# Articles

## Random, Defect-Free Ethylene/Vinyl Halide Model Copolymers via Condensation Polymerization

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ABSTRACT: The synthesis of ethylene vinyl halide (EVH) copolymers containing fluorine, chlorine, and bromine via the ADMET copolymerization of halogen containing $\alpha-\omega$-dienes with 1,9-decadiene is presented. The statistically random nature of the copolymers was established from their $^{13}C$ NMR spectra. Thermal analysis via differential scanning calorimetry points to a distinct difference in the crystallization behavior of these random copolymers when compared to their compositionally matched precise analogues. In this case, sharp melting peaks typical of homopolymer-like crystallization of the precise analogues are no longer observed in Cl- and Br-based random copolymers and are replaced by broader peaks indicating a mechanism based on the selection of long crystallizable sequences. The results presented herein thus point to the utility of these random ADMET copolymers as suitable models for industrially relevant PE copolymers based on the perfectly linear, defect-free, and statistically random copolymer composition.

### Introduction

Polyolefins represent the largest class of industrially produced polymers, and their importance is manifested in diverse applications ranging from packaging to biomaterials and electronics.[1] Even though polyethylene (PE) itself possesses a broad and dynamic property set, additional application specific variations can be introduced through copolymerization with other vinyl monomers.[2,3] Specifically, copolymerization with polar vinyl monomers can be used to vary the mechanical and physical properties of the polymer.[4,5] However, direct copolymerization via common free-radical methods often leads to poorly defined polymers with limited compositional ranges based on reactivity differences between ethylene and polar monomers as well as the numerous defects (e.g., branching) introduced through free-radical techniques.[5,6] Therefore, a variety of other polymerization methods have been employed in an effort to model the properties of such copolymers.[7,8] Olefin metathesis has emerged as an attractive method for modeling ethylene copolymers containing polar groups, based on the functional group tolerance of the employed late-transition-metal catalysts and the fidelity of the reaction, which provides perfectly linear polymers, free of structural defects.[9]

Using acyclic diene metathesis (ADMET), we have pursued halogen-containing ethylene polymers, and we have capitalized on the ability of ADMET to produce precision polymers in which fluorine, chlorine, and bromine atoms are separated by a constant methylene sequence.[10−13] In such systems, we have observed unique crystallization and thermal behavior attributed to the homopolymer-like behavior of these precise ethylene/vinyl halide (EVH) polymers. Here we extend these EVH polymers for use as effective models for industrial polymers via copolymerization of halogen-containing $\alpha-\omega$-dienes with 1,9-decadiene to yield random and defect-free EVH polymers. Such polymers are more relevant as model systems for chain-addition EVH polymers produced by free radical techniques based on the ability to attain continuous methylene sequences of significant length and broad distributions of length. Variation in halogen size and content allows us to more accurately derive structure−property relationships in such polymers. The defect-free nature of the polymer backbone allows the use of NMR analysis to prove the random nature of the polymers, while thermal analysis via differential scanning calorimetry (DSC) provides insight into the compositional dependence of the thermal properties in these random polymers relative to their precise analogues.

### Results and Discussion

**Polymer Synthesis.** The synthesis of the statistically random copolymers is shown in Scheme 1. Copolymerization was carried out using a halogen-containing monomer (abbreviated [X]) and 1,9-decadiene (abbreviated [H]). Synthesis of the fluorine,[13] chlorine,[12] and bromine[11] containing monomers has been previously reported. Copolymerization was carried out using Grubb’s first-generation ruthenium catalyst to yield the unsaturated ADMET polymers **RUPE15X** and **RUPE21X**. Following ADMET polymerization, the fluorine and chlorine

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**Scheme 1**

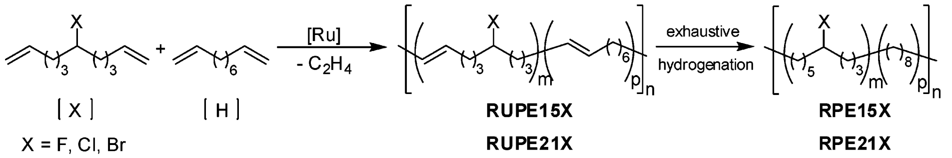
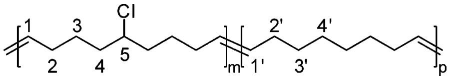


**Table 1. Molecular Mass and Thermal Characterization of Random Polymers**

| sample | $M_w \times 10^3$ | $M_w/M_n$ | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_f$ (J/g) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|---|
| **RPE21F** | 21.6[a] | 1.6 | 127 | 119 | 157 | 170 |
| **RPE15F** | 7.9[a] | 2.5 | 120 | 107 | 151 | 163 |
| **RPE21Cl** | 118.5[b] | 2.2 | 88 | 73 | 78 | 86 |
| **RPE15Cl** | 73.6[b] | 2.1 | 71 | 56 | 68 | 76 |
| **RPE21Br** | 55.5[b] | 1.7 | 56, 74 | 63 | 56 | 71 |
| **RPE15Br** | 72.1[b] | 1.8 | 33, 50 | 32 | 36 | 45 |

[a] GPC vs PE in DCB. [b] GPC vs PS in THF.

