Hydrogenolysis of linear low-density polyethylene during heterogeneous catalytic hydrogen-deuterium exchange

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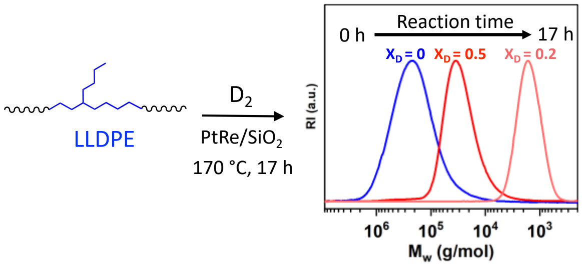
TOC Graphic



Abstract

Exchange of deuterium (D) for hydrogen (H) on polyolefins enabled by heterogeneous catalysts is a versatile and relatively inexpensive technique to obtain matched pairs of isotopically labeled and unlabeled polymers. A bimetallic ultra-wide pore silica-supported platinum-rhenium catalyst (PtRe/SiO_2), originally designed for the hydrogenation of polystyrene (PS), can be used as an isotope exchange catalyst with various saturated hydrocarbon polymers, most notably polyethylene (PE). Recently, we discovered that under certain conditions a commercial linear low-density polyethylene (LLDPE) undergoes severe chain degradation during the H/D exchange reaction. In this study we explored the effects of reacting various polymers on the PtRe/SiO_2 catalyst. First, the extent of hydrogenolysis accompanying deuterium exchange was studied under the most severe reaction conditions (1:1 PtRe/SiO_2-to-polymer by weight, 170 °C) with four different polymers: narrow-dispersity PS, perfectly linear PE, poly(ethylene-*alt*-propylene) (PEP), and a commercial LLDPE. PS was fully saturated to yield poly(cyclohexylethylene) (PCHE) without any detectable hydrogenolysis. Among the polyolefins, linear PE showed the least degradation, PEP incurred an intermediate extent of hydrogenolysis, and LLDPE experienced severe chain degradation; at these reaction conditions the LLDPE was reduced in weight average molecular weight from 120 kg/mol to under 11 kg/mol. A time-resolved experiment also revealed exchange of hydrogen for deuterium on LLDPE coincident with hydrogenolysis following initial uptake of the heavy isotope. This loss of deuterium is due to the interaction of the hydrogenous solvent with the catalyst. Subsequently, the H/D exchange reaction conditions were varied to probe the process leading to LLDPE hydrogenolysis. For this purpose, Pt/SiO_2 and PtRe/SiO_2 catalysts were compared. When using Pt/SiO_2, LLDPE maintained its molecular integrity at all catalyst loadings (1:1, 0.2:1, 0.1:1 catalyst-to-polymer by weight) and reaction temperatures (130 and 170

°C). In the case of $PtRe/SiO_2$, reducing the catalyst loading decreased but did not eliminate hydrogenolysis of LLDPE. Kinetic experiments and microstructural analysis of the hydrogenolysis products implicated a degradation mechanism involving C-C chain scission away from the tertiary carbon associated with the short (C_4H_9) chain branches. These findings suggest a degradation mechanism mediated by the cooperative adsorption of the 4-carbon side chain and backbone units on the catalyst surface. The results of this study set important limitations on the conditions that can be employed to exchange deuterium for hydrogen on LLDPE and other polyolefins using the high surface area wide pore $PtRe/SiO_2$ heterogeneous catalyst.

Introduction

Deuterium labeled polymers are essential ingredients in small angle neutron scattering (SANS) experiments as probes that provide scattering contrast. Blends of labeled and unlabeled polymers enable the analysis of single chain conformations, block copolymer self-assembly in bulk or in solution, and determination of thermodynamic interactions in polymer blends, among other applications.[1] Deuterium labeling of polymers is generally achieved through one of three methods: 1) polymerization with deuterated monomers, 2) saturation of unsaturated polymer precursors with deuterium, or 3) catalytic hydrogen/deuterium (H/D) exchange. The first technique is generally expensive due to the high cost of deuterated monomers. Moreover, it can be challenging to obtain exactly matched pairs of labeled and unlabeled polymers due to variations in reaction conditions. These limitations are particularly problematic when dealing with commercial materials such as polyethylene (PE). The second technique is able to provide a matched pair of labeled and unlabeled polymers by separately saturating the same polymer precursor with deuterium and hydrogen. However, this method is limited to unsaturated precursors, such as polybutadiene, polyisoprene, or polystyrene. Catalytic H/D exchange is applicable to saturated polymers, and provides a versatile and relatively inexpensive method to obtain chemically matched isotopically labeled polymer pairs, provided the molecular structure (architecture, molecular weight, and dispersity) of the polymer is preserved.

While catalytic H/D exchange with low molecular weight alkanes has been studied extensively,[2] exchange reactions with saturated polyolefins are relatively unexplored. The earliest examples were presented by Case and Atlas,[3] where polypropylene was H/D exchanged up to 3% using a Nickel/Kieselguhr catalyst. Tanzer and Crist[4] and Nicholson and Crist[5] used a heterogeneous rhodium catalyst and pressurized deuterium gas, obtaining 5% H/D exchange on poly(ethylethylene) (PEE).[4] This yield was improved when deuterated cyclohexane was used as the solvent, producing up to 60% isotope exchange on PE.[5] Several years ago our group showed that a heterogeneous bimetallic catalyst, platinum-rhenium supported on ultra-wide porous silica (PtRe/SiO_2), induces efficient H/D exchange on polyolefins, leading to up to 80% deuterium content on PE, apparently without altering the polymer structure.[6–9]

PtRe/SiO_2 was originally developed as a robust hydrogenation catalyst for polystyrene (PS), offering additional stability relative to Pt/SiO_2, in producing poly(cyclohexylethylene) (PCHE) and PCHE-containing block copolymers on a commercial scale.[10–13] The bimetallic nature of the catalyst was found to improve the catalyst lifetime compared to Pt/SiO_2, and rendered the catalyst more tolerant to polar impurities.[13] The ultra-wide pore size of the silica support (pore diameter ≈ 3000 – 4000 Å) allows facile diffusion of polymers in and out of the pores, while providing for relatively high metal content and surface area, thus enabling reduced catalyst loading and short reaction times (ca. 0.1:1 catalyst:polymer (wt:wt), <1h, respectively) compared to other hydrogenation catalysts such as palladium supported on calcium carbonate (5:1 catalyst:polymer (wt:wt), 12-40 hours).[11]

Our group has been using both Pt/SiO_2 and PtRe/SiO_2 catalysts extensively, mainly for hydrogenation of polydienes, polystyrene, and related block copolymers.[14–23] For the H/D exchange reactions we have almost exclusively used the PtRe/SiO_2 catalyst, and identified several factors that affect the isotope exchange efficiency with polyolefins. Habersberger *et al.* reported H/D exchange on polyethylene, isotactic polypropylene (*i*PP), and poly(ethylene-*alt*-propylene) (PEP), and showed that the type of solvent employed strongly influences the extent of H/D exchange.[6] Later, Habersberger and Baugh also showed the importance of the solvent type in preserving tacticity before and after catalytic H/D exchange on *i*PP.[24] Zeng *et al.* reported preferred H/D exchange of the methyl protons on saturated poly(butadiene) with variable ethyl branch content,[9] and reported an overall decrease in the level of H/D exchange with increasing branch fraction. The molecular weight of the polymer chains also was found to affect the extent of exchange,[7–9] which increased with higher polymer molecular weight.

Generally, the H/D exchange reaction is performed in a high-pressure reactor, using a saturated hydrocarbon solvent such as isooctane or cyclohexane with a catalyst-to-polymer loading ranging from 0.1:1 to 0.4:1 (wt:wt).[6–9] The reaction mixture is kept under pressurized deuterium gas and heated to 170 °C for 17 h. This protocol was adopted from hydrogenation reactions optimized for polystyrene homo-,[21] random-,[14] and block copolymers, for which hydrogen gas is used instead of deuterium.[15–18,23] Most of these copolymers contained polybutadiene blocks, which were fully saturated to yield polyethylene blocks upon hydrogenation without damaging the polymer integrity. These hydrogenation conditions also were successful for the preparation of other model polyolefin block polymers, for example, poly(ethylene-*alt*-propylene)-*b*-poly(ethylene-*ran*-ethylethylene) (PEP-*b*-PEE_E), starting from a 1,4-poly(isoprene)-*b*-1,2-poly(butadiene) (PI-*b*-$PB_{1,2}$) diblock copolymer precursor that contained 70-80% 1,2-butadiene addition.[25] However, during the recent hydrogenation of a related copolymer, 1,4-poly(isoprene)-*b*-1,4-poly(butadiene), hydrogenolysis (i.e., polymer degradation) was observed, even though the reaction was performed following the same 'standard' protocol (Figure S1). The degradation was suppressed when the temperature was lowered to 100 °C and the reaction time reduced from 17 to 6 h. These results, however, were puzzling since use of a 1:1 catalyst-to-polymer loading for H/D exchange on poly(ethylene-*ran*-ethylethylene) (PEE_E) homopolymers with a range of ethylene branch content proceeded without any significant polymer degradation.[9] These observations motivated us to explore the occurrence of polymer degradation during H/D exchange as a function of polymer molecular structure and reaction conditions.

