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Precision Phosphonic Acid Functionalized Polyolefin Architectures

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ABSTRACT: Polyethylene structures containing precisely placed phosphonic acids were synthesized varying both the frequency of acid appearance along the backbone and the architecture associated with each position. Single, geminal, and benzyl attachment schemes are described with symmetry of placement being an important feature. Altering these precision primary structures has a direct effect on secondary structure where changes in thermal behavior become obvious, particularly in terms of crystallization behavior. It is evident that strong interactions between polymer chains exist, effecting polymer crystallization and solubility depending upon both the length of methylene run-lengths between symmetrically placed acids and whether or not the acid group is protected as the ester or free to participate in hydrogen bonding, which directly influences interchain interaction.

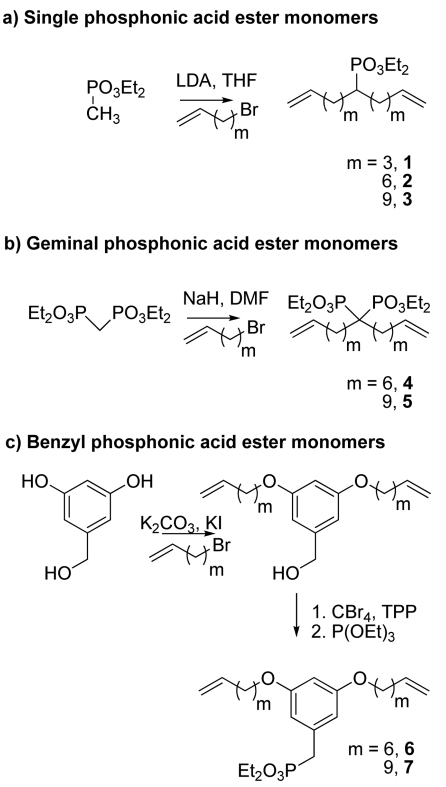
Introduction

The wide range of chemical and physical properties make polyolefins, specifically polyethylene, the highest volume commercial synthetic polymer produced today.[1] The number of commercial applications can be increased by varying the architecture and functionality, thereby enhancing the chemical and physical properties of the otherwise unreactive hydrocarbon backbone.[2−5] Functionalization of polyolefins is typically achieved using polymerization techniques having common pathways of comonomer incorporation or postpolymerization modifications.[3,6−8] There are advantages and disadvantages to each approach. Although polymer composition is easily tunable using comonomer incorporation, monomer reactivity and catalyst activity represent possible challenges. Modifying an existing polymer may result in chain breakage, cross-linking, and unknown amounts of functionality incorporation.

Polymers containing exact placement of functional groups can be obtained using a step-growth metathesis polycondensation technique.[9−11] This approach has been utilized to synthesize strictly linear and otherwise challenging polyethylene (PE) copolymers. After incorporating several traditional ethylene/vinyl repeat units into a single symmetrical α,ω-diene monomer, polymerization via metathesis polycondensation followed by hydrogenation yields a precisely functionalized PE copolymer. This technique not only allows for the precise and tunable incorporation of functional groups but also results in unique polymer structures and morphologies.[12,13]

To further study PE crystallization in the presence of interactive hydrogen bonding groups,[14−16] a family of polyethylenes functionalized with phosphonic acids has been synthesized. Phosphonic acid-containing polymers already have multiple applications as membranes for ion transport, exchange, or barriers,[17−21] as well as biomaterials for dental cements, bone integration or cell adhesion.[22−24] Accordingly, creating a well-defined family of precisely functionalized phosphonic acid-containing polymer architectures, discussed herein, potentially increases the range of applications for such polymers,[25] as recently it was shown that order and crystallinity can dramatically improve the proton mobility by generating defined proton pathways.[26] This study comprises a systematic investigation relating primary and secondary structure of these polymers in the presence of resilient, highly interactive phosphonic acid groups.

Scheme 1. Efficient Monomer Syntheses



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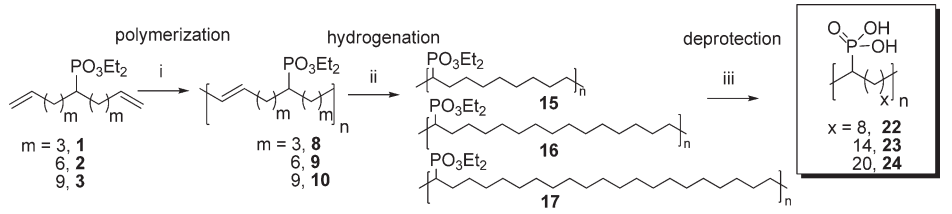

Figure 1. Phosphonic ester and acid polymer family: (i) 0.25 mol % $(Cy_3P)_2Cl_2Ru{=}CHPh$, 50 °C, 10^{-3} mmHg; (ii) $RhCl(PPh_3)_3$, H_2 (40 bar), toluene; (iii) (1)TMSBr, CH_2Cl_2, 24 h, (2) MeOH, 24 h.

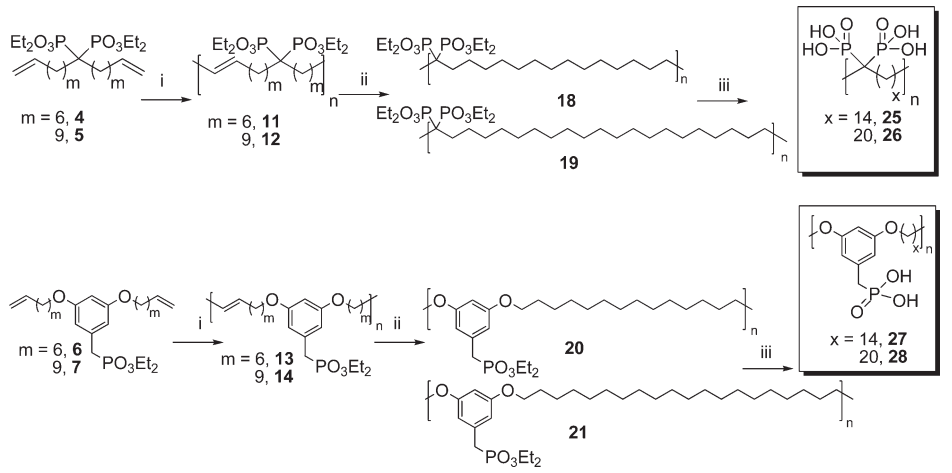

Figure 2. Phosphonic ester and acid variations in functionality and architecture: (i) 0.25 mol % $(Cy_3P)_2Cl_2Ru{=}CHPh$, 50 °C, 10^{-3} mmHg; (ii) $RhCl(PPh_3)_3$, H_2 (40 bar), toluene; (iii) (1) TMSBr, CH_2Cl_2, 24 h, (2) MeOH, 24 h.

Results and Discussion

Synthesis. Structure control begins with the synthesis of 7 monomers, the attachment of protected phosphonic acid groups being varied between protected single acids (**1**−**3**), protected geminal acids (**4** and **5**), and protected benzyl acids (**6** and **7**). Methylene spacing between these symmetrically placed protected phosphonic acid groups is determined using appropriate alkenyl synthons (Scheme 1). Singly attached phosphonic acid ester monomers were synthesized by a two-step, one-pot alkylation reaction.[27] Geminal phosphonic acid ester monomers were prepared using a hydride base for the alkylation, and benzyl phosphonic acid ester monomers were introduced via an etheral benzene linkage. Specifically, after alkylation chemistry to prepare the diene benzyl alcohol, bromination using an Appel reaction followed by an Arbuzov reaction yielded the monomers **6** and **7**.