**Scheme 2**



containing copolymers were exhaustively hydrogenated via diimide reduction,[14] while Wilkinson's catalyst[11] was used for hydrogenation of the bromine containing polymers to yield the fully saturated copolymers **RPE15X** and **RPE21X**. In the acronyms, R indicates random, U indicates unsaturation, and PE15X and PE21X indicate random polyethylene backbones with halogen contents equivalent to the precise analogues with a halogen on each and every 15th or 21st carbon. Molecular weight data are given for all six of the random copolymers in Table 1.

**Primary Structure Characterization.** The primary structure of these random copolymers **RUPE15X**, **RUPE21X**, **RPE15X**, and **RPE21X** was established using a combination of $^1$H NMR, $^{13}$C NMR, elemental analysis, IR spectroscopy, and TGA (thermogravimetric analysis). In-depth analysis by $^1$H and $^{13}$C NMR described below confirms the statistically random nature of the copolymers presented.

The assignment of the signals in the $^1$H and $^{13}$C NMR spectra was based on the $^1$H−$^{13}$C correlations seen in the gradient heteronuclear multiple bond coherence (gHMBC) spectra, and it is discussed in detail in the Supporting Information. The $^{13}$C chemical shifts are given in Table 2. The numbering of the positions is given in Scheme 2: plain numbers for the 6-chloroundeca-1,10-diene moiety (Cl moiety) and prime numbers for the 1,9-decadiene moiety (H moiety). We add a *t* or a *c* after this number to mark the *trans* or *cis* configuration of the closest double bond. If this double bond connects to a 1,9-decadiene moiety, *t* becomes *t′* and *c* becomes *c′*. The H moiety:X moiety ratio ([H]:[X]) derived from $^1$H NMR integration is given for all random polymers (X = Cl, F, and Br moieties) in Table 3.

The alkene region of the $^{13}$C NMR spectra for **RUPE15Cl** and **RUPE21Cl** (Figure 1 top and bottom, respectively) shows four major signals and four minor ones, whose assignments are given in the figure. The signals of *1t*, *1′t* + *1t′*, and *1′t′* correspond to the XX, HX, and HH diads, respectively; therefore, the integrals of these signals can be used to determine the degree of randomness (DR) in the copolymers. Because of the signal overlap, three integrals can be measured reliably, corresponding to *1′t*, *1t* + *1′t′*, and *1t′*. Therefore, we define $\mathrm{DR} = 2(\mathrm{XX} + \mathrm{HH})/\mathrm{HX}/(r + 1/r)$, where XX + HH is the integral for *1t* + *1′t′*, HX is the sum of the integrals for *1′t* and *1t′*, and $r$ is the ratio of the H and X monomers. For a random copolymer DR = 1, for an alternating polymer DR = 0, and for a block copolymer DR = ∞. The values of DR given in Table 3 indicate a random distribution for all of these copolymers.

Analysis of the chemical shifts data, given in the Supporting Information, indicates that the $^{13}$C chemical shifts in polymers of the type $(=\mathrm{CH{-}CH_2{-}CH_2{-}CH_2{-}CHX{-}CH_2{-}CH_2{-}CH_2{-}CH{=}})_n(=\mathrm{CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH{=}})_m$ can be calculated with a precision of ±0.02 ppm by adding the effect of the halogen and the effect of the configuration of the double bond in the closest diad. The corresponding increments are given in Table 4. As an example, the chemical shift for *C3c* in the Cl copolymers is the sum of 29.64 (base), −3.21 (position 3 in a Cl moiety), −0.07 (position 3′ relative to the other unit in the diad which is also a Cl moiety), and 0.15 (increment cis for position 3), total 26.51 vs 26.52 (observed). For *C1′t* in the Br copolymers, the chemical shift is 130.34 + 0.80 = 131.14 vs 131.12 (observed).