This report examines the efficacy and limitations of the ultra-wide pore $PtRe/SiO_2$ catalysts in conjunction with H/D exchange reactions on saturated hydrocarbon polymers. We describe the unexpected hydrogenolysis observed with a commercial linear low-density polyethylene (LLDPE) when $PtRe/SiO_2$ is used at high catalyst loading, and compare these results with the behavior of this catalyst when applied to a perfectly linear high-density polyethylene (PE), poly(ethylene-*alt*-propylene) (PEP), and polystyrene (PS). Then we discuss the relative H/D exchange efficiencies of both Pt/SiO_2 and $PtRe/SiO_2$ catalysts on LLDPE with several variations of catalyst loading, reaction temperature, and polymer concentration. Finally, we propose a mechanism leading to the hydrogenolysis of LLDPE based on the microstructural analyses of the degradation products.

Materials and methods

Materials

High purity linear low-density polyethylene (LLDPE) was provided by ExxonMobil (Exceed 1018). The manufacturer describes the polymer as an ethylene/1-hexene copolymer with relatively homogeneous branch distribution.[8] The microstructure of the polymer was confirmed via ^1H and

^{13}C DEPT135 NMR spectroscopy (Figure S2 and S3, respectively) as 1 butyl sidechain per 80 backbone carbon atoms. Poly(ethylene-*alt*-propylene) (PEP) was prepared by hydrogenation of a poly(isoprene) precursor (95% 1,4-addition) synthesized via anionic polymerization as described previously.[26] Linear polyethylene (PE) was synthesized by ring opening metathesis polymerization of cyclooctene followed by hydrogenation with the homogeneous catalyst *p*-toluenesulfonyl hydrazide, similar to previously reported methods (^{1}H NMR spectrum provided in Figure S7).[27] Polystyrene (PS) was synthesized by anionic polymerization. PtRe/SiO_2 and Pt/SiO_2 were provided by the Dow Chemical Co. and were used as received. All solvents (isooctane or cyclohexane from Sigma Aldrich), H_2 (Matheson Gas) and D_2 (Cambridge Isotope Laboratories, Inc.) gases were used without further purification.

Hydrogen/deuterium (H/D) exchange reaction

General procedure. A representative reaction procedure is as follows. A 0.3 L stainless steel reactor equipped with a magnetic stirrer was loaded with 1 g of polymer and 130 mL solvent (a concentration of 0.0076 g/mL) (isooctane for LLDPE, PE, and PEP), followed by the addition of 1 g of catalyst (PtRe or Pt/SiO_2). The reactor was sealed and purged with argon gas for 30 min. Then, the reactor was filled with 500 psig of deuterium (or hydrogen) gas at room temperature and heated to 170 °C and stirred for 17 h. Once cooled to room temperature, the reactor was depressurized, then purged with argon for 15 min, and unsealed. For LLDPE and PE, the reaction mixture was filtered at room temperature to remove isooctane since it has a relatively low boiling point and is not suitable for hot filtration. The polymer and catalyst residue were then re-dissolved in xylene at 130 °C, and subsequently filtered through 0.22 μm filter paper (Express Plus Membrane, Millipore) at 130 °C and precipitated in a 10-fold volumetric excess of methanol. Recovered polymer products were dried under dynamic vacuum for at least 24 h prior to further analysis. For PEP, the reaction mixture was filtered gravitationally at room temperature to remove catalyst residue and the filtrate was subsequently precipitated in 10-fold volumetric excess of methanol.

Time-resolved H/D exchange reaction. 5 g of LLDPE, 500 mL isooctane (a concentration of 0.0099 g/mL), and 5 g PtRe/SiO_2 (or Pt/SiO_2) were added to a 1 L Parr reactor equipped with a magnetic stir bar. Subsequently, the reactor was filled with 500 psig of deuterium gas at room temperature and heated to 170 °C for 17 h. The reaction was monitored by collecting samples at different times throughout the course of the reaction, every 2 – 3 h up to 17 h. Aliquots were collected by transferring small amounts (ca. 5–10 mL) of the reaction solution from the 1 L reactor into a 0.3 L Parr reactor through a 1 ft long section of copper tubing (0.25 in. i.d.), which connected the sample ports of the two reactors. The 0.3 L reactor was purged with argon for 10 min prior to each sample collection. During sample collection, the tubing was kept at 130 °C using heating tape to prevent precipitation of polymer. A freshly cleaned copper tube was used for each sample collection. The polymer samples were then filtered, dried, and characterized.

Saturation of polystyrene. A 0.3 L stainless steel reactor equipped with a magnetic stirrer was loaded with 1 g of polymer and 130 mL isooctane followed by 1 g of PtRe/SiO_2 catalyst. The reactor was sealed and purged with argon gas for 30 min. Then, the reactor was filled with 500 psig of deuterium gas at room temperature. (When saturating with H_2 cyclohexane was used as solvent following standard procedures optimized in our laboratories).[21] The reactor was heated to 170 °C and the contents stirred for 17 h. Once cooled to room temperature, the reactor was depressurized, purged with argon, and unsealed. The catalyst residue was removed through gravitational filtration. The filtrate was then added dropwise in a 10-fold volumetric excess of methanol to precipitate the polymer product. Recovered polymer was dried under dynamic vacuum at 50 °C for at least 24 h prior to further analysis.

Characterization

Size exclusion chromatography (SEC). Measurements were conducted with LLDPE and PE at 135 °C using an Agilent PL-GPC 220 High Temperature GPC/SEC System equipped with a refractive index detector with 1,2,4-trichlorobenzene as the mobile phase. The measured elution time was compared against polystyrene standards. The weight-average molecular weights (M_w) were calibrated using Mark-Houwink parameters for linear polyethylene $K = 59.7\times10^{-3}$ (mL/g), $\alpha = 0.695$,[28] and polystyrene $K = 12.1\times10^{-3}$ (mL/g), $\alpha = 0.707$.[29] The weight-average molecular weights and dispersities ($Đ$) of PEP and PS were determined by SEC at 25 °C with tetrahydrofuran (THF) as the solvent on an Agilent 1260 Infinity system. The eluents were monitored by a Wyatt Optilab T-rEX refractive index detector, and the corresponding molecular weights and distributions were determined using Zimm plots based on data obtained from a Wyatt Dawn Heleos II multiangle laser light scattering (MALS) detector. Refractive index increments ($\mathrm{d}n/\mathrm{d}c$) in THF were measured using the Optilab T-rEX refractive index detector with a wavelength of 633 nm, and were determined as 0.102 mL/g, 0.187 mL/g and 0.120 mL/g for PEP, PS, and PCHE respectively.

Fourier Transform Infrared Spectroscopy (FTIR). Spectra were recorded on a Bruker Alpha Platinum ATR spectrometer with 4 cm^{-1} resolution over 16 scans. The level of H/D exchange was determined by comparing relative integral areas of the CH (3000 – 2550 cm^{-1}) and CD (2250 – 2000 cm^{-1}) stretching signals.

Differential Scanning Calorimetry (DSC). Measurements were performed using a TA Instruments Discovery system. Hermetically sealed aluminum pans were loaded with 5 – 10 mg of sample.

Samples were heated from 50 to 300 °C at a rate of 10 °C/min. Second heating runs were used for the analysis of melting points and enthalpies.

Nuclear Magnetic Resonance Spectroscopy (NMR). ^{1}H NMR spectra were collected on a Bruker Avance HD III 400 MHz (AX-400) spectrometer. High temperature ^{1}H and ^{13}C NMR spectra were collected on a Bruker Avance HD III 400 MHz (AM-400) spectrometer equipped with a variable temperature probe. All high temperature NMR measurements were conducted at 358 K. For the ^{13}C DEPT135 experiments the Bruker *deptsp135* pulse sequence was employed and data were collected over an average of 256 scans. Quantitative ^{13}C NMR analyses were performed on a Bruker Avance III 500 MHz (AV-500) spectrometer using the *C13IG* pulse sequence over 1024 scans with d1 for 4.5 s and acquisition time 1.5 s. Each peak was integrated over a range of 0.6 ppm. The signal to noise ratio (SNR) was calculated using the MestReNova SNR calculation script. Relative uncertainty (ΔR/R) was calculated according to,[30]

$$\frac{\Delta R}{R} = \frac{\left[\frac{1}{SNR_{CH}} - \frac{R}{SNR_{CH}}\right]}{R} \tag{1}$$

where R is ratio of the integral area of the backbone methylene carbon at 29.3 ppm to the methine carbon, and SNR_{CH} is the SNR calculated relative to the methine peak at 37.7 ppm.

