.[25,26] Recently, the nature of defects in such precisely defined polyolefins and their dynamics was elucidated by ^2H and ^{13}C solid-state NMR.[26] In the analogous system with CD_3 instead of $PO(OH)_2$ groups, the chain defects are highly mobile close to the melting point. Whereas in the systems studied here, hydrogen bonding apparently precludes such chain mobility. No peak was found at about 65 ppm (OCH_2 unit), hence indicating successful deprotection of the former ester group. This is further supported by the ^{31}P MAS NMR spectrum that shows *one* fairly sharp resonance at 36.0 ppm (fwhh = 887 Hz) typically found for phosphonic acid-containing polymers.[14] In addition, no indication of anhydride formation is found.[4]

Quantitative deprotection was also examined using IR spectroscopy (Figure 3). Ester monomer **1a** reveals a characteristic ester P═O stretching vibration at 1243 cm^{-1} (Figure 3a) that shifts and broadens to lower frequency at 1143 cm^{-1} in the corresponding acid compound **1b** (Figure 3b). Monomer **1a** also shows further P−O−C ester absorbances at 957, 1029, and 1163 cm^{-1}, while the acid **1b** exhibits the P−OH absorbances of 939 and 1004 cm^{-1}. Additional P−O−H absorbances at 2998 and 2800 cm^{-1} are less pronounced. Upon polymerization and hydrogenation to yield ester copolymer **3a** (Figure 3c), the absorbances attributed to ester functionality match those in the ester monomer **1a**, as expected. Notably after hydrolysis, peaks due to the former ester functionality are removed and replaced by absorbances characteristic of the acid (Figure 3d). In addition, the olefin out-of-plane C−H wag at 967 cm^{-1} is no longer

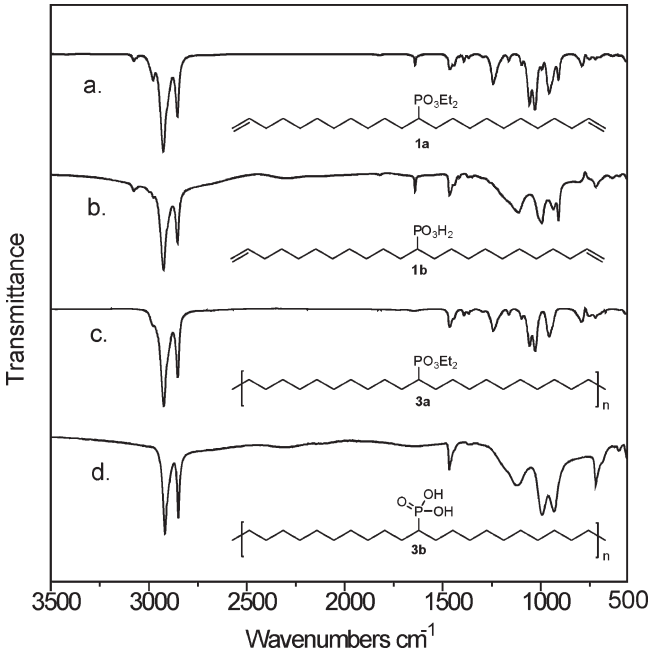

Figure 3. Infrared spectra of (a) protected monomer **1a**, (b) deprotected monomer **1b**, (c) protected copolymer **3a**, and (d) deprotected copolymer **3b**. Samples a, b, and c prepared by $CHCl_3$ solution cast onto KBr disks; spectrum d obtained via ATR.

present, indicating the backbone hydrogenation was complete. These results confirm complete deprotection evidenced by solid-state NMR and support the overall synthesis of precisely defined poly(ethylene-*co*-vinylphosphonic acid) containing a phosphonic acid on every 21st carbon.

Conclusions

Solid-state NMR and FTIR spectroscopic techniques clearly demonstrate the successful synthesis of polyethylene possessing precisely spaced phosphonic acid groups and support the unprecedented structural control in acid-containing polylolefins by the metathesis polycondensation method. Prior work on precision poly(ethylene-*co*-acrylic acid) containing a carboxylic acid on every 21st carbon showed this level of structural control leads to a new morphology.[19] Because of the interplay of precise primary structure and hydrogen-bonded chain immobilization indicated by solid-state NMR, we anticipate the same will hold true for these copolymers and now have begun a series of experiments to compare structure of a variety of acid-containing precision polyolefins.

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Supporting Information Available: Monomer synthetic details; monomer deprotection hydrolysis details; protected and deprotected monomer characterization including ^{1}H, ^{13}C, and ^{31}P NMR, elemental analysis; polymer deprotection details. This material is available free of charge via the Internet at http://pubs.acs.org.

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