The IR spectra in Figure 2 also provide characteristic information regarding the primary structure of the polymers. Here the **RPE15X** polymers are shown as representative examples. In each case, characteristic peaks support the presence of the expected halogens. For **RPE15F**, a peak at 1068 cm$^{-1}$ corresponds to C−F stretching vibrations.[15] For **RPE15Cl**, the

**Table 2. $^{13}$C Chemical Shifts in Copolymers**

|  | 1 | 2 | 3 | 4 | 5 | 1′ | 2′ | 3′ | 4′ |
|---|---|---|---|---|---|---|---|---|---|
| F ($^1J_{C-F}$) |  |  | *4.0* | *20.9* | *167.6* |  |  |  |  |
| t | 130.30 | 32.34 | 25.05 | 34.63 | 94.29 | 131.00 | 32.59 | 29.59 | 29.05 |
| t′ | 129.65 | 32.36 | 25.08 | 34.63 | 94.29 | 130.34 | 32.61 | 29.64 | 29.05 |
| c | 129.78 | 26.99 | 25.20 | 34.74 | 94.29 | 130.49 | 27.25 | 29.71 | 29.19 |
| c′ | 129.17 | 26.96 | 25.23 | 34.74 | 94.29 | 129.88 | 27.22 | 29.75 | 29.19 |
| Cl |  |  |  |  |  |  |  |  |  |
| t | 130.24 | 32.03 | 26.38 | 37.96 | 63.92 | 131.06 | 32.58 | 29.57 | 29.05 |
| t′ | 129.51 | 32.05 | 26.43 | 37.96 | 63.92 | 130.32 | 32.61 | 29.64 | 29.05 |
| c | 129.72 | 26.69 | 26.52 | 38.05 | 63.92 | 130.56 | 27.26 | 29.70 | 29.19 |
| c′ | 129.02 | 26.65 | 26.56 | 38.05 | 63.92 | 129.86 | 27.22 | 29.75 | 29.19 |
| Br |  |  |  |  |  |  |  |  |  |
| t | 130.25 | 31.90 | 27.44 | 38.60 | 58.42 | 131.12 | 32.57 | 29.56 | 29.04 |
| t′ | 129.46 | 31.92 | 27.50 | 38.60 | 58.42 | 130.32 | 32.60 | 29.63 | 29.04 |
| c | 129.72 | 26.57 | 27.60 | 38.68 | 58.42 | 130.61 | 27.26 | 29.69 | 29.18 |
| c′ | 128.96 | 26.53 | 27.63 | 38.68 | 58.42 | 129.86 | 27.22 | 29.74 | 29.18 |

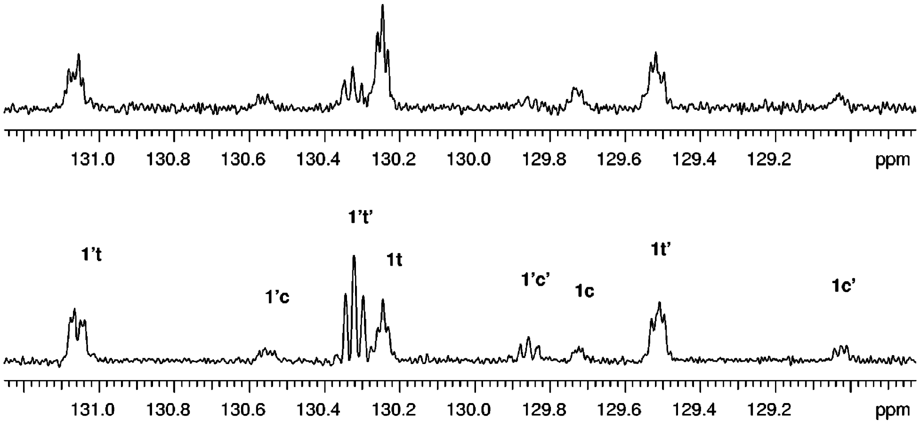


**Figure 1.** Expansion of the $^{13}$C NMR for **RUPE15Cl** (top) **and RUPE21Cl** (bottom).

**Table 3. Monomer Ratio, Degree of Randomness (DR), and *Trans*:*Cis* Ratio in Copolymers**

| copolymer | F | Cl | Br |
|---|---|---|---|
| ratio H:X in **RUPE15X** | 0.70 | 0.64 | 0.43 |
| ratio H:X in **RUPE21X** | 1.40 | 1.28 | 1.04 |
| (XX + HH)/HX in **RUPE15X** | 1.01 | 1.19 | 1.08 |
| (XX + HH)/HX in **RUPE21X** | 1.08 | 0.99 | 1.06 |
| DR in **RUPE15X** | 0.95 | 1.08 | 0.78 |
| DR in **RUPE21X** | 1.02 | 0.96 | 1.06 |
| ratio *trans:cis* in **RUPE15X** | 3.34 | 3.68 | 3.72 |
| ratio *trans:cis* in **RUPE21X** | 3.29 | 3.46 | 2.82 |

peaks at 612 and 664 cm$^{-1}$ correspond to C−Cl stretching vibrations.[16] Finally, peaks at 537 and 615 cm$^{-1}$ for **RPE15Br** correspond to C−Br stretching vibrations.[17] Characteristic peaks at ∼720 and ∼1470 cm$^{-1}$, which correspond to vibrational modes of methylene sequences in PE analogues, are also observed for each of the samples. For **RPE15F**, the doublets observed at 729−721 and 1472−1463 cm$^{-1}$ are the same as observed in orthorhombic crystalline PE.[18,19] Singlets observed at 722, 1467 cm$^{-1}$ and 722, 1466 cm$^{-1}$ for **RPE15Cl** and **RPE21Cl**, respectively, indicate a change in crystal packing when compared to **RPE15F**.

