

Precision Ethylene/Vinyl Bromide Polymers

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Abstract: Here we report the synthesis of precision ethylene/vinyl bromide (EV/B) polymers *via* metathesis chemistry followed by exhaustive hydrogenation. The polymer primary structures are supported by ¹H NMR, ¹³C NMR, elemental analysis, TGA, and IR. Thermal analysis by DSC shows that a linear trend exists between increasing bromine content and decreasing melting temperature as bromine is incorporated (as a defect) in the crystalline lattice. In reference to the defect-free chain, a change in phase structure causes a dramatic decrease in the observed heat of fusion and a smooth decrease within the Br series. This study describes the first family of precise EV/B polymers reported in the literature.

Keywords: ADMET polymerization; ethylene/vinyl bromide; olefin metathesis; polyethylene

The importance of polyolefins in industry is reflected by the enormous volumes of these polymers that are produced on an annual basis.^[1] While polyethylene (PE) is the most abundant of these polymers, polyethylenes modified with halogens such as poly(vinyl chloride), are extensively employed as a result of the tailored sets of properties they possess.^[2,3] Ethylene/vinyl bromide (EV/B) polymers have received significantly less attention than their ethylene/vinyl fluoride (EVF) or ethylene/vinyl chloride (EVC) counterparts because they are difficult to synthesize, especially those having a well-defined structure.^[4]

No direct synthetic copolymerization methods exist that combine vinyl bromide and co-monomers;^[5] instead a variety of post-polymerization bromination strategies have been employed. The most common techniques employ either bromination of a suspension of PE, or solution bromination.^[6] Similarly, solution

hydrobromination of polyoctenamer has been used.^[7] Additionally, surface bromination of thin PE films with bromine vapor has been described.^[8] Another somewhat different approach to these polymers involves reductive debromination of poly(vinyl bromide).^[5]

Deficiencies in the above techniques can be attributed to the incorporation of structural defects in the polymer precursor (e.g., branching, cyclic defects caused by back-biting) as well as the uncontrolled chemical events that accompany post-polymerization bromination.^[5] Further, the uncontrolled incorporation of bromine, which is assured when using these techniques, leads to polymers with a non-uniform distribution of bromine or even a blocky primary structure.^[6] Consequently, the pursuit of optimized routes to well-defined EV/B co-polymers remains relevant. For example, EV/B co-polymers could serve as the precursor to a variety of modified polyolefins *via* substitution of the bromine atom,^[9,10] or they could prove useful in selective cross-linking. In addition, the EV/B co-polymers could find direct materials applications stemming from the flame retardancy induced in bromine-containing materials,^[11] or more generally based on the modified physical properties and their influence on adhesion, wettability, and surface energy.^[8]

Olefin metathesis offers distinct advantages over previously used methods for the synthesis of EV/B polymers. Acyclic diene metathesis polymerization (ADMET) is now widely accepted as a route to polyolefins having a precisely defined primary structure, for it entails mild chemistry, which does not lead to side reactions involving the reactive bromine functionality. Thus far we have produced a precise EV/B ADMET polymer with a bromine atom located on each and every 19th carbon along the polyethylene backbone.^[12] We now extend this study to a larger family of EV/B polymers in order to examine the effect of bromine content and sequence distribution

on the thermal and crystalline properties of this novel class of polymers.

Synthesis of the necessary brominated ADMET α - ω diene monomers is illustrated in Scheme 1. The alcohol precursors (**4–6**) were prepared according to the methods previously described^[13] and converted to the corresponding bromine monomers (**7–9**) by reaction with carbon tetrabromide and triphenylphosphine.^[12] Bulk polymerization with Grubbs' first generation ruthenium catalyst, followed by exhaustive hydrogenation under mild conditions with Wilkinson's catalyst led to the precise EV/B polymers **PE9Br**, **PE15Br**, and **PE21Br** containing a bromine atom on each and every 9th, 15th, and 21st carbon along the PE backbone, respectively. The primary structure of the polymers was confirmed by ¹H NMR, ¹³C NMR, and elemental analysis (see Supporting Information).

The primary structure of these polymers was confirmed further by thermogravimetric analysis (TGA) (Figure 1a) and infrared spectroscopy (Figure 1b). All three polymers exhibit a two-stage TGA weight loss where the first stage corresponds to the loss of HBr and the second stage marks the catastrophic decomposition of the polymer. Analogous to our previous work on ethylene/vinyl halide polymers^[12] and the reported decomposition of poly(vinyl bromide),^[11,14] the mass loss in the first stage quantitatively reflects the halogen content of the polymer. The observed values for mass loss in the first stage are found to be in agreement with the calculated HBr content for each of the polymers at 39%, 28%, and 22% for **PE9Br**, **PE15Br**, and **PE21Br** respectively.