Figure 1 shows the step-growth metathesis polycondensation technique using protected singly attached phosphonic acid monomers **1**−**3**. Polymerization yields unsaturated polymers **8**−**10**, which upon saturation with hydrogen yields precisely spaced phosphonic acid ester polymers **15**−**17**. Quantitative deprotection using reaction (iii)[27,28] yielded precisely functionalized phosphonic acid polymers **22**−**24** with the spacing between acids containing exactly 8, 14, or 20 methylenes. Polymers **22**−**24** were isolated as insoluble highly interactive polymers after evaporating the methanol and washing with acetone.

The methodology used to alter the architecture of such precision phosphonic acid polymers is shown in Figure 2, where geminal acids are introduced as well as benzyl acids. Polymerization of protected geminal monomers **4** and **5** containing twice the functionality content yielded geminal phosphonic acid ester polymers **11** and **12**, which upon hydrogenation affords polymers **18** and **19**. Upon deprotection, precision geminal phosphonic acid polymers **25** and **26** are obtained as insoluble polymers. Hydrogenation was also performed to yield **20** and **21** and these were subsequently deprotected to generate insoluble precision benzyl phosphonic acid polymers **27** and **28**.

Table 1. Soluble Phosphonic Ester Molecular Weight and Molecular Weight Distribution Data

	GPC data[a]		
polymer	M_n	M_w	PDI
15	10.6	17.1	1.61
16	23.6	40.4	1.68
17	17.9	34.5	1.93
18	6.2	11.4	1.82
19	19.5	33.3	1.71
20	10.6	20.6	1.94
21	7.3	16.4	2.23

[a] In kg/mol obtained in THF relative to PS standards.

As such, solution characterization techniques were utilized on the soluble phosphonic acid ester polymers in supporting primary structure, including functionality content. Additional bulk techniques were utilized in probing acid polymer structure.

Structure. Table 1 shows molecular weight and polydispersity data for the soluble, protected phosphonic acid *ester* polymers. Throughout, monomodal traces were obtained with polydispersity indices (PDIs) of about 2 consistent with the step-growth polymerization technique with the slight variations due to competing reactions. In general, protected single phosphonic acid ester polymers have higher molecular weights with degrees of polymerizations (DPs) of about 50, while an increase in functionality (either as geminal or etheral groups) apparently leads to catalyst deactivation. The exception within single phosphonic acid ester polymers include **16** and **17** with **17** exhibiting a lower DP attributed to inhibition of ethylene removal. However sufficient molecular weights for property comparison were obtained after an

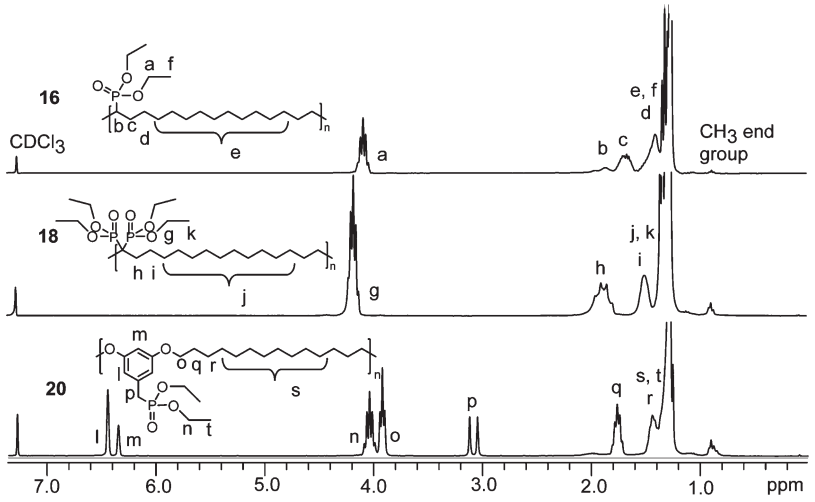

Figure 3. Solution ^{1}H NMR spectra in $CDCl_3$ of soluble ester polymers **16**, **18**, and **20**.

iterative addition of 0.25 mol % catalyst halfway through the polymerization.[29] In the extreme case when geminal and benzyl monomers containing three methylene units underwent polymerization attempts (not shown), only oligomers were obtained. High concentration of functional groups relative to olefin led to the oligomerization under typically ideal bulk polymerization conditions. Following the path of lowering the concentration using solvent was not followed as this would theoretically increase the formation of cyclic structures specifically preformed into the structure by geminal substitution and the Thorpe−Ingold effect.

Representative soluble, protected phosphonic acid *ester* polymer ^{1}H NMR spectra confirm molecular weight via CH_3 end-group integration, hydrogenation shown by the absence of olefin signal at ~4.5 ppm and correct phosphonic acid ester functionality content (Figure 3). The spectrum of single phosphonic acid ester polymer **16** shows the clean polymer structure including methine (b), α-methylene (c), *β*-methylene (d), and unresolved backbone methylene (e) protons along with the ethyl ester CH_2 (a) and CH_3 (f). The spectrum of geminal ester polymer **18** contains α-protons coupled to the two phosphorus atoms (h), *β*-methylene (i) and unresolved backbone methylene (j) protons along with the ethyl ester CH_2 (g) and CH_3 (k). The spectrum of benzyl ester polymer **20** contains benzene protons (l and m); etheral oxygen backbone α- (o), *β*- (q), *γ*- (r), and unresolved (s) protons; benzyl protons (p); and ethyl ester CH_2 (n) and CH_3 (t). Additionally, all ^{31}P NMR spectra showing a single resonance indicated that phosphonic acid esters remained intact prior to hydrolysis.

Functional group identity (protected ester compared to deprotected acid) was further probed using FT-IR and ATR-IR (Figure 4). The most interesting absorbances result from the functional group comparing the ester polymers (**16**, **18**, and **20**) to acid polymers (**17**, **19**, and **21**) within the representative 14-methylene spaced polymers (see Supporting Information for all polymers). The protected single phosphonic acid ester polymer **16** contains absorbances including P═O stretching vibrations at 1243 cm^{-1} and P−O−C aborbances at 955, 1026, and 1164 cm^{-1} with the geminal (**18**) and benzyl (**20**) ester polymers displaying similar motions. Benzyl ester polymer **20** is complicated by 1,3,5-trisubstituted benzene ring motions: strong benzene in-plane C−H bending band at 1054 cm^{-1}, weak symmetric C−O−C stretch at 1040 cm^{-1}, strong etheral C−O−C strong asymmetric stretch at 1247 cm^{-1}. Other benzene motions include C═C ring stretches at 1456, and 1603 cm^{-1}, along with

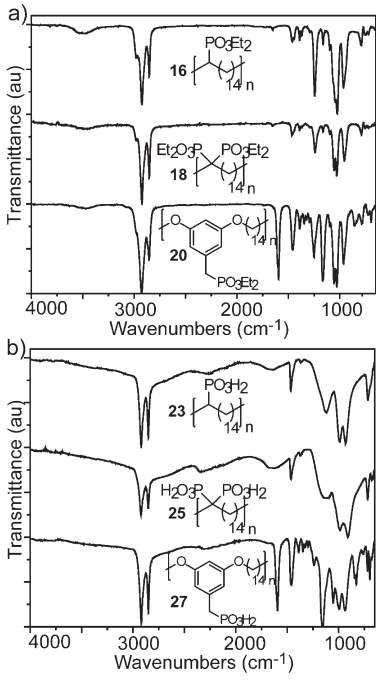

Figure 4. IR spectra comparing the 14-methylene spaced polymers with (a) FT-IR of ester polymers and (b) ATR-IR of acid polymers.

weaker out-of-plane C−H bending bands at 780 and 851 cm^{-1}. Within the representative acid polymers (**17**, **19**, and **21**), the P═O stretch broadens to lower frequency at about 1143 cm^{-1}, and P−OH stretches are observed at ~939 and ~1004 cm^{-1}.