**Thermal Analysis (TGA).** Figure 3 shows the TGA data for all six random polymers. It can be observed that all six polymers undergo two-step degradation processes, marked by the initial loss of HX (X = F, Cl, Br) and followed by catastrophic decomposition.[10] The first stage loss of HX is a good measure of primary structure composition. In all cases the mass loss corresponding to HX conforms closely to the theoretically calculated value based on the monomer feed ratios in each polymer. For **RPE21Br** and **RPE15Br**, the first stage mass loss gave approximately 22 and 28% mass loss, respectively, in agreement with the calculated HBr in the chain. For **RPE21Cl** and **RPE15Cl**, the first stage mass loss gave approximately 11 and 15% mass loss, respectively, in accord with the calculated HCl. For **RPE21F** and **RPE15F**, the first stage mass loss gave approximately 6 and 9% mass loss, respectively, in accord with the calculated amount of HF.

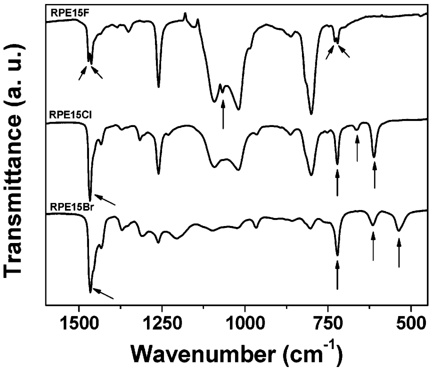


**Figure 2.** IR spectra for **RPE15F** (top), **RPE15Cl** (middle), and **RPE15Br** (bottom).

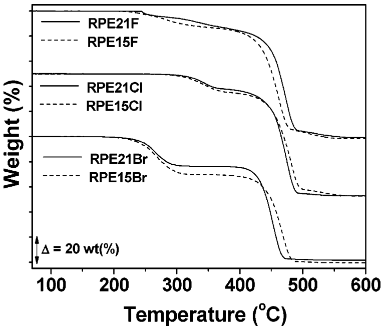


**Figure 3.** TGA results for all six random polymers, **RPE21X** (solid lines) and **RPE15X** (dashed lines), where X = F (top), Cl (middle), and Br (bottom).

**DSC.** The thermal properties of these random copolymers have been further investigated by DSC. Here the most interesting results are observed when compared to their precise analogues, as illustrated in Figure 4. A tabular summary of the data is also given in Table 1. Figure 4a shows the melting transitions for **RPE21Cl**, **PE21Cl**, **RPE15Cl**, and **PE15Cl**. Several observations can be made in the comparison of the melting behavior of the direct analogues. First, it can be seen, as previously reported,[12] that **PE21Cl** has a $T_m$ 18 °C higher than **PE15Cl** due to lower incorporation of Cl into the crystalline lattice of the **PE21Cl**. Accordingly, these precise polymers behave as homopolymers and display sharp melting transitions. Notice with the random copolymers, that much broader melt transitions are observed. When comparing direct analogues (either **RPE21Cl**

**Table 4. Increments for the Calculus of the $^{13}$C Chemical Shifts in Copolymers**

| | 1 | 2 | 3 | 4 | 5 | 1′ | 2′ | 3′ | 4′ |
|---|---|---|---|---|---|---|---|---|---|
| base | 130.34 | 32.61 | 29.64 | 29.05 | 29.49 | 130.34 | 32.61 | 29.64 | 29.05 |
| incr F | −0.69 | −0.25 | −4.56 | 5.58 | 64.80 | 0.66 | −0.02 | −0.05 | 0.00 |
| incr Cl | −0.83 | −0.56 | −3.21 | 8.91 | 34.43 | 0.74 | −0.03 | −0.07 | 0.00 |
| incr Br | −0.88 | −0.69 | −2.14 | 9.55 | 28.93 | 0.80 | −0.03 | −0.07 | 0.00 |
| incr *cis* | −0.52 | −5.34 | 0.15 | 0.09 | 0.00 | −0.51 | −5.32 | 0.13 | 0.14 |