Results and Discussion

Effect of polymer structure

To explore the extent of hydrogenolysis on different types of polymers, we performed H/D exchange on three structurally different polyolefins: a perfectly linear polyethylene (PE), a poly(ethylene-*alt*-propylene) (PEP), and a linear low-density polyethylene (LLDPE) (Table 1). All the comparative reactions were run at 170 °C under 500 psig deuterium (D_2) (or H_2 gas) for 17 h in the presence of the PtRe/SiO_2 catalyst at the highest catalyst-to-polymer loading reported, 1:1 wt:wt.[9] As a control, we saturated a narrow-dispersity polystyrene (PS) sample to establish whether hydrogenolysis occurred when the PtRe/SiO_2 catalyst was used to prepare poly(cyclohexylethylene) (PCHE).

Table 1. Characteristics of polymers subjected to H/D exchange or hydrogenation with 1:1 PtRe/SiO_2:polymer (wt:wt) catalyst loading at 170 °C for 17 h. Reactions were conducted with 1 g of polymer and 130 mL isooctane in a 0.3 L reactor charged with 500 psig D_2 (or H_2).

Sample[a]	**M_w (kg/mol)**	**Đ**	**X_D**[d]
PS[b]	81	1.02	-
PE[c]	128	3.3	-
PEP[b]	127	1.04	-
LLDPE[c]	120	2.5	-
d-PCHE[b,e]	88 (88)[e]	1.02 (1.02)[e]	0.40 (0)[e]
d-PE[c]	98	4.2	0.40
d-PEP[b]	74	1.2	0.40
d-LLDPE[c]	6, 7.4 (11)[e]	2.4, 1.7, (1.5)[e]	0.20, 0.53 (0)[e]

a) Deuterium labelled polymers are denoted by the prefix d-

b) Molecular weight and dispersity values determined using THF SEC MALS.

c) Values determined using high temperature SEC calibrated against PS standards. Values converted using Mark-Houwink parameters for PS ($K=13.1\times10^{-3}$ mL/g, $\alpha = 0.707$)[29] and for linear PE ($K= 57.9 \times10^{-3}$ mL/g, $\alpha = 0.695$).[28]

d) Fraction of deuterium determined using ATR-FTIR and integrated areas of the CH stretching (3000 – 2550 cm^{-1}) and CD stretching (2250 – 2000 cm^{-1}) signals.

e) Values in parenthesis are results from the saturation reaction performed with hydrogen gas.

Quantitative saturation of the narrow-dispersity PS to PCHE was confirmed via ^{1}H NMR and FTIR spectroscopies (Figures S4 and S5). The dispersity of d-PCHE was found to be exactly the same as its precursor PS (both 1.02), confirming that the polymer backbone integrity was preserved (Table 1). The SEC curve of d-PCHE was slightly shifted toward higher elution times than that for PS (Figure 1a), which reflects the combined effects of solvent quality and a smaller statistical segment length, b_{PCHE} = 4.6 Å[20] versus b_{PS} = 6.7 Å.[31] A similar effect has been observed during hydrogenation of poly(vinyl ethylene) to poly(ethyl ethylene).[32] To ensure that this shift is not an artifact of saturating the polymer with deuterium we repeated the reaction using hydrogen gas. The resulting SEC trace had a dispersity of 1.02 and the shifted curve precisely overlapped the d-PCHE result (Figure S6).

Unlike PS, the polyolefins underwent varying degrees of hydrogenolysis during the 17 h H/D exchange reaction at 170 °C with a catalyst:polymer loading (wt:wt) of 1:1 (Table 1). The extent of hydrogenolysis showed a strong dependence on the polymer structure. The perfectly linear PE underwent a minor amount of degradation, where the SEC curve broadened slightly and shifted toward longer retention times (Figure 1b); M_w dropped from 128 to 98 kg/mol. In comparison, PEP showed a greater molecular weight reduction (127 to 74 kg/mol) along with an increase in dispersity (Figure 1c). LLDPE underwent extensive hydrogenolysis, where the SEC data revealed a drop in the average molecular weight of more than an order of magnitude (Figure 1d). Three separate experiments yielded reductions in molecular weight from 120 kg/mol to 6.0, 7.4, and 11 kg/mol (Table 1). The source of the variability in product M_w between reactions is not known, although inhomogeneous mixing of the catalyst/solution slurry and catalyst poisoning are likely candidates.

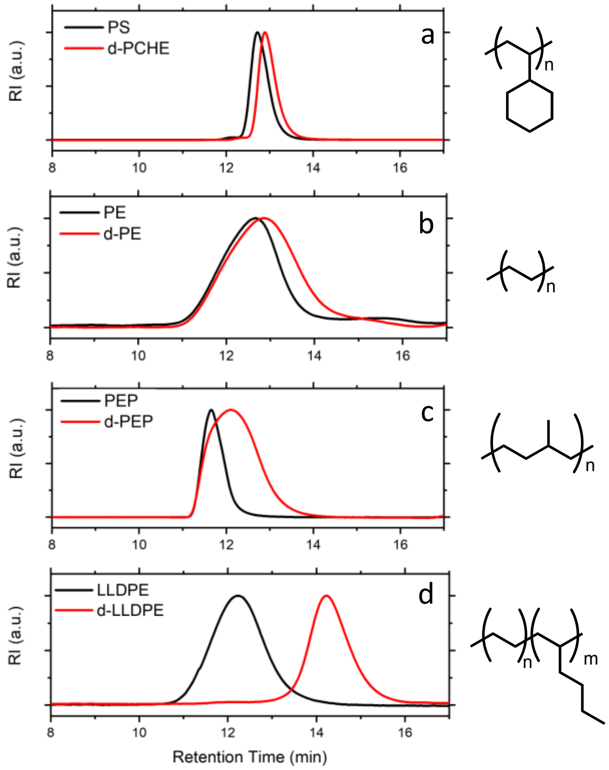


Figure 1. SEC traces before (black curves) and after (red curves) reaction with deuterium for 17 h over a PtRe/SiO_2 catalyst at a 1:1 catalyst-to-polymer (wt:wt) loading at 170 °C. a) PS (black curve) and PCHE (red curve) before and after saturation. b) Perfectly linear PE, c) PEP, and d) LLDPE with 1 butyl side chain per 80 backbone carbon atoms. Repeat unit structures are shown beside each panel of SEC results. The small shoulder in the PE curve (panel b) at long retention times is likely due to a small fraction of cyclic polymers that formed during the synthesis of poly(cyclooctene), a known consequence of ROMP of cyclooctene.

The level of H/D exchange, denoted X_D (fraction of deuterium versus total amount of deuterium and hydrogen), was determined using infra-red spectroscopy by comparing the integral areas of the CH stretching (3000–2550 cm^{-1}) and CD stretching (2250–2000 cm^{-1}) signals. Example spectra are shown in Figure 2, where the CH and CD stretching region of PE is evident before and after H/D exchange. All polymers except for LLDPE reached an average of $X_D = 0.40$ (Figures S8 and S9, respectively). A comparison of the ^1H NMR data for PEP before and after the isotope exchange reaction showed that the relative ratios of methyl (-CH_3), methylene (-CH_2-), and methine (-CH-) hydrogens remained essentially constant (Figure S10), indicating that on average all hydrogens of PEP have a similar propensity towards isotope exchange, consistent with previous reports.[6] LLDPE, however, displayed significant variability in the amount of deuterium exchanged over the PtRe/SiO_2 catalyst at 170 °C and the 1:1 loading when reacted for 17 h, ranging from $X_D = 0.07$ to 0.53. As discussed in the following sections, the extent of H/D exchange also was found to be dependent on the reaction conditions, such as catalyst loading, polymer concentration, temperature, and reaction time.