Thermal Properties. The primary structures of all polymers are exact and precisely defined, stemming from the features of metathesis polycondensation chemistry. Trends in secondary structure variation with respect to decomposition and crystallinity become apparent in the thermal properties probed by TGA and DSC.

TGA data is particularly valuable relating the profile shape and decomposition to the acid polymer functionality amount as titration of insoluble materials was not feasible. The TGAs of all protected phosphonic acid polymers show a two-step decomposition profile, attributed to ester and backbone decomposition, yet dependent on the exact identity of either single, geminal or benzyl acid ester polymers

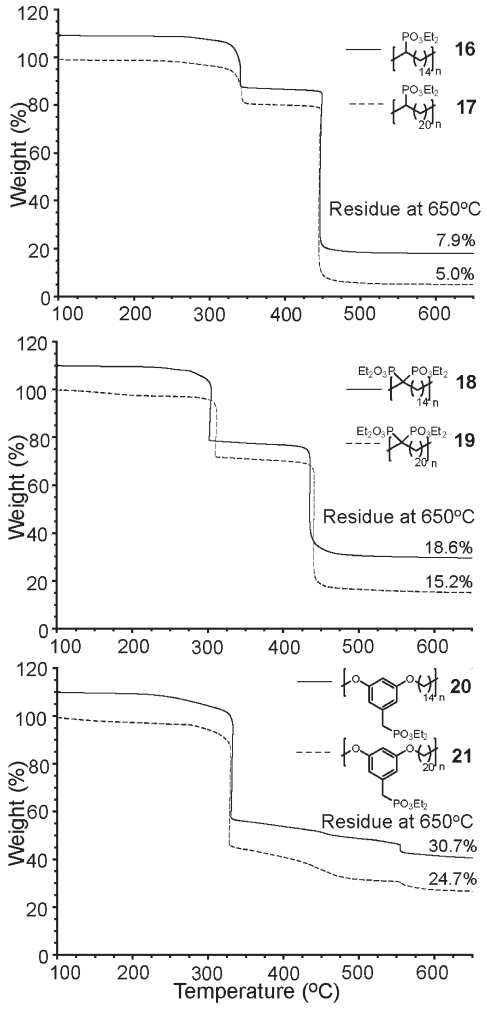

Figure 5. Thermogravimetric analysis comparing phosphonic acid ester polymers containing 14 and 20 methylenes.

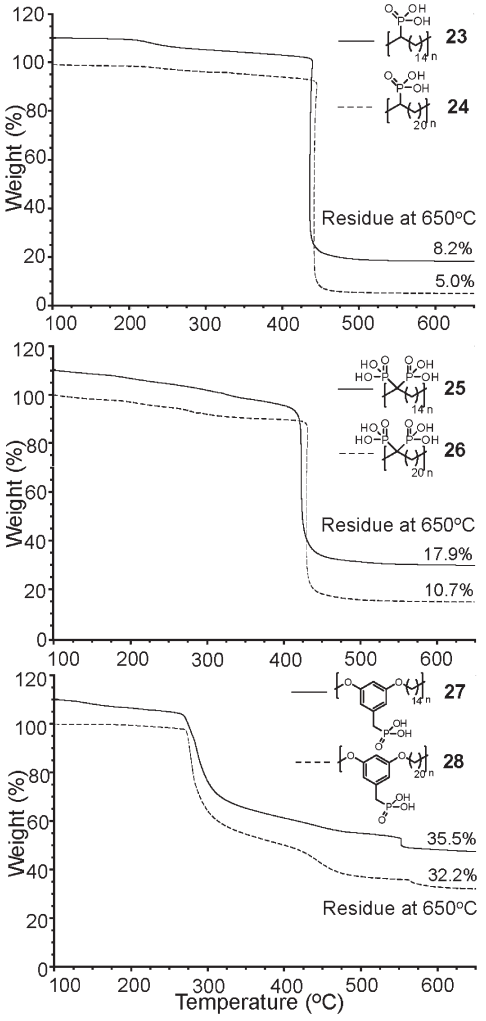

Figure 6. Thermogravimetric analysis comparing phosphonic acid polymers containing 14 and 20 methylenes.

(Figure 5). Each single, geminal or benzyl acid ester polymer profile differs drastically from the corresponding deprotected acid polymer profiles (Figure 6).

Shown in Figure 5, the protected single phosphonic acid ester polymers and geminal ester polymers **16**−**19** first decompose at roughly 300 °C from the loss of ethylene from the ethyl esters.[30] The ether linkage effects benzyl ester polymers **20** and **21** as the first decomposition is much greater than the ester content. Because of the complexity of decomposition in all of these functional polymers, this first mass loss does not exactly correlate as observed in simpler precision halogen substituted structures.[31] *However, when comparing all of the ester polymers* **16**−**21**, *the residue remaining is highest in polymers containing the most functionality*; i.e., polymers possessing more frequent functional groups with 14 methylenes have more residue than those with 20 methylenes, polymers having geminal attachment have more residue than those with single attachment, and polymers having benzyl attachment have the most residue due to the ether linked benzyl ester. The mass % loss of the step decompositions does not quantitatively correlate to any assumed ethyl, ethoxide, or phosphonate cleavage. The remaining residue also does not correlate exactly to specific decomposition products but the general shape of the decomposition profile correlates to the functionalization.

Within the deprotected acid polymers shown in Figure 6, the decomposition profile shape corresponds to a broad undefined loss of functionality coupled to loss of water (presumably through anhydride formation), followed by a sharper one-step decomposition resulting from polymer backbone decomposition. In all cases, there are no similarities in acid decomposition profile shape to ester profile shape. Quantitatively, the functionality content by mass % loss again did not match exactly particular expected acid fragments. However, the trend relating the highest residues remaining to the most functional polymers is upheld.

While the TGA profiles appear similar between specific simple, geminal, and benzyl esters and acids, DSC reveals differences in the crystallization behavior throughout the complete protected ester and deprotected acid families (Table 2).

Table 2. Summary of DSC thermal analysis

esters[a]	T_g[b] (°C)	T_m[c] (°C)	ΔH_m (J/g)	acids[a]	T_g[b] (°C)	T_m[c] (°C)	ΔH_m (J/g)
15	−57			**22**	44		
16	−61			**23**	45		
17	-	11, 13	55	**24**[d]		48,67	23,22
18	−42			**25**	32		
19	−48	47	30	**26**[d]		87	120
20	−25			**27**	43		
21		2	47	**28**[d]		46	42

[a] Second heat shown at 10 °C/min, except where noted otherwise. [b] C_p (J/g°C) were between 0.07 and 0.12. [c] Peak melting temperature. [d] First heat at 10 °C/min after annealing at room temperature for72 h attaining reproducible endotherms.