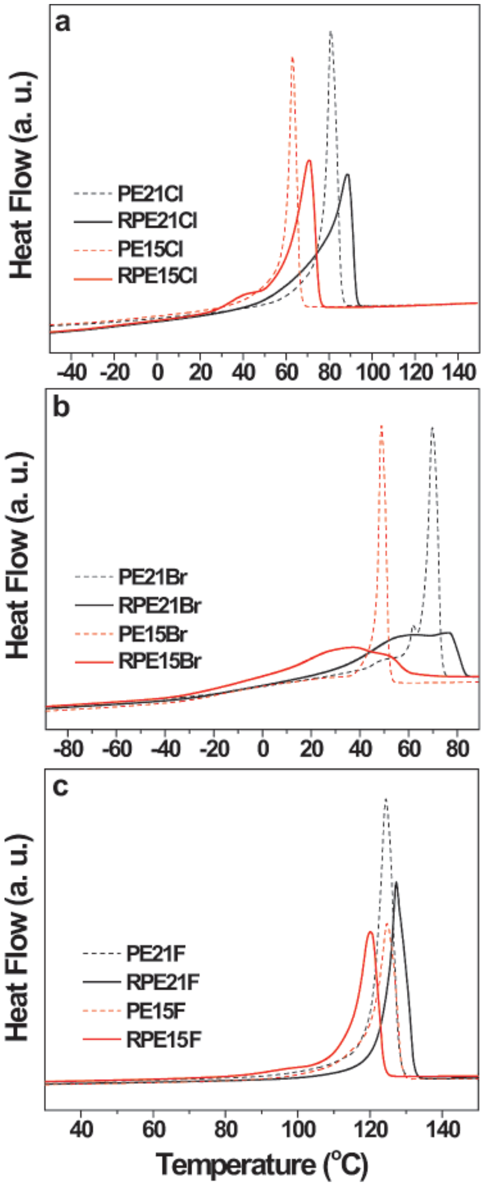


**Figure 4.** Melting comparison of random copolymers and precise analogues: (a) **RPE21Cl**, **RPE15Cl**, **PE21Cl**, **PE15Cl**; (b) **RPE21Br**, **RPE15Br**, **PE21Br**, **PE15Br**; (c) **RPE21F**, **RPE15F**, **PE21F**, **PE15F**. Heat flow is represented in arbitrary units (au).

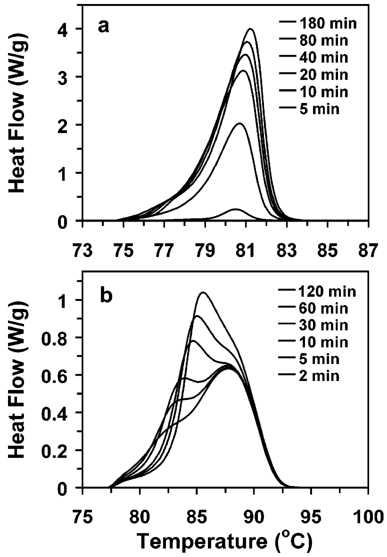


**Figure 5.** Melting thermograms of precise **PE21Cl** (a) and random copolymer analogue **RPE21Cl** (b), isothermally crystallized at 76 and 73 °C, respectively, for the times indicated.

and **PE21Cl** or **RPE15Cl** and **PE15Cl**), it can be seen that the random copolymer displays a higher $T_m$ than the precise polymer, despite the same overall composition. This feature was also observed for methyl branched precise vs random analogues[8] and provides additional evidence in support of very different crystallization mechanisms for these two types of polymers. Polymers with precisely placed halogens crystallize as homopolymers, as evidenced in our earlier work.[10] However, despite the feasibility of halogen participation in the crystal lattice, the crystallization of random copolymers is led by an early selection of sequences with the least constraints to form ordered arrays. Primarily methylene sequences are selected first, followed by sequences with higher halogen contents. This sequence selection leads to a broader melt due to the variable composition of the crystalline phase with crystallites defined by a range of Cl contents. The broad melt is a reflection of the changing composition of the melt phase, which is originally rich in Cl but becomes progressively closer to the composition of the overall copolymer. The final melting temperature of the random copolymers is higher than that of the precise polymers due to the presence of lower defect content crystallites generated via sequence selection. A final melting comparison to make is between **RPE15Cl** and **RPE21Cl**, where a $T_m$ 17 °C higher is observed for the latter. This is expected due to the higher concentration of Cl in **RPE15Cl**, leading to more defected crystals and a melt richer in Cl.