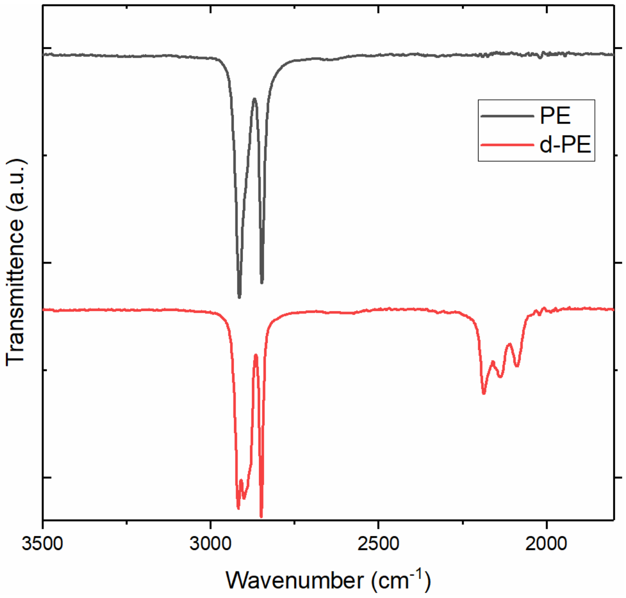


Figure 2 ATR-IR data of linear PE before (top) and after H/D exchange (bottom) using PtRe/SiO_2 at 170 °C with 1:1 (wt:wt) catalyst-to-polymer loading. Spectra are shifted vertically for clarity.

These results reveal a curious trend of increasing extent of hydrogenolysis from PE to PEP to LLDPE. The primary difference between these polyolefins is the number and spacing of tertiary carbon centers along the polymer backbone. The linear PE is composed of a single long sequence of methylene (-CH_2-) units (except for the chain ends) and no tertiary carbon atoms. PEP has a tertiary carbon center (-CH-) connected to a methyl group (CH_3) on every fourth carbon along the backbone; there also is approximately one isopropyl group per 100 backbone carbon atoms. The LLDPE specimen has a structure nominally very similar to the linear PE, with just one tertiary center on average per 80 backbone carbon atoms, connected to a four-carbon long alkyl branch. It appears that the branched repeat units affect the extent of hydrogenolysis experienced by each polyolefin chain. We associate the relative stability of PE to hydrogenolysis with a lack of short chain branches and the associated tertiary carbon centers. Surprisingly, LLDPE degrades much more extensively than PEP, despite having a much lower fraction of tertiary carbon atoms relative to methylene groups in the backbone. Thus, the extent of LLDPE hydrogenolysis likely reflects factors in addition to the presence of tertiary carbon centers, which may include the distance between the branch points, the branch length (butyl vs methyl), steric hindrance upon adsorption on the catalyst surface, and perhaps the local conformation of the polymer chain. One other possibility is unzipping of the polymer backbone induced by dehydrocyclization of the butyl side-chains.[33] While these hypotheses require further analysis, the above results clearly show that the reaction conditions optimized for PS-containing copolymers can disrupt the chain integrity of polyolefins.

For the remainder of this article we examine: 1) the reaction conditions that optimize H/D exchange on LLDPE while maintaining polymer integrity, focusing on the effect of catalyst type, catalyst loading, and reaction concentration and temperature; and 2) the mechanism of degradation using a time-resolved analysis of the reaction and characterization of the microstructure of the degradation products.

H/D exchange and hydrogenolysis of LLDPE

As noted above, the ultra-wide pore silica supported PtRe/SiO_2 and Pt/SiO_2 catalysts were developed to enable hydrogenation of PS homopolymer and block copolymers on a commercial scale.[10–13] Our groups have been using both catalysts for hydrogenation of various model polymers,[14–23] but only the PtRe/SiO_2 catalyst was exploited for H/D exchange reactions.[6,8,9] Here, both catalysts are compared for the ability to promote H/D exchange in conjunction with the effect on polymer chain integrity. For this analysis, isotope exchange was evaluated on LLDPE under three sets of conditions: (*i*) catalyst-to-polymer ratios of 1:1, 0.2:1, and 0.1:1 (wt:wt); (*ii*) polymer concentrations of 0.0076 and 0.0015 g/mL; (*iii*) reaction temperatures of 130 and 170 °C. The molecular weights, dispersities, and deuterium levels achieved with these reactions are listed in Table 2.

Table 2. Reaction conditions for catalytic H/D exchange on LLDPE conducted for 17 h in a 0.3 L reactor charged with 500 psig D_2 (or H_2).

Sample[a]	**Catalyst**	**Catalyst:Polymer (wt:wt)**	**Polymer conc. (g/mL)**	**T (°C)**	**M_w**[b] **(kg/mol)**	**Đ**[b]	**X_D**[c]
LLDPE	-	-	-	-	120	2.5	-
i-PtRe-1	PtRe	1:1	0.0076	170	6.0, 7.4 (11)[e]	2.4, 1.7 (1.5)[e]	0.20, 0.53 (0)[e]
i-PtRe-0.2		0.2:1			70	3.0	0.56
i-PtRe-0.1		0.1:1			100	2.5	0.53
i-Pt-1	Pt	1:1			110	3.0	0.46
i-Pt-0.2		0.2:1			120	2.6	0.58
i-Pt-0.1		0.1:1			110	2.7	0.13
ii-PtRe-1	PtRe	1:1	0.0015	170	1.2[d],	1.2[d],	0.41
ii-Pt-1	Pt				110	2.8	0.74
iii-PtRe-1	PtRe	1:1	0.0076	130	100, 117[f]	3.4, 2.1[f]	0.47, 0.22[f]
iii-Pt-1	Pt				120	3.4	0.38

a) An example of sample nomenclature is i-Pt-1, where the Roman numeral refers to the group of experiment, Pt (or PtRe) symbolizes the catalyst used, and the last set of numbers is the catalyst loading.

b) Determined using high temperature SEC calibrated against PS standards. Values converted using Mark-Houwink parameters for PS ($K = 13.1\times10^{-3}$ mL/g, $\alpha = 0.707$)[29] and for linear PE ($K = 57.9\times10^{-3}$ mL/g, $\alpha = 0.695$).[28]

c) Fraction of deuterium determined using ATR-FTIR measurements and relative integral areas of the CH stretching (3000 – 2550 cm^{-1}) and CD stretching (2250 – 2000 cm^{-1}) signals.

d) Molecular weight and dispersity may reflect limit of size exclusion for the high temperature SEC columns.

e) Values in parenthesis are results from the saturation reaction performed with hydrogen gas.

f) Reactions performed in 1L reactor.

i) Effect of catalyst and catalyst loading

H/D exchange with LLDPE was studied using Pt/SiO_2 and $PtRe/SiO_2$ at catalyst-to-polymer loadings (wt:wt) of 1:1, 0.2:1, and 0.1:1 under 500 psig D_2 at 170 °C and a reaction time of 17 h. All reactions resulted in exchange of deuterium for hydrogen over the range $X_D = 0.13 – 0.58$, as determined by FTIR spectroscopy (Figure S11). The Pt/SiO_2 catalyst showed the least H/D exchange ($X_D = 0.13$) at the lowest (0.1:1) catalyst loading. However, we cannot draw firm conclusions regarding the exchange reactions due to the variability in deuterium labeling from run to run under nominally identical conditions. For example, the $PtRe/SiO_2$ produced $X_D = 0.20$ and

0.53 at the 1:1 loading condition. With the exception of these two cases, roughly half the hydrogen atoms were exchanged for deuterium using both catalysts at the three different catalyst to polymer loadings.

In contrast, the molecular weights of the reaction products were strongly influenced by the choice of catalyst and loading at 170 °C. Figure 3 shows SEC traces of the final products. With the Pt/SiO_2 catalyst LLDPE molecular integrity was maintained at every catalyst loading (Figure 3a). On the other hand, PtRe/SiO_2 caused degradation of the LLDPE at every catalyst loading. A 1:1 catalyst:polymer loading reduced the molecular weight from 120 kg/mol to 6 kg/mol as shown in Figure 3b; separate reactions (using H_2) led to 7.4 and 11 kg/mol (Table 1 and 2). At lower PtRe/SiO_2 catalyst loadings the extent of hydrogenolysis was reduced although the molecular weight of the products were still distinctly lower than the starting material; a 0.2:1 catalyst loading produced $M_w \approx 70$ kg/mol versus 120 kg/mol for the starting polymer. Reducing the catalyst loading further to 0.1:1 dropped the extent of degradation, yielding polymer with $M_w \approx 100$ kg/mol.

These results indicate that both catalysts are capable of promoting H/D exchange. With Pt/SiO_2 the polymer structure remains intact, while PtRe/SiO_2 induces both H/D exchange and hydrogenolysis. The effect of Re addition to Pt on activating C–C bond breaking or hydrocracking has been well documented.[34–36] Recent discoveries suggest that Re may be providing a Brønsted acidic function to an otherwise non-acidic Pt/SiO_2 catalytic system.[37] Thus, enhanced activity of PtRe/SiO_2 toward hydrogenolysis may be an effect of the acidic character of the added rhenium. Moreover, Re is a known cracking catalyst that binds to hydrocarbons strongly. Thus, it is not surprising that PtRe induces hydrogenolysis.