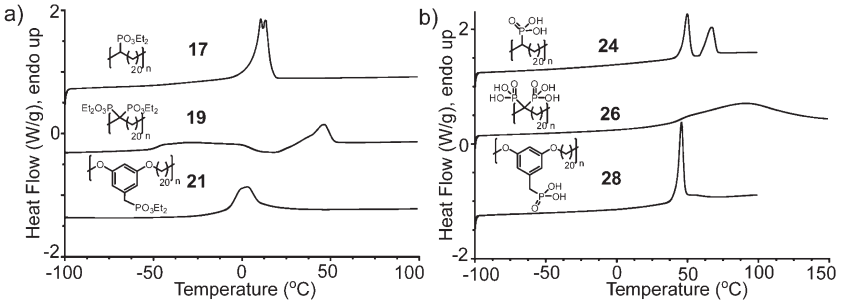

Figure 7. DSC thermograms with arbitrary offsets of (a) semicrystalline ester polymers, second heat shown (b) semicrystalline acid polymers, first heat after 72 h annealing at room temperature shown.

Amorphous ester polymers are obtained for those spaced with 8 and 14 methylenes (polymers **15**, **16**, **18**, and **20**) with glass transitions ranging from −62 to −24 °C. Semicrystalline ester polymers are obtained once the functionality is spaced by 20 methylenes (polymers **17**, **19**, and **21**) with crystallization being attributed to the 20-methylene run-length. Upon hydrolysis to the acid family, amorphous and semicrystalline trends are upheld yet with transitions at higher temperatures. The glass transition temperatures of the amorphous polymers increase by more than 50 °C, ranging from 32 to 45 °C.

The thermal behavior of semicrystalline polymers is complicated by the strongly interacting phosphonic acid functional groups, which causes the melting temperature to increase (Table 2) and also affects the crystallization time scale. In a previous random phosphonic acid-modified polyethylene polymer study containing lower incorporation levels (2.8, 1.8, and 0.8 acids per 100 carbon atoms) than the precision 20-methylene spaced polymers (5 acids per 100 carbons), crystallization kinetics were significantly affected and found to be strongly influenced by annealing and the thermal history.[14] It was also observed that when phosphonic acid frequency was increased to 7.4 acids per 100 carbons, similar to 14-methylene spaced polymers, no crystallization was observed. In the precision single, geminal, and benzyl phosphonic acid polymer family presented here, a similar behavior is observed when the run-length is reduced below 20 methylenes. As noted by MacKnight, incorporating acid groups more frequently, increasing the overall acid content, results in amorphous polymers from this inability to cocrystallize with short polyethylene segments due to increased hydrogen bonding and decreased diffusional motion. Indeed, an amorphous polymer is obtained when the acid content is effectively doubled with more frequent singly attached groups along the backbone (see Figure 1, polymers **22** and **24**). *But when the architecture is altered from singly attached polymer* **24** *with twice the acid content via geminal attachment* (**26**) *or with benzyl attachment* (**28**), *the 20-methylene run-length still ensures crystallization.*

For the acid polymers containing a run-length of 20 methylenes (Figure 7b), a typical experiment after erasing thermal history results in no recrystallization in the subsequent cooling cycle and thus no melting until 72 h have passed. After 72 h or longer, a reproducible endotherm is observed on the first heating cycle, indicating that an equilibrium structure has been achieved (see Supporting Information). The acid endotherms shown in Figure 7b were acquired after erasing thermal history, slow cooling, annealing at room temperature for 72 h and heating at 10 °C/min.

Comparing parts a and b of Figure 7, the acid polymer **24** melts at higher temperature with well-resolved endotherms compared to the ester polymer **17**. Although the precise geminal ester polymer **19** shows more complex behavior upon heating, with a glass transition leading to cold crystallization prior to melting, a broad single endotherm is exhibited by the geminal acid polymer **26**. Geminal ester polymer **19** and geminal acid polymer **26** both have endotherms higher than the single and benzyl polymers. Perhaps this is due to an organized structure lending from geminal enhancement of chain folding. Also noteworthy, even though the acid content is doubled, crystallinity is retained yet less perfect as indicated by the broadened melting endotherm. In addition, acid polymer **28** again melts at a higher temperature compared to the ester polymer **21**.

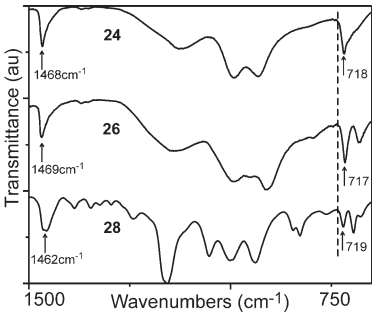

Figure 8. ATR-IR spectra expansion of 20-methylene spaced semicrystalline acid polymers.

Backbone variations associated with crystallinity between single, geminal and benzyl acid polymers with the same thermal history as the DSC samples (prior to heating) were further investigated by ATR-IR (Figure 8). Singlets at ~718 cm^{-1} are apparent in all 20-methylene spaced acid polymers in contrast to the typical orthorhombic PE doublet that arises from long trans CH_2 sequences rocking at 719 cm^{-1} and sequences of 5 or more CH_2 rocking at 730 cm^{-1}.[32,33] Singlets at 1468 cm^{-1} are also apparent in all 20 methylene spaced acid polymers in contrast to the typical orthorhombic PE doublet associated with methylene bending at ~1460 cm^{-1}. The singlet peaks present in all spectra suggests similar structural features, yet disorganized compared to orthorhombic PE.[34] With the exact identity of the unit cell remaining unknown from these data, we have shown a dependency on run-length in these highly interactive polymers.

Conclusions

Precision protected phosphonic acid ester and deprotected phosphonic acid polymer families were synthesized with varying frequency and architecture. The highly interactive acid primary structures have implications on secondary structure probed by thermal behavior. Commonalities in thermal behavior between esters and acids are found in polymers possessing 14 and 20 methylenes between attachment points. The precision acid

polymers containing 20 methylenes display PE endotherms strongly dependent on annealing. Additionally, this run-length of 20 methylenes ensures reproducible endotherms attributed to melting, even in polymer structures containing geminal acid groups or a benzyl acid group. Further analysis by diffraction, scattering, and microscopic techniques will delineate these crystallinity differences and give a more accurate quantification of crystallinity than simple comparison to the heat of fusion of purely orthorhombic PE. Compared to the layered morphology observed previously with dimerized carboxylic acid groups,[12] the resilient, highly interactive phosphonic acid hydrogen bonds appear to display higher ordered structures concomitant with PE crystallization, lending toward model studies and materials design in particular applications.

Experimental Section

Materials and Methods. All ^{1}H (300 MHz) and ^{13}C (75 MHz) solution NMR spectra were recorded on a Varian Associates Mercury 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR were referenced to residual signals from $CDCl_3$ (^{1}H = 7.27 ppm and ^{13}C = 77.23 ppm). Thin layer chromatography (TLC) was performed on EMD silica gel-coated (250 μm thickness) glass plates. Developed TLC plates were stained with iodine adsorbed on silica to produce a visible signature. Reaction progress and relative purity of crude products were monitored by TLC and ^{1}H NMR.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters Associates GPCV2000 liquid chromatography system equipped with a differential refractive index detector (DRI) and an autosampler. These analyses were performed at 40 °C using two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm ID, 300 mm length) with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/minute. Injections were made at 0.05−0.07% w/v sample concentration using a 220.5 μL injection volume. Retention times were calibrated versus narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA).