The IR spectra also display characteristic information regarding the primary structure of the polymers. The absence of a peak at 967 cm⁻¹ for all three polymers indicates complete hydrogenation, based on the disappearance of the out-of plane olefin C–H wag, observed in the unhydrogenated polymers **UPE9Br**, **UPE15Br**, and **UPE21Br** (see Supporting Information). Characteristic peaks corresponding to C–Br stretching are found in the region from 700–450 cm⁻¹

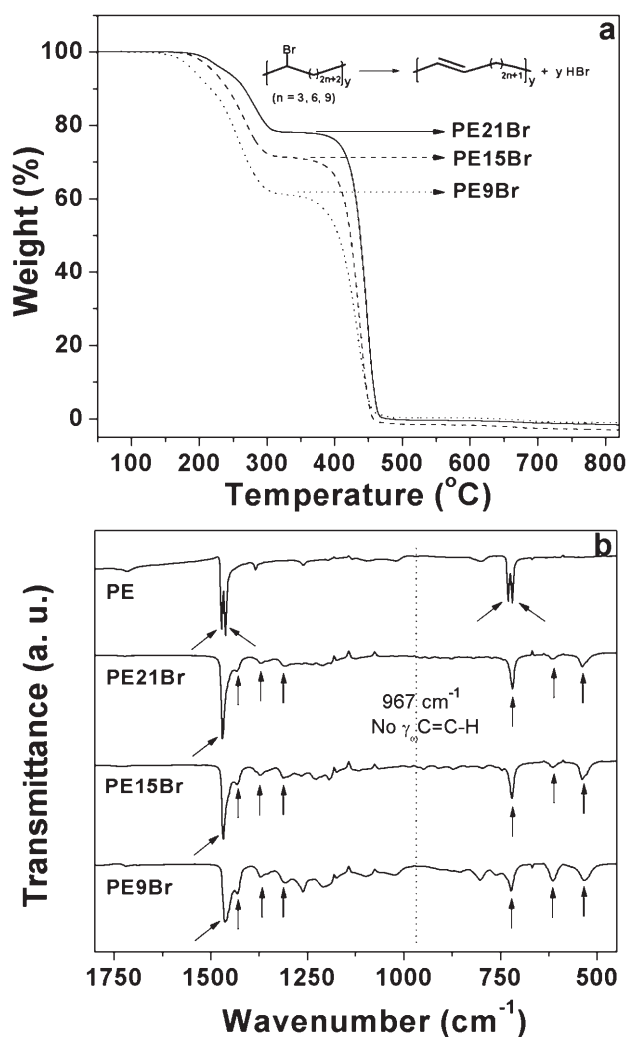
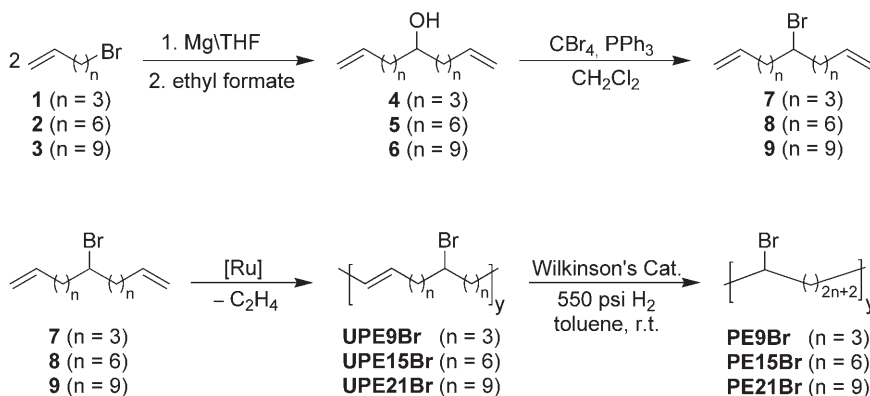


Figure 1. (a) TGA for **PE21Br** (solid line), **PE15Br** (dashed line), and **PE9Br** (dotted line). (b) IR spectra for PE, **PE21Br**, **PE15Br**, and **PE9Br**.