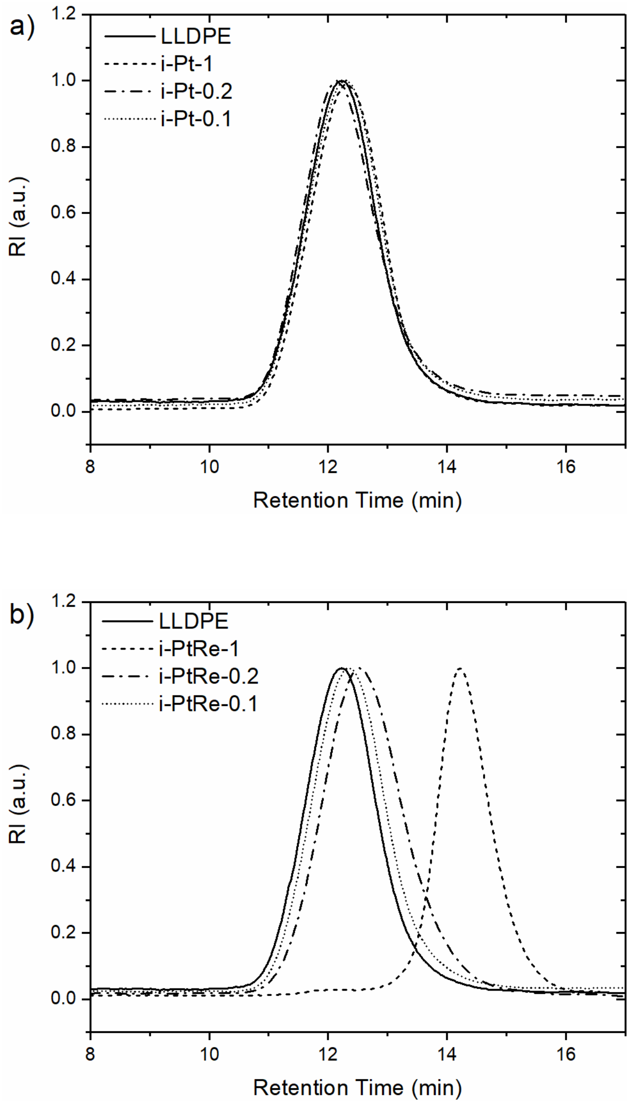


Figure 3. High temperature SEC curves of LLDPE before (solid curves) and after H/D exchange using (a) Pt/SiO2 and (b) PtRe/SiO2 catalyst at 170 °C with 1:1 (dashed curve), 0.2:1 (dash-dotted curve), and 0.1:1 (dotted curve) catalyst-to-polymer (wt:wt) loading.

ii) Effect of polymer concentration

Polyethylene can exhibit a lower critical solution temperature (LCST) in alkanes under high pressure and elevated temperatures, ranging from 80 to 270 °C depending on the saturated hydrocarbon solvent, and the molecular weight and branch fraction of the PE.[38–40] A PE with M_w $\approx$ 100 kg/mol was shown to have an LCST of about 150 °C in *n*-pentane at volume fractions around

0.025 – 0.05.[38] For the reactions reported in the previous sections the concentration of polymer was 0.0076 g/mL. If this concentration places the solution close to the LCST boundary, the polymer may phase separate, potentially enhancing adsorption onto the catalyst surface and creating a favorable environment for C–C bond breaking reactions. In other words, due to a change in solvent-polymer interactions, the polymer may not readily desorb from the catalyst, which could enhance chain breaking. If this hypothesis were correct, reducing the polymer concentration while keeping the temperature and catalyst loading constant, might move the solution farther away from a possible phase boundary, thus avoiding the hydrogenolysis event.

To assess this possibility, we performed the isotope exchange reaction at a five-fold lower polymer concentration, i.e., 0.0015 g/mL in isooctane, while maintaining the temperature at 170 °C and a 1:1 catalyst-to-polymer ratio. As seen in Figure 4 and Table 2, extensive hydrogenolysis occurred at the lower concentration. However, the molecular weight of the Pt/SiO_2 catalyzed reaction product at this lower concentration (also at 170 °C and 1:1 catalyst-to-polymer) was indistinguishable from the molecular weight of the starting material, indicating absence of chain degradation. Hydrogenolysis with the bimetallic PtRe/SiO_2 catalyst was more severe at the lower polymer concentration, resulting in an apparent molecular weight of just $M_w \approx 1.2$ kg/mol (Table 2). We note however that the measured dispersity $Đ = 1.2$ is not consistent with random cleavage of the LLDPE chains from which a dispersity closer to 2 would be anticipated. We posit three possible explanations for this result: (*i*) fractionation and loss of polymer during sample recovery; (*ii*) approaching the size exclusion limit of the high temperature SEC (Figure S12); (*iii*) a limiting molecular weight for polymer adsorption on the catalyst surface. As described further in the Supporting Information, we favor point (*iii*). Overall, lowering the polymer concentration from roughly c* (~ 0.01 g/mL) to the dilute limit (c < c*) apparently enhances chain degradation during the PtRe/SiO2 catalyzed reaction. An FT-IR trace corresponding to this run is provided in Figure S13.

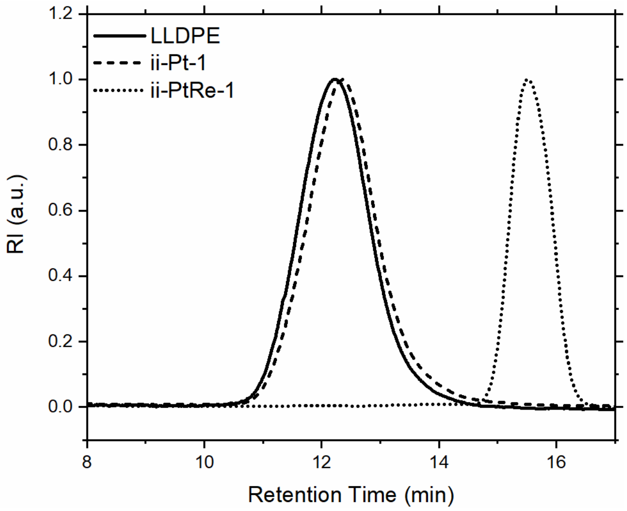


Figure 4. High temperature SEC curves of LLDPE before (solid curve) and after H/D exchange using Pt/SiO2 (dashed curve) and PtRe/SiO2 (dotted curve) catalyst at 170 °C with 1:1 catalyst-to-polymer (wt:wt) loading at a polymer volume fraction of 0.002. The narrow distribution of the degraded LLDPE is discussed in the Supporting Information.

iii) Effect of temperature

The effects of reducing the reaction temperature to 130 °C on chain degradation and isotope exchange were investigated at a 1:1 catalyst-to-polymer ratio and a polymer concentration of 0.0076 g/mL. Both catalysts yielded products with molecular weights similar to the starting material (Table 2). The SEC trace of the product of the PtRe/SiO2 catalyzed reaction shows a small low molecular weight shoulder, indicative of a slight amount of degradation (Figure 5), which is also reflected in a slightly lower molecular weight, suggesting that a minor amount of hydrogenolysis occurred. The molecular weight and molecular weight distribution of the LLDPE appears to be unaffected by the reaction with Pt/SiO2 at 130 °C.

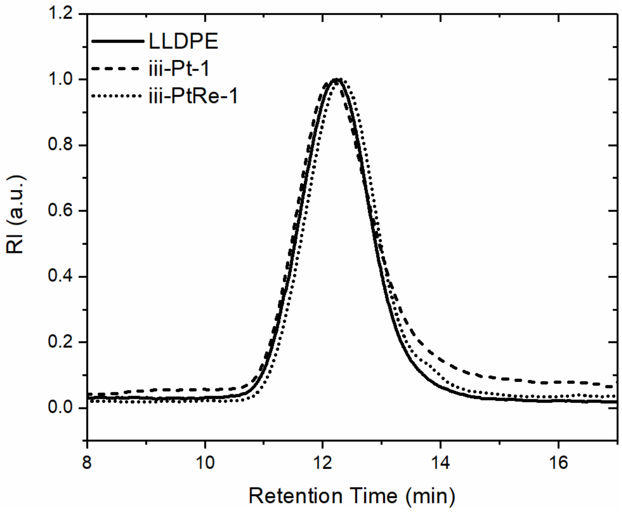


Figure 5. High temperature SEC curves of LLDPE before (solid curve) and after isotope exchange at 130 °C using Pt/SiO_2 (dashed curve) or PtRe/SiO_2 (dotted curve) catalyst at 1:1 catalyst-to-polymer (wt:wt) loading.