Infrared spectra were obtained on a Perkin-Elmer Spectrum One FTIR equipped with a $LiTaO_3$ detector. Samples were dissolved in chloroform and cast on a KBr disk by slow solvent evaporation. Because of rather poor solubility, the spectrum of the deprotected polymer was obtained by means of an ATR accessory.

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q5000 using high resolution dynamic resolution under nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed using a TA Instruments Q1000 at a heating rate of 10 °C/min under nitrogen purge. Temperature calibrations were achieved using indium and freshly distilled *n*-octane while the enthalpy calibration was achieved using indium. All samples were prepared in hermetically sealed pans (4−7 mg/sample) and were run using an empty pan as a reference.

Synthesis. All materials were purchased from Aldrich and used as received, unless noted otherwise. Tetrahydrofuran (THF) was obtained from a MBraun solvent purification system. Lithium diisopropyl amide (LDA) was prepared prior to monomer synthesis. Grubbs' first generation ruthenium catalyst, bis(tricyclohexylphosphine)benzylidine ruthenium(IV)-dichloride, was a generous gift from Materia, Inc. Wilkinson's rhodium catalyst, $RhCl(PPh_3)_3$, was purchased from Strem Chemical.

General Synthesis of Monomer Containing Single Directly Attached Phosphonic Acid Ester. The synthesis was previously reported with the exception of appropriate alkenyl halide synthon choice for each monomer.[27] In a flame-dried 3-necked flask equipped with a magnetic stir bar, 2.2 mL (15 mmol, 1 equiv) of diethyl methane phosphonate and 3.3 mL (15 mmol, 1 equiv) of 11-bromoundecene were stirred in15 mL of dry THF under argon. After bringing the solution to −78 °C, 0.9 equiv of LDA was added dropwise over 30 min and stirred for 30 min additional. The solution was then warmed to 0 °C and stirred for 1 to 2 h until monoalkylation was observed and alkenyl bromide disappeared by TLC. After bringing the solution back to −78 °C, 0.9 equiv of 11-bromoundecene was added slowly and allowed to dissolve. With the solution at −78 °C, 0.9 equiv of LDA was added dropwise over 30 min and stirred for 30 additional minutes. The solution was then warmed to 0 °C and stirred for 2 to 3 h until the conversion from monoalkylation to diene product was no longer observed. The reaction was quenched by adding ice cold water. This mixture was then extracted (3 × 50 mL) with diethyl ether, dried over magnesium sulfate and concentrated to a colorless oil. Column chromatography, using 2:1 ethyl acetate:hexane as the eluent, afforded dialkylation product **1** in 43% recovered yield.

Diethyl Undeca-1,10-dien-6-ylphosphonate (1). Column chromatography, using 3:1 ethyl acetate:hexane as the eluent, afforded dialkylation product **1** in 56% recovered yield. ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, 6H), 1.49 (br, 6H), 1.64−1.75 (br, 4H), 2.03 (q, 4H), 4.07 (p, 4H), 4.92−5.03 (m, 4H), 5.72−5.85 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.74 ($^3J_{CP}$ 5.8 Hz), 27.08 ($^2J_{CP}$ 9.1 Hz), 27.97, 28.02, 33.98, 36.10 ($^1J_{CP}$ 138 Hz), 61.51 ($^2J_{CP}$ 6.9 Hz), 114.91, 138.65. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 33.99. Anal. Calcd for $C_{15}H_{29}O_3P$: C, 62.48; H 10.14; O, 16.65; P, 10.74. Found: C, 61.98; H, 10.36. HRMS: calcd for $C_{15}H_{29}O_3P$ [$(M + H)^+$] = 289.1927; found = 289.1942.

Diethyl Heptadeca-1,16-dien-9-ylphosphonate (2). Column chromatography, using 5:2 ethyl acetate:hexane as the eluent, afforded dialkylation product **2** in 50% recovered yield. ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, 6H), 1.39 (br, 21H), 1.62−1.69 (br, 4H), 2.02 (q, 4H), 4.08 (p, 4H), 4.90−5.00 (m, 4H), 5.73−5.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.74 ($^3J_{CP}$ 5.9 Hz), 27.77 ($^2J_{CP}$ 9.3 Hz), 28.43($^3J_{CP}$ 5.9 Hz), 29.08, 29.13, 29.77, 33.98, 36.20 ($^1J_{CP}$ 138 Hz), 114.39, 139.31. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.56. Anal. Calcd for $C_{21}H_{41}O_3P$: C, 67.71; H 11.09; O, 12.88; P, 8.31. Found: C, 67.75; H, 11.20. HRMS: calcd for $C_{21}H_{41}O_3P$ [$(M + H)^+$] = 373.2866; found = 373.2903.

Diethyl Tricosa-1,22-dien-12-ylphosphonate (3). Column chromatography, using 2:1 ethyl acetate:hexane as the eluent, afforded dialkylation product **3** in 43% recovered yield. ^{1}H NMR ($CDCl_3$): δ = 1.26−1.36 (br, 38H), 1.63−1.69 (m, 4H), 1.98−2.06 (q, 4H), 4.07 (p, 4H), 4.89−5.00 (m, 4H), 5.73−5.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.72 ($^3J_{CP}$ 5.9 Hz), 27.79 ($^2J_{CP}$ 9.3 Hz), 28.39($^3J_{CP}$ 3.6 Hz), 29.13, 29.33, 29.63, 29.67, 29.75, 29.91, 34.01, 36.14 ($^1J_{CP}$ 138 Hz), 61.46 ($^2J_{CP}$ 6.8 Hz), 114.86, 138.59. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.70; Anal. Calcd for $C_{27}H_{53}O_3P$: C, 71.01; H 11.70; O, 10.51; P, 6.78. Found: C, 70.96; H, 11.72. HRMS: calcd for $C_{27}H_{53}O_3P$ [$(M + H)^+$] = 457.3805; found = 457.3783.

General Synthesis of Monomer Containing Geminally Substituted Phosphonic Acid Esters. Again the appropriate alkenyl halide synthon was used for each monomer. In a flame-dried 3-necked flask equipped with a magnetic stir bar, 75 mL of DMF was stirred at 0 °C under a constant argon flow. Using a powder funnel under continued constant argon flow, 2.4 g of 60% NaH powder (100 mmol, 5 equiv) was added to the flask. Upon resealing the flask, 5 mL (20.2 mmol, 1 equiv), tetraethyl methylenediphosphonate was added dropwise over 30 min. After an additional hour of stirring at 0 °C, 9.7 mL (44.4 mmol, 2.2 equiv) of 11-bromoundecene was added dropwise over 30 min. The reaction was allowed to warm to room temperature over 4 h and then allowed to stir at room temperature overnight. Reaction progress was monitored by TLC noting the disappearance of starting materials. The reaction was quenched at 0 °C by first diluting the mixture with hexane 75 mL and then adding 750 mL of deionized water. The reaction mixture was then extracted (3 × 75 mL) hexane. After washing the hexane

with water, the crude mixture was concentrated to a light yellow oil.

Tetraethyl Heptadeca-1,16-diene-9,9-diyldiphosphonate (4). Column chromatography, using 20:1 ethyl acetate:methanol as the eluent, afforded dialkylation product **4** in 24% recovered yield.