A more dramatic example of the differences in crystallization between precise and random analogues is given by the melting traces after isothermal crystallization shown in Figure 5 for increasing crystallization times. Single sharp melting peaks along the kinetic process of **PE21Cl** crystallized at 73 °C are characteristic of homopolymers. The double melting of isothermally crystallized **RPE21Cl** is a general feature of random ethylene copolymers with comonomers that are totally or partially excluded from the crystalline regions.[20,21] It is explained as a result of partitioning of crystallizable sequences.[20] Long crystalline sequences, primarily methylene-based, are selected first and form the early crystalline structure that further melts at the highest temperatures in Figure 5b. The remaining crystallizable sequences form a second population of crystallites with slower kinetics, richer in Cl, and morphologically different from the first. The lower melting endotherms of Figure 5b are associated with this second population of crystallites. They are formed to a large extent from sequences pinned to the initially formed crystallites. Note that while the area under the high melting peak is basically constant with time, the lower melting endotherm increases continuously, reflecting large differences in kinetics. At the isothermal crystallization temperature of 76 °C, the initial selection of primarily long methylene sequences is very fast. However, pinning of the remaining sequences to the first population of crystallites imposes constraints in the melt topology for gathering additional sequences richer in Cl with a concomitant decrease in kinetics as reflected in the melting behavior.

The Br containing polymers behave similarly (Figure 4b). It is observed that while the precise polymers show sharp, well-defined melt transitions, the random analogues show broad double-melting transitions. As discussed for Cl copolymers, this is evidence of a different mechanism for crystallization between the precise polymers and the random copolymers. The lack of a sharp $T_m$ in **RPE21Br** and **RPE15Br** is evidence that the homopolymer-like crystallization of their precise analogues is no longer operative as is expected to be replaced by a mechanism based on selection of long most crystallizable sequences, as described above for the Cl polymers.

In the case of the fluorine containing polymers, large differences in melting behavior are not expected on the basis of the small size of the fluorine atom, which does not introduce a large strain on incorporation into the crystal lattice.[13] In Figure 4c, results are shown for **RPE21F**, **PE21F**, **RPE15F**, and **PE15F**. Several observations can be made in this case. First, it is clear that all fluorine containing random copolymers and precise polymers display sharp, well-defined melt transitions. Second, the peak melting temperatures of all four polymers are very close (in the range 120−127 °C). Looking more closely, for a comparison of **RPE21F** and **PE21F**, it is observed that the random copolymer melts 3 °C higher than its precise analogue (127 °C vs 124 °C). It is expected that the random polymer will display a higher $T_m$ than its precise analogue, which has been shown to display homopolymer-like crystallization due to a mechanism of selection of long crystallizable sequences, which is expected to operate in such random polymers. The two $T_m$ values are suspected to be so close on the basis of the small size of the F atom and its ability to enter into the crystalline lattice with a minimum of disruption. Note that despite the low strain exerted to the lattice by the F atom, the $T_m$ of **RPE15F** is 7 °C lower than the value of **RPE21F**, in agreement with the sequence selection-based crystallization behavior of a random copolymer and the lower molar mass of **RPE15F**. The early formed crystallites of **RPE15F** are in equilibrium with a melt with a composition in F richer than comparable crystallites from **RPE21F**. Thus, **RPE15F** crystals melt at lower $T_m$.

**Conclusion and Outlook.** Here we have shown that ADMET copolymerization of a halogen containing $\alpha-\omega$-diene and 1,9-decadiene is a useful method for the synthesis of industrially relevant model PE copolymers. As evidenced by NMR studies on the unsaturated precursor polymers, a statistically random distribution of comonomers is achieved in a defect-free perfectly unbranched polymer backbone. Thermal analysis via DSC confirms the distinct difference between precise and random EVH polymers produced via ADMET. In the case of precise polymers, sharp and well-defined melt transitions show a homopolymer-like crystallization in which all halogens are equally partitioned between crystalline and noncrystalline regions, while the random copolymers show broad melting transitions that conform to a mechanism of crystallization based on the selection of long crystallizable sequences. Future work will focus on elucidating the crystal structures of the random polymers via X-ray diffraction and developing a quantitative measure of the distribution of halogens between the crystalline and amorphous phases via solid-state NMR.

## Experimental Section

**Chemicals.** Chemicals were purchased from the Aldrich Chemical Co. and used as received unless noted. Grubbs' first-generation ruthenium catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride, was purchased from Strem Chemical and stored in an argon-filled drybox prior to use. Wilkinson's catalyst $RhCl(PPh_3)_3$ was purchased from Strem. Methylene chloride and *o*-xylene were distilled over $CaH_2$.