Isotope exchange levels of the reaction products at 130 °C were X_D = 0.22 and 0.47 for the PtRe/SiO_2 catalyzed reactions, and 0.38 with Pt/SiO_2 (Figure S14). These values, including the variability, are consistent with what was obtained at 170 °C.

Time-resolved study

The preceding sections demonstrate that PtRe/SiO_2 is a more active catalyst than Pt/SiO_2 with respect to hydrogenolysis, while both catalysts promote H/D exchange. We postulate two different mechanisms that may be associated with chain degradation. 1) A single chain adsorbs onto the catalyst and undergoes multiple chain scission events before the products desorb. This mechanism would lead to a single SEC peak that emerges at larger elution times. Over the course of the reaction, the intensity of this peak would increase while the SEC signal from the pristine polymer would decrease in intensity. 2) The chains continuously adsorb, react, and desorb, undergoing multiple hydrogenolysis reactions across multiple adsorption steps. This reaction path would lead to a gradual decrease in the molecular weight, hence a steady shift of the SEC peak to larger elution times. During either of these hydrogenolysis reaction pathways, the chains can undergo continuous H/D exchange. To gain a better understanding of the progress of the hydrogenolysis and the H/D exchange reactions, we conducted time-resolved experiments with the LLDPE polymer at the highest catalyst loading at 170 °C. A batch reaction was performed in a 1 L reactor (the other reactions were carried out in a 0.3 L reactor) with a polymer concentration of 0.0099 g/mL and small aliquots were sampled during a 17 h reaction period. The results of these experiments are summarized in Table 3.

Table 3. Time-resolved H/D exchange reaction of LLDPE at 0.0099 g/mL in isooctane with PtRe/SiO$_2$ at a 1:1 catalyst-to-polymer loading at 170 °C.

PtRe/SiO$_2$ at 170 °C			
Time (hours)	M_w [a]	$Đ$ [a]	X_D [b]
0	120	2.5	-
2	64	2.8	0.53
4	30	1.9	0.48
7	16	3.6	0.35
10.5	3	1.5	0.21
13.5	4.8	1.3	0.16
17	1.3	1.3	0.07

[a] Determined using high temperature SEC calibrated against PS standards. Values converted using Mark-Houwink parameters for PS ($K = 13.1\times10^{-3}$ mL/g, $\alpha = 0.707$)[29] and for linear PE ($K = 57.9\times10^{-3}$ mL/g, $\alpha = 0.695$).[28] [b] Fraction of deuterium determined using ATR-FTIR measurements and relative integral areas of the CH stretching (3000 – 2550 cm^{-1}) and CD stretching (2250 – 2000 cm^{-1}) signals.

The time-resolved study supports the continuous chain degradation mechanism. As seen in Figure 6, the SEC traces move to longer elution times and remain generally monomodal as a function of reaction time, indicating a continuous interaction of the chains with the catalyst through adsorption-reaction-desorption cycles. (The specimen extracted at 7 h contains a small shoulder at short retention times which we attribute to residual polymer trapped in the sampling port during the previous sample extraction). Most surprisingly, the results reveal that at 170 °C the polymer chains quickly attained a high level of H/D exchange, reaching $X_D = 0.53$ within the first 2 h of the reaction. As the reaction progressed, the level of isotope exchange decreased monotonically, until most of the deuterium atoms were replaced with hydrogen resulting in $X_D = 0.07$ after 17 h (Figure 7); corresponding FT-IR curves are presented in Figure S15.

These results show that PtRe/SiO_2 promotes two competing reactions at 170 °C: isotope exchange and hydrogenolysis. Early in the reaction, the chains undergo isotope exchange, swapping about half of the hydrogen atoms for deuterium while simultaneously undergoing hydrogenolysis. After 2 hours the molecular weight was approximately halved (M_w = 64 kg/mol). Assuming a linear relationship between catalyst concentration and reaction rate, we would anticipate it would take roughly 2.6 h to achieve this extent of hydrogenolysis based on the result obtained after 17 h with the 0.2:1 catalyst:polymer loading (M_w = 70 kg/mol, Table 2). This falls within the sizable uncertainty associated with the reaction rates. At longer reaction times the polymer chains continue to interact with the catalyst and hydrogenolysis and H/D exchange are both operative. By 17 h the nominal molecular weight dropped to M_w = 1.3 kg/mol, considerably lower than the values obtained under the same conditions in the 0.3 L reactor (Tables 1 and 2). (As noted earlier the associated dispersity $Đ = 1.3$ is considered in the Supporting Information). We do not have a concrete explanation for this difference but suspect that variations in the mixing characteristics of the 0.3 and 1 L reactors are responsible.

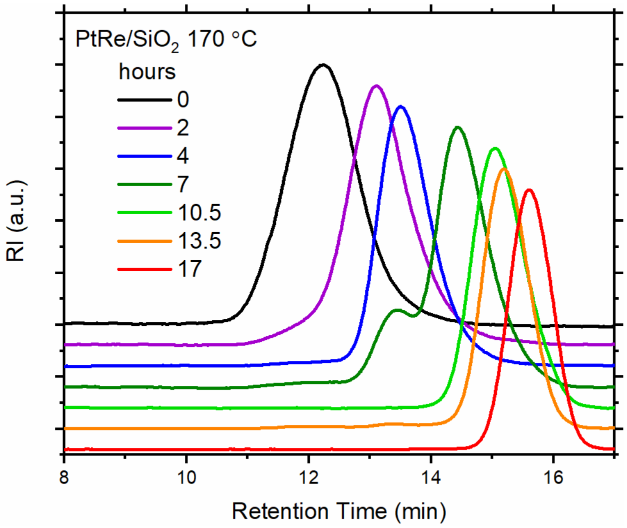


Figure 6. High temperature SEC curves of aliquots collected during time-resolved H/D exchange reaction performed on LLDPE using PtRe/SiO_2 at 170 °C at 1:1 catalyst-to-polymer (wt:wt) loading. Curves have been shifted vertically for clarity.

We propose the following mechanism for isotope exchange. Strong adsorption of polymer on the catalyst surface at the early stages of the reaction along with dissociated deuterium result in the rapid exchange of deuterium for hydrogen. With time, relatively small amounts of adsorbed isooctane will exchange hydrogen onto the catalyst surface, which will then start displacing deuterium from the polymer. At very long times, this process will result in nearly all the deuterium being bound to the solvent, which represents the vast majority of C-H(D) bonds, with very little remaining on the polymer. Reducing the temperature of the reaction to 130 °C virtually eliminates hydrogenolysis and loss of deuterium with both the PtRe/SiO_2 and Pt/SiO_2 catalysts over the 17 h reaction time, as shown by time-dependent experiments presented in the Supporting Information (Figures S16 and S17, and Tables S1 and S2).

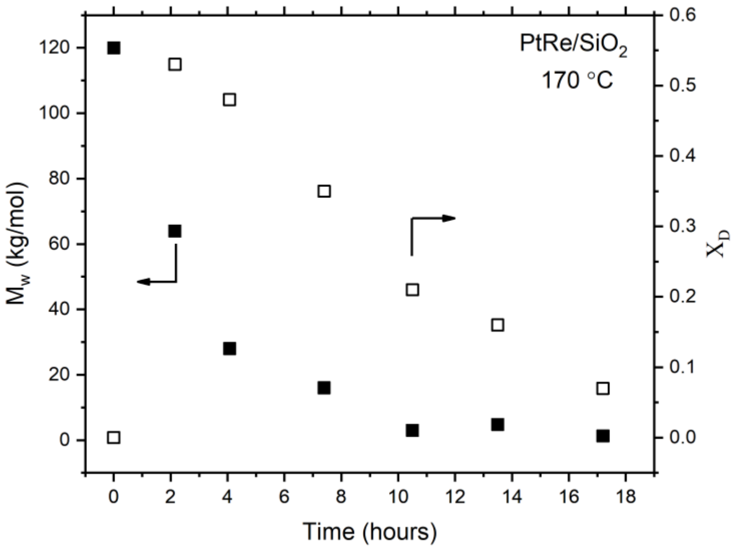


Figure 7. Weight average molecular weight (M_w) and fractional isotope exchange (X_D) of aliquots collected during time-resolved H/D exchange reaction performed on LLDPE using PtRe/SiO_2 at 170 °C at 1:1 catalyst-to-polymer (wt:wt) loading.