^{1}H NMR ($CDCl_3$): δ = 1.32 (br, 24H), 1.50 (br, 4H), 1.88 (m, 4H), 2.04 (q, 4H), 4.17 (p, 8H), 4.92−5.02 (m, 4H), 5.75−5.88 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.73 (t), 24.42 (t), 29.07, 29.12, 30.29 (t), 34.00 45.99 (t, $^1J_{CP}$ 123 Hz), 62.55 (t), 114.41, 139.39. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 26.72. Anal. Calcd for $C_{25}H_{50}O_6P_2$: C, 59.04; H 9.91; O, 18.87; P, 12.18. Found: C, 59.03; H, 9.92. HRMS: calcd for $C_{25}H_{50}O_6P_2$ [(M+H)$^+$] = 509.3102; found = 509.3116.

Tetraethyl Tricosa-1,22-diene-12,12-diyldiphosphonate (5). Column chromatography, using 50:1 ethyl acetate:methanol as the eluent, afforded dialkylation product **5** in 28% recovered yield. ^{1}H NMR ($CDCl_3$): δ = 1.27(br, 40H), 1.88 (m, 4H), 2.05 (q, 4H), 4.16 (p, 8H), 4.91−5.02 (m, 4H), 5.74−5.88 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.68 (t), 24.40 (t), 29.14, 29.34, 29.53, 29.65, 29.75, 30.23 (t), 30.57, 45.96 (t, $^1J_{CP}$ 123 Hz), 62.46 (t), 114.28, 139.41. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 26.74.; Anal. Calcd for $C_{31}H_{62}O_6P_2$: C, 62.81; H 10.54; O, 16.19; P, 10.45. Found: C, 62.21; H, 10.67. HRMS: Calcd for $C_{31}H_{62}O_6P_2$ [(M + H)$^+$] = 593.4094; found = 593.4049.

General Synthesis of Monomer Containing Benzyl-Substituted Phosphonic Acid Ester. The phosphonic acid ester was prepared in three steps detailed from alkylation of alcohol with the appropriate alkenyl halide synthon, to bromide, to phosphonic acid ester.

3,5-Bis(10-undecenyloxy)phenyl)benzyl Alcohol. In a 200 mL round-bottom flask equipped with a magnetic stir bar, 2.8 g (20 mmol, 1 equiv) of 3,5-dihydroxybenzyl alcohol was dissolved in 80 mL acetonitrile. To this mixture, 6.91 g (50 mmol, 2.5 equiv) of K_2CO_3 and 0.83 g (5 mmol, 0.25 mmol) of KI were added. After partial dissolution due to insolubility at room temperature, 7.72 mL (46 mmol, 2.3 equiv) of 11-bromoundecene was then added and a reflux condenser attached. After refluxing at 100 °C for 24 h under argon, the reaction was allowed to cool to room temperature. After filtering residual K_2CO_3 and KI and adding deionized water, the mixture was extracted with (3 × 50 mL) ethyl acetate. Upon concentrating the crude mixture to an oil, the crude product was passed through a plug of silica. Using 1:1 hexane:dichloromethane, excess alkenyl bromide was removed. Switching to 1:1 hexane: ethyl acetate led to isolation of product concentrated as a yellowish oil in 82% yield. ^{1}H NMR ($CDCl_3$): δ = 1.27 (br, 24H), 1.68 (m, 4H), 1.95 (m, 4H), 3.83 (m, 4H), 4.51 (d, 2H), 5.02−5.15 (m, 4H), 5.82−5.97 (m, 2H), 6.46 (m, 1H), 6.53 (d, 2H). ^{13}C NMR ($CDCl_3$): δ = 25.97, 29.27, 33.77, 65.31, 68.02, 100.54, 104.94, 114.14, 139.17, 143.16, 160.50.

(3,5-Bis(pent-4-enyloxy)phenyl)benzyl Alcohol. ^{1}H NMR ($CDCl_3$): δ = 1.75−1.95 (m, 8H), 2.27 (q, 4H), 3.98 (m, 4H), 4.64 (d, 2H), 5.01−5.13 (m, 4H), 5.80−5.96 (m, 2H), 6.46 (m, 1H), 6.53 (d, 2H). ^{13}C NMR ($CDCl_3$): δ = 28.44, 30.11, 65.4, 67.27, 100.65, 105.15, 115.21, 137.80, 143.27, 160.46.

(3,5-Bis(10-undecenyloxy)phenyl)benzyl Bromide. In a 200 mL round-bottom flask equipped with a magnetic stir bar, the benzyl alcohol derivative obtained was dissolved in 40 mL of THF. Under a blanket of argon, 1.5 equiv of CBr4 was added. Upon cooling to 0 °C, 1.5 equiv of triphenyl phosphine was added. After warming the mixture to room temperature, progress was monitored by TLC. After being stirred overnight, the reaction was quenched by precipitating the triphenyl phosphine oxides in pentane, filtering off the solids, and concentrating the remaining solution. Purification via column chromatography using a 1:1 hexane:dichloromethane solvent system allowed for product isolation in 67% yield as a yellowish oil. ^{1}H NMR ($CDCl_3$): δ = 1.35 (br, 24H), 1.74 (m, 4H), 2.03 (m, 4H), 3.90 (br, 4H), 4.38 (s, 2H), 5.01−5.13 (m, 4H), 5.80−5.96 (m, 2H), 6.36 (m, 1H), 6.51 (d, 2H). ^{13}C NMR ($CDCl_3$): δ = 25.99, 29.14, 33.75, 68.10, 101.36, 107.39, 114.11, 139.20, 139.45, 160.37.

(3,5-Bis(pent-4-enyloxy)phenyl)benzyl Bromide. ^{1}H NMR ($CDCl_3$): δ = 1.46 (br, 8H), 1.80 (p, 4H), 2.08 (m, 4H), 3.96 (t, 4H), 4.43 (s, 2H), 4.94−5.08 (m, 4H), 5.77−5.93 (m, 2H), 6.40 (m, 1H), 6.54 (d, 2H). ^{13}C NMR ($CDCl_3$): δ = 28.27, 30.11, 33.70, 67.16, 101.42, 107.38, 115.20, 137.67, 139.54, 160.27.

Diethyl 3,5-bis(10-undecenyloxy)phenyl) benzyl Phosphonate (7). In a 50 mL round-bottom flask equipped with a magnetic stir bar, benzyl bromide was added with 1.3 equiv of triethyl phosphite. After refluxing the solution for 72 h, the residual triethyl phosphite was removed under vacuum and the phosphonate was obtained in quantitative yield with no further purification necessary. ^{1}H NMR ($CDCl_3$): δ = 1.26 (br, 30H), 1.67 (p, 4H), 1.98 (m, 4H), 2.92 (d, 2H), 3.82 (t, 4H), 3.95 (m, 4H), 4.94−5.06 (m, 4H), 5.76−5.92 (m, 2H), 6.38 (q, 1H), 6.45−6.47 (t, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.79, 26.42, 29.73, 33.87, 33.99 ($^1J_{CP}$ = 137 Hz), 34.15, 62.53, 68.47, 100.51, 108.80, 114.46, 133.79, 139.59, 160.72. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 25.49. Anal. Calcd for $C_{33}H_{57}O_3P$: C, 70.18; H 10.17; O, 14.16; P, 5.48. Found: C, 68.06; H, 9.93. HRMS: calcd for $C_{33}H_{57}O_3P$ [(M + H)$^+$] = 565.4022; found = 565.4022.