and in all cases the peaks at ~613 cm⁻¹ and ~538 cm⁻¹ can be assigned to secondary bromines in the *gauche* and *trans* configuration, respectively.^[15] From these



Scheme 1.

data it becomes clear that with increasing bromine content, the ratio of *gauche* C–Br ($\sim 613\text{ cm}^{-1}$) increases relative to *trans* C–Br ($\sim 538\text{ cm}^{-1}$). Corresponding methylene peaks at 1368 cm^{-1} and 1308 cm^{-1} also indicate the presence of *gauche* and *trans* conformations, specifically the symmetric and antisymmetric wagging modes of *gauche-trans-gauche* triads.^[16] Other characteristic methylene peaks are assigned for all polymers at $\sim 1470\text{ cm}^{-1}$ and $\sim 1432\text{ cm}^{-1}$ for methylene bending modes,^[17,18] and at $\sim 720\text{ cm}^{-1}$ for methylene rocking.^[19] Importantly, these spectra suggest, in accord with our previous work on **PE19Br**, that these three precise E/VB polymers possess a triclinic rather than an orthorhombic crystal structure based on the absence of doublets at $1463\text{--}1472\text{ cm}^{-1}$ and $721\text{--}730\text{ cm}^{-1}$.^[12,17]

The proposed triclinic structure is also supported by differential scanning calorimetry (DSC) as well (Figure 2). Melting points (T_m) observed on the second cycle of heating and cooling are plotted relative to the bromine content of the polymers (Figure 2a). A linear decrease in T_m is evident with increasing bromine content. This linear trend has been observed for a series of precise *methyl*-branched PE derivatives synthesized *via* ADMET^[20] (see Supporting Information); and here, the correlation of the trends is accentuated by the *similarity in the size of the bromine atom and the methyl group*. The decrease in T_m can be explained using the same arguments proposed for **PE19Br** and similar halogenated ADMET polyolefins,^[12] specifically, that increased bromine content in the crystal is the direct consequence of polymer composition and the larger incorporation of defects leads to a proportionally decreasing T_m . Bromine side groups were also found to enter the crystals of random EV/B polymers.^[21] Figure 2b shows the relationship between the enthalpy of fusion (ΔH_f) and the bromine content. Here the ΔH_f (on a weight basis) shows a dramatic decrease as bromine content is increased at low mole fractions, while increases in bromine content at high mole fraction show markedly smaller changes in ΔH_f . The initial large decrease in ΔH_f for **PE21Br** relative to PE reflects a predicted change in the crystal structure from orthorhombic to triclinic as we previously observed with **PE19Br**.^[12]

Owing to the participation of multiple repeating units in the crystalline unit cells of the brominated ADMET polyolefins, most useful will be the comparison of thermodynamic ΔH_f data, per mole of crystalline repeating unit, for the same triclinic crystal structures. Since these values are at the present time unknown, we use the observed heats of melting to infer trends with length of repeating unit. From the observed values, 17989 J mol^{-1} (**PE21Br**), 10140 J mol^{-1} (**PE15Br**) and 4248 J mol^{-1} (**PE9Br**), ΔH_f scales proportionally to the number of CH_2 groups in the repeating unit. The value of **PE9Br** is nearly one fourth