Characterization of the degradation product microstructure

As the time-resolved study revealed, LLDPE undergoes multiple hydrogenolysis events throughout the course of the reaction. Moreover, the SEC curves remain monomodal as the reaction progresses. To gain a better understanding of the reaction mechanism the polymer microstructure was investigated following reaction of LLDPE with H_2 (to simplify characterization) over PtRe/SiO_2 in the 0.3 L reactor. These reactions duplicated the most severe conditions employed with D_2: a polymer concentration of 0.0076 g/ml, and 500 psig H_2 at a 1:1 (wt:wt) catalyst-to-polymer ratio at 170 ºC. Three separate experiments were performed with varying reaction times, 17 h, 48 h, and 5 d, and the products were analyzed using high temperature SEC, and high temperature ^1H and ^{13}C NMR spectroscopies.

High temperature SEC results (Figure S18, Table S3) from these reactions reveal monomodal curves, as obtained in the previous reactions. M_w of LLDPE decreased to 11 kg/mol after 17 h, which is nearly twice the values reported in Table 2 for reactions conducted under the same conditions with D_2 (Table 2). The products obtained after 48 h and 5 d reactions were 7.1 and 5.5 kg/mol, respectively. Taken together, the results of all the reactions performed at 170 °C with a 1:1 PtRe/SiO_2:polymer catalyst loading exhibit a high degree of variability in the molecular weight generated by hydrogenolysis, ranging from 1.3 kg/mol to 11 kg/mol after 17 h of reaction. Moreover, the molecular weights obtained after reaction times of 48 h (7.1 kg/mol) and 5 d (5.5 kg/mol) exceed what would be anticipated with simple reaction kinetics based on the results shown in Figure 7. We do not have definitive explanations for these differences. However, we note that such heterogeneous catalytic reactions are sensitive to mixing effects and catalyst poisoning. The results shown in Figure 7 indicate a degraded LLDPE with M_w = 1.2 kg/mol, substantially below the values listed in Table 2 (6.0, 7.4, and 11 kg/mol). This may be a consequence of using a 1 L reactor for this kinetic experiment versus a 0.3 L reactor. Both reactors are mixed using magnetic stir bars. However, the state of catalyst suspension during the reactions may vary between these two reaction vessels. Notwithstanding these variations, all the reactions resulted in at least an order of magnitude reduction in M_w.

^1H NMR spectra of the H_2 reaction products are shown in Figure 8. Signals for methylene (-CH_2-) and methyl (-CH_3) groups are plainly evident with an increase in the ratio of methyl-to-methylene protons. This result indicates that the number of methyl groups increases as a result of hydrogenolysis, which is associated with an increased number of chain ends. (Individual spectra and integration results are provided in Figures S2, S19, S21, and S23). The number of methine protons (-CH-) is difficult to quantify from the ^{1}H NMR, since the associated peak overlaps with the methylene peaks.

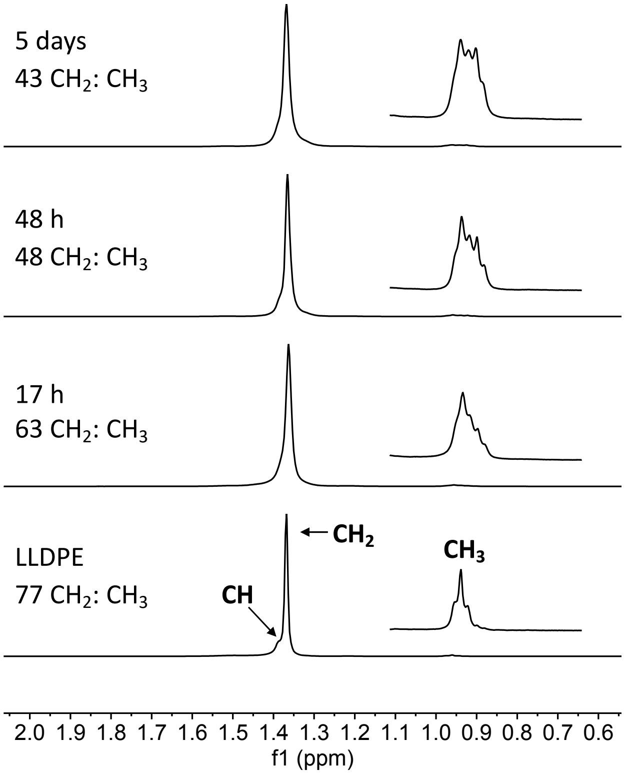


Figure 8. ^{1}H NMR (d-toluene) of LLDPE and the hydrogenolysis products from the reaction of LLDPE with PtRe/SiO$_2$ at a 1:1 catalyst:polymer (wt:wt) loading under pressurized H$_2$ at 170 °C. Spectra are shifted for clarity. The insets above each curve correspond to the expanded region between $\delta = 1.1–0.65$.

A comparison of the ^{13}C NMR spectra obtained from the original LLDPE and the hydrogenolysis products supports the conclusion drawn from the ^{1}H NMR results. Figure 9 shows the ^{13}C DEPT135 spectra and the 5 d hydrogenolysis product (individual ^{1}H and ^{13}C DEPT135 spectra for the 0 h, 17 h, 48 h, and 5 d hydrogenolysis products can be found in Figures S3, S20, S22, and S24, respectively). Here, peaks pointing down arise from carbon atoms bonded to an odd numbers of protons (i.e., methine (CH), and methyl (CH$_3$) groups) and the peaks pointing up arise from methylene (CH_2) carbons; peak assignments were made as reported previously.[41] The strongest peak at 29.7 ppm results from the backbone methylene carbons, while the resonance farthest downfield at 37.8 ppm (labelled **1**) is due to methine carbon atoms. The remaining peaks are associated with methylene or methyl carbons situated within four bonds from the methine branch point. Those derived from the butyl branches are labeled **2** through **5**, and the signals coming from the methylene units along the backbone are labelled with Greek letters **α**, **β**, and **γ**. Note that the **α**, **β**, and **γ** peak intensities are approximately twice those of the **2**, **3**, and **4** methylene carbons due to double the number of backbone methylene carbon atoms adjacent to each methine junction. We can assign the methine carbon, all the carbon atoms of the branch units, and the backbone carbons up to three bonds away from the branch point, suggesting that the branch units are homogenously distributed along the backbone.

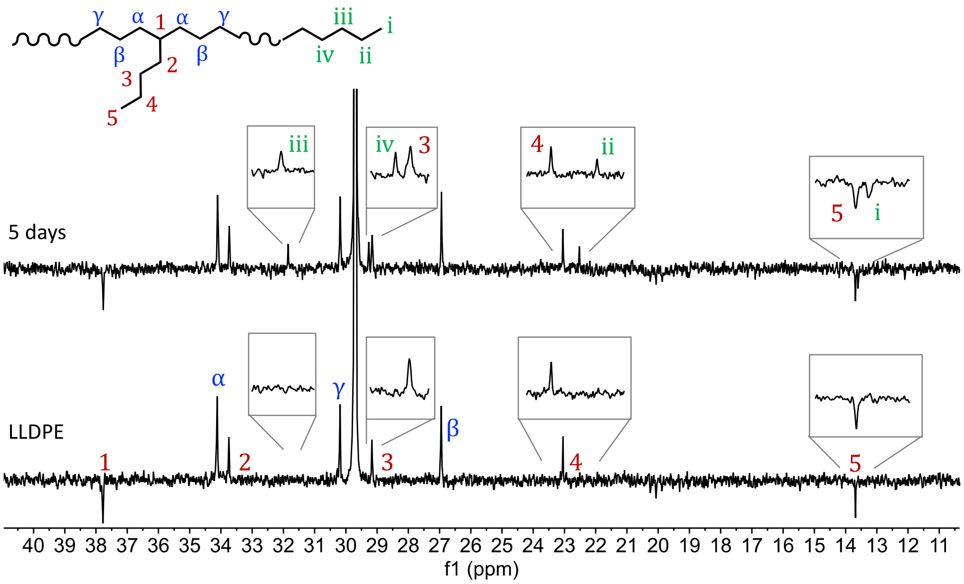


Figure 9. ^{13}C DEPT 135 NMR (toluene-d_8) of LLDPE (bottom) and the 5 d hydrogenolysis product (top) loading under pressurized H_2 with $PtRe/SiO_2$ at a 1:1 catalyst:polymer (wt:wt) at 170 °C. The insets are zoomed-in regions as highlighted. Spectra are shifted for clarity.