**Instrumentation.** Unsaturated samples' NMR spectra were acquired on a Varian Inova spectrometer, operating at 500 MHz for $^1H$ and 125 MHz for $^{13}C$, equipped with a 5 mm indirect detection probe and with *z*-axis gradients. The temperature was 25 °C and the solvent chloroform-*d*. $^1H$ and $^{13}C$ chemical shifts were carefully referenced to internal TMS. $^1H$ spectra were collected in one transient, with a relaxation delay of 10 s and an acquisition time of 5 s. Baseline correction was applied prior to integration. $^{13}C$ spectra were collected in 60 000 transients, with zero relaxation delay and an acquisition time of 3 s, which produced a digital resolution of ∼1 ppb/point. gHMBC spectra were collected with 4096 points over a spectral window of 2600 Hz in $f_2$ and 4096 increments over a spectral window of 15 000 Hz in $f_1$, with 16 transients per increment. The relaxation delay was 1 s. The experiment was optimized for a long-range $^1H-^{13}C$ coupling of 8 Hz. Saturated polymer samples' solution $^1H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were recorded on a Mercury 300 spectrometer. All chemical shifts for $^1H$ and $^{13}C$ NMR were referenced to residual signals from $CDCl_3$ ($^1H = 7.27$ ppm and $^{13}C = 77.23$ ppm) and to residual signals from $C_6D_5CD_3$ ($^1H = 2.09$ ppm and $^{13}C = 137.86$ ppm) with an internal reference TMS 0.03% v/v to internal TMS standard for 0. In all the NMR work the solvents were chloroform-*d* or toluene-$d_8$ the temperatures were 25 or 80 °C.

Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

The GPC measurements for samples in THF were taken on a Waters GPCV 2K instrument. Samples were run with HPLC grade THF at 40 °C on Water Styragel HR 5E columns relative to polystyrene standards. Polymer molecular weights reported vs polyethylene standards were measured using a Waters Associates 150C high-temperature gel permeation chromatograph equipped with three Polymer Laboratories mixed bed type B columns and an internal DRI detector. The mobile phase was BHT-inhibited 1,2,4-trichlorobenzene (135 °C, flow rate 1.0 mL/min, typical sample concentration 2 mg/mL).

IR data were obtained from spin-coated films from methylene chloride (chlorine and bromine containing polymers) or dichlorobenzene (fluorine containing polymers) using a Perkin-Elmer Spectrum One FTIR outfitted with a $LiTaO_3$ detector. Measurements were automatically corrected for water and carbon dioxide. Thermogravimetric analysis (TGA) data were obtained with a Perkin-Elmer 7 series thermal analysis system. The TGA samples (2−5 mg) were heated from 50 to 800 °C at 10 °C/min.

Melting and crystallizations were obtained at 10 °C/min in a differential scanning calorimeter TA Instruments DSC-Q1000 V9.6 Build 290 under nitrogen flow and calibrated with indium.

**General Procedure for Bulk Polymerization.** Monomers and Grubbs' first-generation catalyst were combined in a ratio of 500:1 under an argon atmosphere for chlorine and bromine containing polymers. The polymerization was conducted at 35−40 °C under vacuum with stirring for 5 days. The reaction was then stopped, and 50 mL of toluene was added to dissolve the polymer with stirring. The reaction was allowed to cool to room temperature. The polymers were then precipitated by dripping the toluene solution into cold acidic methanol. They were then isolated by filtration and dried.

**General Procedure for Solution Polymerization.** Monomers and Grubbs' first-generation catalyst (500:1 ratio) were dissolved in toluene for fluorine containing polymers under argon and stirred at 45 °C for 5 days. The same amount of catalyst was added into the solution every 24 h. The same procedure as described above was used to isolate the polymer.

**RUPE15F.** Synthesized by the solution method as above using 0.624 g ($3.66 \times 10^{-3}$ mol) of 6-fluoroundeca-1,10-diene,[13] 0.376 g ($2.72 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.05 \times 10^{-2}$ g ($1.28 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**RUPE21F.** Synthesized by the solution method as above using 0.454 g ($2.67 \times 10^{-3}$ mol) of 6-fluoroundeca-1,10-diene,[13] 0.546 g ($3.95 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.09 \times 10^{-2}$ g ($1.32 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**RUPE15Cl.** Synthesized by the bulk method as above using 0.964 g ($5.16 \times 10^{-3}$ mol) of 6-chloroundeca-1,10-diene,[12] 0.536 g ($3.87 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.48 \times 10^{-2}$ g ($1.81 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**RUPE21Cl.** Synthesized by the bulk method as above using 0.711 g ($3.81 \times 10^{-3}$ mol) of 6-chloroundeca-1,10-diene,[12] 0.789

g ($5.71 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.56 \times 10^{-2}$ g ($1.90 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**RUPE15Br.** Synthesized by the bulk method as above using 1.035 g ($4.48 \times 10^{-3}$ mol) of 6-bromoundeca-1,10-diene,[11] 0.465 g ($3.36 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.29 \times 10^{-2}$ g ($1.57 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**RUPE21Br.** Synthesized by the bulk method as above using 0.791 g ($3.42 \times 10^{-3}$ mol) of 6-bromoundeca-1,10-diene,[11] 0.709 g ($5.13 \times 10^{-3}$ mol) of 1,9-decadiene, and $1.40 \times 10^{-2}$ g ($1.71 \times 10^{-5}$ mol) of Grubbs' first-generation catalyst. Analytical yield.