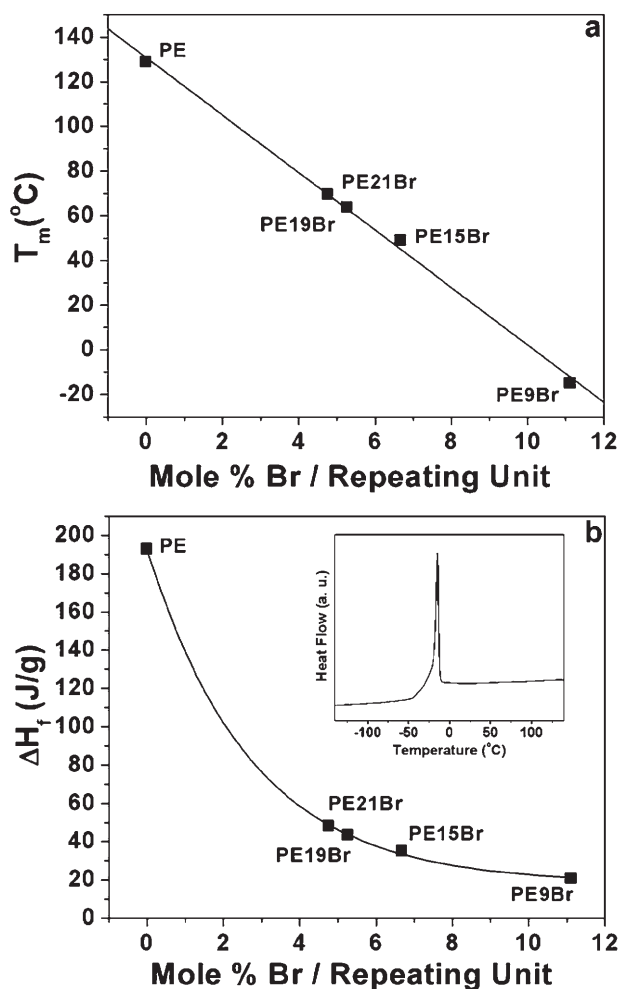


Figure 2. (a) Relationship of the melting point (T_m) with the mole percentage of bromine in the repeating unit for PE, **PE21Br** (4.8% bromine), **PE19Br** (5.3% bromine), **PE15Br** (6.7% bromine) and **PE9Br** (11.1% bromine). (b) Relationship of ΔH_f with the mole percentage of bromine in the repeating unit for PE, **PE21Br** (4.8% bromine), **PE19Br** (5.3% bromine), **PE15Br** (6.7% bromine) and **PE9Br** (11.1% bromine). The inset shows the second heating cycle for **PE9Br**.

of ΔH_f of **PE21Br** denoting that, as the crystals of the same structure incorporate more defects (bromine), the energy required to disorder the all-*trans* packing of the backbone repeating unit is dramatically decreased. Concomitantly, the associated entropy of melting (in $\text{J mol}^{-1}\text{K}$) decreases from $52.5\text{ J mol}^{-1}\text{K}$ (**PE21Br**) to $16.4\text{ J mol}^{-1}\text{K}$ (**PE9Br**) following the expected impact of Br side groups in reducing the configurational entropy of the melt (see Supporting Information).

Comparatively, the crystalline properties of this series of precision brominated polyethylenes follow the behavior of *trans*-poly(alkenamers) for which the melting temperatures increase with the number of

carbon atoms in the repeating unit for the same crystal structure. The enthalpy and entropy of fusion increase with the size of the repeating unit. However, the value of ΔS per single bond remains effectively constant.^[22,23] It appears that this feature may also hold for the precision Br samples as the calculated average ΔS per bond in the series is $2.2 \pm 0.3 \text{ J mol}^{-1} \text{ K}$.

The results presented here illustrate that metathesis chemistry is an efficient method for the synthesis of precisely defined EV/B polymers. The regular structure of these materials is reflected in the primary structure characterization and thermal analysis indicating strong correlations between properties and bromine content. Further work will serve to definitively establish the crystal and phase structure of these polymers utilizing WAXS and solid-state ^{13}C NMR techniques, and also to begin to define potential applications for such polymers.

Experimental Section

Detailed procedures for the synthesis of monomers **7**, **8**, and **9**, shown in Scheme 1, are given in the Supporting Information.

For polymerization, monomer and Grubbs' first generation catalyst were combined in a ratio of 500:1 under an argon atmosphere. Grubbs' first generation catalyst was used based on previous work in our group showing that this catalyst does not cause olefin isomerization, which is a critical point in obtaining a precisely defined primary structure.^[24] The polymerization was conducted at $35\text{--}40^\circ\text{C}$ under vacuum with stirring for 5 days. The reaction was then stopped and 5 mL of toluene were added to dissolve the polymer with stirring. The reaction mixture 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. Polymers were then redissolved in 50 mL of toluene and treated with THP [tris(hydroxymethyl)phosphine] in order to remove any residual catalyst.^[25] The polymers were then reprecipitated into acidic methanol, filtered and dried.

Full characterization (^1H NMR, ^{13}C NMR, and GPC results vs. PS) are given in the supporting information for the unhydrogenated polymers **UPE9Br**, **UPE15Br**, and **UPE21Br**.

The polymers were then 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 a nitrogen blanket. Finally, 20 mL of toluene were added. The vessel was sealed and attached to a grade 5 hydrogen tank and purged with hydrogen several times. The bomb was charged with 550 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.

Full characterization (^1H NMR, ^{13}C NMR, elemental analysis and GPC results vs. PS) are given in the supporting information for the hydrogenated polymers **PE9Br**, **PE15Br**, and **PE21Br**.

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