Diethyl 3,5-bis(oct-7-enyloxy)benzylphosphonate (6). ^{1}H NMR ($CDCl_3$): δ = 1.26−1.31 (t, 6H), 1.42 (br, 12H), 1.78 (m, 4H), 2.06 (m, 4H), 3.05−3.14 (d, 2H), 3.91−3.97 (t, 4H), 3.99−4.11 (m, 4H), 4.94−5.06 (m, 4H), 5.76−5.92 (m, 2H), 6.35−6.37 (q, 1H), 6.45−6.47 (t, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.55, 26.03, 28.97, 29.34, 33.84, 34.16 ($^1J_{CP}$ = 137 Hz), 62.53, 68.07, 100.23, 108.41, 114.43, 133.59, 139.11, 160.38. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 25.78. Anal. Calcd for $C_{27}H_{45}O_3P$: C, 67.47; H 9.44; O, 16.64; P, 6.44. Found: C, 66.26; H, 9.51. HRMS: calcd for $C_{27}H_{45}O_3P$ [(M + H)$^+$] = 481.3077; found = 481.3097.

General Homopolymerization Conditions. In a flame-dried 50 mL round-bottom flask, an exact amount of monomer was weighed. Using a 400:1 monomer:catalyst ratio (0.25 mol %), Grubbs' first generation catalyst was added and mixed into the monomer while under a blanket of argon. A magnetic stir bar was placed into the mixture while a Schlenk adapter was fitted to the round-bottom. After sealing the flask under argon it was moved to a high vacuum line. The mixture was stirred and slowly exposed to vacuum over an hour at room temperature. After stirring for an hour at room temperature under eventual high vacuum (10^{-3} Torr), the flask was lowered into a prewarmed 50 °C oil bath for an appropriate number of days allowing removal of ethylene bubbling through viscous polymer. Polymers were quenched by dissolution of polymer in an 1:10 ethyl vinyl ether:toluene solution under argon. Upon precipitation into an appropriate solvent, the polymers were isolated.

Polymerization of Diethyl Undeca-1,10-dien-6-ylphosphonate (8). After 5 days of polymerization of 0.548 g of monomer **1** with 400:1 Grubbs first generation catalyst, unsaturated polymer **8** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, 6H), 1.44 (br, 4H), 1.64−1.69 (br, 4H), 1.96 (br, 4H), 4.07 (p, 4H), 5.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.75 ($^3J_{CP}$ 5.7 Hz), 27.08 ($^2J_{CP}$ 9.1 Hz), 27.88, 28.37, 29.95, 32.90, 36.10 ($^1J_{CP}$ 137 Hz), 61.51 ($^2J_{CP}$ 6.8 Hz), 129.89, 130.37. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.42. GPC data (THF vs polystyrene standards): M_w = 14100 g/mol; PDI (M_w/M_n) = 1.75.

Polymerization of Diethyl Heptadeca-1,16-dien-9-ylphosphonate (9). After 6 days of polymerization of 0.973 g pf monomer **2** with 400:1 Grubbs first generation catalyst, unsaturated polymer **9** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.27−1.39 (br, 23H), 1.65 (br, 4H), 1.95 (br, 4H), 4.06 (p, 4H), 5.37 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.74 ($^3J_{CP}$ 5.7 Hz), 27.84 ($^2J_{CP}$ 9.1 Hz), 27.88, 28.46, 29.25, 29.87, 32.81, 36.10 ($^1J_{CP}$ 137 Hz), 61.49 ($^2J_{CP}$ 6.8 Hz), 130.50, 130.05. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.52. GPC data (THF vs polystyrene standards): M_w = 33800 g/mol; PDI (M_w/M_n) = 1.68.

Polymerization of Diethyl Tricosa-1,22-dien-12-ylphosphonate (10). After 6 days of polymerization of 0.860 g pf monomer **3** with 400:1 Grubbs first generation catalyst, unsaturated polymer **10** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.27−1.40 (br, 35H), 1.67−1.72 (m, 4H), 1.97 (br, 4H), 4.09 (m, 4H), 5.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.73 ($^3J_{CP}$ 5.8 Hz), 27.80 ($^2J_{CP}$ 9.3 Hz), 28.44($^3J_{CP}$ 3.6 Hz), 29.43, 29.56, 29.68, 29.82, 29.95, 32.84, 36.20 ($^1J_{CP}$ 136 Hz), 61.46 ($^2J_{CP}$ 6.9 Hz), 130.07, 130.53. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.85. GPC data (THF vs polystyrene standards): M_w = 28700 g/mol; PDI (M_w/M_n) = 1.82.

Polymerization of Tetraethyl Heptadeca-1,16-diene-9,9-diyldiphosphonate (11). After 6 days of polymerization of 0.880 g of monomer **4** with 400:1 Grubbs first generation catalyst, an additional portion of catalyst was added. After the polymerization was quenched after an additional 6 days, unsaturated polymer **11** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.32 (br, 24H), 1.48 (br, 4H), 1.84−1.95 (br, 8H), 4.17 (p, 8H), 5.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ =16.72 (t), 24.43 (t), 27.46, 29.22, 29.32, 29.95, 30.53, 32.85, 46.00 (t, $^1J_{CP}$ 123 Hz), 62.52 (t), 130.05, 130.52. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ =26.67. GPC data (THF vs polystyrene standards): M_w = 10500 g/mol; PDI (M_w/M_n) = 1.78.

Polymerization of Tetraethyl Tricosa-1,22-diene-12,12-diyldiphosphonate (12). After 5 days of polymerization of 1.00 g of monomer **5** with 400:1 Grubbs first generation catalyst, unsaturated polymer **12** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.27−1.34(br, 36H), 1.48 (br, 4H), 1.94 (br, 8H), 4.16 (p, 8H), 5.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.68 (t), 24.43 (t), 27.46, 29.48, 29.59, 29.65, 29.75, 30.28 (t), 30.61, 32.86, 45.97 (t, $^1J_{CP}$ 123 Hz), 62.46 (t), 130.06, 130.51. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 30.75. GPC data (THF vs polystyrene standards): M_w = 28900 g/mol; PDI (M_w/M_n) = 1.68.

Polymerization of Diethyl 3,5-Bis(oct-7-enyloxy)benzylphosphonate (13). After 5 days of polymerization of 1.02 g monomer **6** with 400:1 Grubbs first generation catalyst, unsaturated polymer **13** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.26−1.31 (t, 6H), 1.28 (br, 12H), 1.78 (m, 4H), 2.03 (br, 4H), 3.08 (d, 2H), 3.93 (t, 4H), 3.99−4.11 (m, 4H), 5.42 (m, 2H), 6.35−6.37 (m, 1H), 6.45−6.47 (t, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.40, 25.95, 27.18, 28.94, 29.09, 29.25, 29.57, 29.70, 32.53, 34.03 ($^1J_{CP}$ = 138 Hz), 62.10, 67.99, 100.10, 108.30, 129.84, 130.31, 133.42, 160.25. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 25.79. GPC data (THF vs polystyrene standards): M_w = 14700 g/mol; PDI (M_w/M_n) = 2.30.