**General Procedure for Hydrogenation.** The polymers containing F or Cl halogens were then hydrogenated using a modified version of the method described by Hahn[14] by dissolving in dry *o*-xylene under argon and adding 3.3 equiv of *p*-toluenesulfonyl hydrazide (TSH) and 4 equiv of tri-*n*-propylamine (TPA). The solutions were refluxed for 9 h and then cooled to room temperature. The hydrogenated polymer was precipitated into ice-cold methanol and isolated by filtration. The dried polymer was then redissolved in toluene and reprecipitated by dipping into ice-cold acidic methanol. A white solid was collected by filtration, and the polymers were isolated in quantitative yield.

The polymers containing Br halogen were hydrogenated using a 150 mL Parr high-pressure reaction vessel equipped with a glass liner and Teflon stirbar. Unsaturated polymer (1.0 g) and Wilkinson's catalyst (0.02 g) were added to the glass liner under nitrogen blanket.[11] Finally, 20 mL of toluene was added. The vessel was sealed and attached to a grade 5 hydrogen tank and purged with hydrogen several times. The bomb was charged with 500 psi of $H_2$ and stirred for 5 days at room temperature. The hydrogenated polymer was dissolved in toluene and precipitated into methanol. The polymer was then filtered and dried under reduced pressure.

**RPE15F.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz toluene-$d_8$): $\delta$ 4.53−4.37 (dp, 1H), 1.8−1.23 (bm, 28H). $^{13}$C NMR (75 MHz, toluene-$d_8$): $\delta$ 95.40, 93.16, 36.27, 35.99, 30.53, 30.41, 30.38, 30.32, 30.26, 26.01, 25.95. Anal. Calcd: C, 78.88; H, 12.80; F, 8.32. Found: C, 71.38; H, 12.16; F, 6.97. $M_w$ (GPC vs PE) = 7900 g/mol. PDI = $M_w/M_n$ = 2.5.

**RPE21F.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz toluene-$d_8$): $\delta$ 4.45−4.28 (dp, 1H), 1.8−1.23 (bm, 40H). $^{13}$C NMR (75 MHz, toluene-$d_8$): $\delta$ 95.41, 93.16, 36.28, 36.00, 30.53, 30.38, 25.97. Anal. Calcd: C, 80.70; H, 13.22; F, 6.08. Found: C, 72.63; H, 12.51; F, 5.35. $M_w$ (GPC vs PE) = 21 600 g/mol. PDI = $M_w/M_n$ = 1.6.

**RPE15Cl.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.89 (p, 1H), 1.69 (m, 4H), 1.60−1.20 (b, 24H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 64.61, 38.76, 29.94, 29.82, 29.76, 29.65, 29.43, 29.38, 26.72. Anal. Calcd: C, 73.58; H, 11.94; Cl, 14.48. Found: C, 69.75; H, 11.74; Cl, 13.52. $M_w$ (GPC vs PS) = 73 600 g/mol. PDI = $M_w/M_n$ = 2.1.

**RPE21Cl.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.90 (p, 1H), 1.70 (m, 4H), 1.60−1.17 (b, 36H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 64.61, 38.76, 29.95, 29.83, 29.77, 29.65, 29.44, 29.39, 26.75. Anal. Calcd: C, 76.66; H, 12.56; Cl, 10.78. Found: C, 75.04; H, 12.55; Cl, 10.84. $M_w$ (GPC vs PS) = 118 500 g/mol. PDI = $M_w/M_n$ = 2.2.

**RPE15Br.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.03 (p, 1H), 1.81 (m, 4H), 1.70−1.00 (bm, 24H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 59.24, 39.40, 29.93, 29.82, 29.73, 29.61, 29.31, 29.25, 27.79. Anal. Calcd: C, 62.28; H, 10.10; Br, 27.62. Found: C, 60.34; H, 9.85; Br, 29.71. $M_w$ (GPC vs PS) = 72 100 g/mol. PDI = $M_w/M_n$ = 1.8.

**RPE21Br.** Hydrogenation was performed as above. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.03 (p, 1H), 1.81 (m, 4H), 1.65−1.15 (bm, 36H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 59.23, 39.41, 29.94, 29.82, 29.74, 29.62, 29.31, 29.25, 27.82. Anal. Calcd: C, 67.54; H, 11.07; Br, 21.40. Found: C, 65.68; H, 10.92; Br, 23.65. $M_w$ (GPC vs PS) = 55 500 g/mol. PDI = $M_w/M_n$ = 1.7.

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**Supporting Information Available:** Detailed NMR characterization data. This information is available free of charge via the Internet at http://pubs.acs.org.

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