Polymerization of Diethyl 3,5-Bis(10-undecenyloxy)phenyl)-benzylphosphonate (14). After 5 days of polymerization of 0.550 g of monomer **7** with 400:1 Grubbs first generation catalyst, unsaturated polymer **14** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.24−1.43 (br, 30H), 1.75 (m, 4H), 1.98 (m, 4H), 2.92 (d, 2H), 3.91 (br, 4H), 4.03 (m, 4H), 5.39 (m, 2H), 6.34 (br, 1H), 6.44 (br, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.79, 26.42, 29.73, 32.27, 34.15 ($^1J_{CP}$ = 137 Hz), 62.53, 68.47, 100.51, 108.80, 114.46, 133.79, 139.59, 160.72. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 25.93. GPC data (THF vs polystyrene standards): M_w = 15000 g/mol; PDI (M_w/M_n) = 2.07.

General Hydrogenation Conditions. A solution of unsaturated polymer was dissolved in toluene and degassed by bubbling a nitrogen purge through the stirred solution for an hour. Wilkinson's catalyst [$RhCl(PPh_3)_3$] was added to the solution along with a magnetic stir bar, and the glass sleeve was sealed in a Parr reactor equipped with a pressure gauge. The reactor was filled to 700 psi hydrogen gas and purged three times while stirring, filled to 700 psi hydrogen, and stirred for an appropriate number of days. After degassing of the solution, the crude solution was isolated, and precipitated into an appropriate solvent.

Hydrogenation of Polymerized Diethyl undeca-1,10-dien-6-ylphosphonate (15). After 5 days, saturated polymer **15** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.26−1.39 (br, 19H), 1.64−1.69 (br, 4H), 4.07 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 16.70 ($^3J_{CP}$ 5.7 Hz), 27.84 ($^2J_{CP}$ 9.1 Hz), 28.54, 29.72, 30.00, 36.10 ($^1J_{CP}$ 137 Hz), 61.55 ($^2J_{CP}$ 6.8 Hz). ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.76. GPC data (THF vs polystyrene standards): M_w = 17100 g/mol; PDI (M_w/M_n) = 1.61.

Hydrogenation of Polymerized Diethyl Heptadeca-1,16-dien-9-ylphosphonate (16). After 6 days, saturated polymer **16** was obtained.^{1}H NMR ($CDCl_3$): δ =1.27−1.39 (br, 31H), 1.65 (br, 4H), 4.06 (m, 4H). ^{13}C NMR ($CDCl_3$): δ =16.74 ($^3J_{CP}$ 5.7 Hz), 27.84 ($^2J_{CP}$ 9.1 Hz), 27.88, 28.46, 29.25, 29.87, 32.81, 36.10 ($^1J_{CP}$ 137 Hz), 61.49 ($^2J_{CP}$ 6.8 Hz), 130.50, 130.05. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.52. GPC data (THF vs polystyrene standards): M_w = 40400 g/mol; PDI (M_w/M_n) = 1.71.

Hydrogenation of Polymerized Diethyl Tricosa-1,22-dien-12-ylphosphonate (17). After 6 days, saturated polymer **17** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.27−1.44 (br, 43H), 1.62−1.84 (m, 4H), 4.10 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 16.73 ($^3J_{CP}$ 5.8 Hz), 27.82 ($^2J_{CP}$ 9.3 Hz), 28.44($^3J_{CP}$ 3.6 Hz), 29.69, 29.89, 29.95, 36.20 ($^1J_{CP}$ 136 Hz), 61.46 ($^2J_{CP}$ 6.9 Hz). ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 34.71. GPC data (THF vs polystyrene standards): M_w = 34500 g/mol; PDI (M_w/M_n) = 1.93.

Hydrogenation of Polymerized Tetraethyl Heptadeca-1,16-diene-9,9-diyldiphosphonate (18). After 6 days, saturated polymer **18** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.32 (br, 24H), 1.48 (br, 4H), 1.84−1.95 (br, 8H), 4.17 (p, 8H), 5.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ =16.72 (t), 24.43 (t), 27.46, 29.22, 29.32, 29.95, 30.53, 32.85, 46.00 (t, $^1J_{CP}$ 123 Hz), 62.52 (t), 130.05, 130.52. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ =26.67. GPC data (THF vs polystyrene standards): M_w = 11400 g/mol; PDI (M_w/M_n) = 1.82.

Hydrogenation of Polymerized Tetraethyl tricosa-1,22-diene-12,12-diyldiphosphonate (19). After 5 days, saturated polymer **19** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.25−1.34 (br, 44H), 1.48 (br, 4H), 1.85 (br, 4H), 4.16 (p, 8H). ^{13}C NMR ($CDCl_3$): δ = 16.67 (t), 24.41 (t), 29.58, 29.88, 29.95, 30.18 (t), 30.60, 32.12, 45.97 (t, $^1J_{CP}$ 123 Hz), 62.47 (t). ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 30.74. GPC data (THF vs polystyrene standards): M_w = 33400 g/mol; PDI (M_w/M_n) = 1.71.

Hydrogenation of Polymerized Diethyl 3,5-Bis(oct-7-enyloxy)-benzylphosphonate (20). After 5 days, saturated polymer **20** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.26−1.31 (br, 26H), 1.78 (m, 4H), 3.08 (d, 2H), 3.93 (t, 4H), 3.99−4.11 (m, 4H), 6.35−6.37 (m, 1H), 6.45−6.47 (t, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.40, 26.30, 29.51, 29.93, 34.03 ($^1J_{CP}$ = 138 Hz), 62.35, 68.28, 100.35, 108.52, 133.42, 160.25. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 26.09. GPC data (THF vs polystyrene standards): M_w = 20600 g/mol; PDI (M_w/M_n) = 1.94.

Hydrogenation of Polymerized Diethyl 3,5-Bis(10-undecenyloxy)phenyl) benzyl phosphonate (21). After 5 days, saturated polymer **21** was obtained. ^{1}H NMR ($CDCl_3$): δ = 1.25−1.44 (br, 34H), 1.77 (m, 4H), 2.92 (d, 2H), 3.91 (br, 4H), 4.03 (m, 4H), 6.34 (br, 1H), 6.44 (br, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.65, 22.93, 26.30, 29.51, 29.67, 29.83, 29.98, 32.15, 34.26 ($^1J_{CP}$ = 138 Hz), 62.37, 68.27, 100.34, 108.53, 133.62, 160.49. ^{31}P NMR ($CDCl_3$, PPh_3 reference): δ = 25.77. GPC data (THF vs polystyrene standards): M_w = 16400 g/mol; PDI (M_w/M_n) = 2.23.

General Hydrolysis Procedure. Into a 2-necked Schlenk round-bottom flask was transferred polymer ester dissolved in dry dichloromethane. Then the flask was equipped with a stir bar and septa. After the flask was flushed with argon, 10 equiv of bromotrimethylsilane was added dropwise by syringe under a continuous flow of argon. After the reaction was stirred with a constant flow of argon for 24 h, the residual reactants were removed under vacuum prior to adding 20 mL of methanol (not anhydrous). The reaction was allowed to stir with a constant flow of argon for another 24 h. Upon removal of residual methanol and trimethylsilyl species, acid polymer was obtained in quantitative yield (99%) without any purification necessary. Following methanolysis, the polymer was precipitated from the sides of the flask with acetone. The precipitated polymer was

rinsed through an osmotic filter with acetone and dried at 50 °C for 24 h. See characterization herein and in the Supporting Information.

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Supporting Information Available: Figures showing protected polymer and deprotected polymer spectra and deprotected polymer annealing thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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