After 5 d of hydrogenolysis the product still shows peaks that exactly match those obtained from the original LLDPE. Moreover, several new peaks emerge, as highlighted in Figure 9 in the magnified regions. The chemical shifts of these peaks are consistent with terminal methyl carbon atoms and neighboring carbons up to three bonds away. These new peaks and the corresponding carbon atoms in the polymer representation are labeled with Roman numerals **i – iv**. Analysis of these terminal carbon species via quantitative ^{13}C NMR (Figure S25) indicates a number average molecular weight around 2000 g/mol, consistent with the SEC results (Table S1). However, the integrations also show that the relative ratio of the tertiary carbons to the backbone methylene carbons (1:72 ± 7.5%) are virtually the same as in the pristine LLDPE (1:80 ± 9.0%) (Figures S25 and S26). These results indicate that the average microstructure of the degradation product is similar to that of the starting LLDPE, despite being one to two orders of magnitude lower in molecular weight.

Differential scanning calorimetry (DSC) analysis of the degradation products revealed relatively sharp melting peaks with a broad low temperature shoulder and melting temperatures (defined as the peak in the melting endotherm) at $T_m \cong 120$ °C, slightly higher than $T_m \cong 116$ °C of the starting LLDPE (Figure 10, Table S4). The extent of crystallinity of the products increased dramatically with reaction time, approaching 90% for the 5 d degradation product, versus 48% for the starting LLDPE material. Increased crystallinity is a known effect of reduced molecular weight, due to the elimination of chain folding and the associated amorphous content and increased chain mobility in the bulk polymer. Surprisingly, T_m remains relatively unchanged with the percent crystallinity. We speculate that this result may be due to the relatively invariant branch content, which could compensate for the higher crystallinity.[42–44]

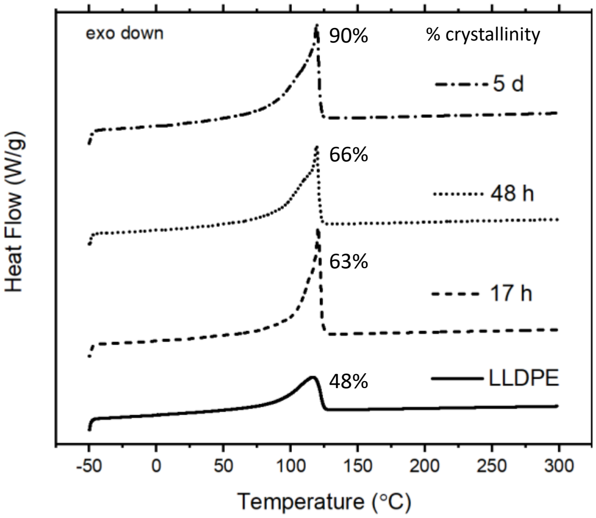


Figure 10. Second heating DSC curves and crystallinities (%) of LLDPE (solid line) and the 17 h (dashed line), 48 h (dotted line), and 5 d (dash dotted line) degradation products. The curves are shifted for clarity.

Collectively, the NMR and DSC analyses indicate that chain scission on the PtRe/SiO_2 catalyst surface occurs primarily through cleavage of methylene bonds along the polymer backbone. As shown earlier, the perfectly linear PE exhibits the least degradation versus PEP and LLDPE, where the latter undergoes the most pronounced degradation. Thus, short chain branches along the LLDPE backbone must play a significant role in the way the polymer interacts with the catalyst. We speculate that the side chains facilitate adsorption of the polymer onto the catalyst, perhaps through the coordinated interaction of the short butyl side chains with the surface in concert with adjacent backbone methylene groups. (See following section for additional discussion of this point). Another contributing factor may be chemisorption of the tertiary carbon centers, activated due to the relatively low C-H bond dissociation energies. A recent study by Habersberger and Baugh showed epimerization of stereoregular polypropylene species during H/D exchange, suggesting that the tertiary carbon centers were involved in the adsorption process.[24] We hypothesize that enhanced adsorption of the branch units could nucleate a “zipper-like” action whereby the adjacent methylene groups cooperatively attach to the catalyst surface. Such cooperative adsorption would increase the residence time of the polymer in contact with the PtRe metal, thus facilitating hydrogenolysis. Here we note that although PEP has far more backbone tertiary carbon atoms, the side chains are methyl groups, which may not coordinate as strongly with the surface as the pendant butyl units in LLDPE. Moreover, the placement of a methyl group at every fourth backbone carbon atom probably would interfere with the proposed "zipper" mechanism, which could explain the reduced levels of hydrogenolysis. Work of Flaherty et al. on small molecule alkanes suggests that less substituted C-C bonds cleave more easily than C-C bonds with substituted carbons (acyclic or cyclic).[45] Moreover, location of the C-C bond scission depends on the rotational entropy of the alkyl chain attached to the C-C bond. Thus, the farther away the C-C bond from the chain ends, the more likely it is to break.[46] Regardless of the actual underlying cause for the remarkable LLDPE degradation, our findings create a basis for future investigation, in particular a study using model polyolefin compounds with systematic variations in branch length (see below) and branch density.

Previous Work with PtRe/SiO_2

The PtRe/SiO_2 ultra-wide pore catalyst was developed by the Dow Chemical Company for the purpose of hydrogenating polystyrene and polystyrene-*b*-polybutadiene triblock and pentablock copolymers.[10-13] As shown in Fig. 1, even under the harshest conditions used in this study, polystyrene can be saturated to PCHE without any detectable chain degradation. Over the past decades this catalyst also has been employed in our laboratory to saturate polystyrene and polydienes, including polybutadiene and polyisoprene containing various microstructures, in the form of both homopolymers and block copolymers. We conclude this article with a brief examination of representative examples drawn from that body of work in the context of the presently reported findings regarding chain degradation.

The impetus for this study was the partial degradation of two 1,4-poly(isoprene)-*b*-1,4-poly(butadiene) (1,4PI-1,4PB) diblock copolymers (Figure S1) during hydrogenation at 170 °C over the PtRe/SiO_2 catalyst in cyclohexane at a catalyst-to-polymer loading of 1:5. We have produced saturated versions of this polymer, referred to as poly(ethylene-*alt*-propylene)-*b*-poly(ethylene) (PEP-PE), for more than 25 years. This material was first prepared using a palladium catalyst (Pd/$CaCO_3$) in cyclohexane at 70 – 80 °C resulting in quantitative (>99%) hydrogenation.[47]Because high temperature SEC was not available at that time (required due to the semicrystalline PE block), lack of chain degradation was not directly confirmed. Nevertheless, the combination of a less reactive metal (Pd versus PtRe), a relatively low reaction temperature (70-80 versus 170 °C), and well-defined morphological and rheological properties for the product materials lead us to conclude that hydrogenolysis was very unlikely. Due to the relatively low surface area associated with the Pd/$CaCO_3$ catalyst, we switched to the PtRe/SiO_2 and Pt/SiO_2 wide-pore catalysts when they became available about 20 years ago. Koo et al. prepared a host of 1,4PB-1,4PI-1,4PB triblock[22]and $(1,4PB\text{-}1,4PI)_n$ multiblock[48] copolymers (n = 1 – 12) and saturated these compounds using PtRe/SiO_2 in cyclohexane at 140 °C for 12 h. The catalyst loading was not identified in these publications although absence of chain degradation was confirmed using high temperature SEC. Apparently, the lower temperature employed by Koo et al. relative to 170 °C for the reaction shown in Fig. S1 circumvented hydrogenolysis, consistent with the trend for LLDPE at 130 °C versus 170 °C. Mahanthappa et al.[49] prepared PCHE-PEP-PE-PEP-PCHE and PCHE-PE-PEP-PE-PCHE pentablock copolymers by hydrogenation of polystyrene/polydiene precursor molecules using a 1:10 loading of PtRe/SiO_2:polymer in cyclohexane at 170 °C for 12

h. (Note that the catalyst-to-polymer loading was not reported in this study. The indicated value was provided by M. Mahanthappa in a personal communication.) High temperature SEC confirmed absence of chain degradation and relatively narrow dispersities. Two factors likely contributed to this outcome. Firstly, the relatively low catalyst loading, and secondly the PS/PCHE blocks attached on either end of the central triblocks, which may alter the residence time of the polymer on the catalyst surface relative to what occurred with the 1,4PI-1,4PB featured in Fig. S1. Xu et al.[25] saturated 1,4PI-1,2PB diblock copolymers using the PtRe/SiO_2 catalyst with cyclohexane as the solvent at 170 °C for 20 h leading to PEP-PEE_E; here 1,2PB represents polybutadiene containing between 70 and 90% 1,2 addition. The catalyst loading was 1:5 PtRe/SiO_2:polymer. (Catalyst loading was not identified in the publication but confirmed by personal communication with J. Xu, who also prepared the polymers shown in Fig. S1). SEC traces of the polydiene precursor and hydrogenated product established that little if any chain degradation occurred.

An intriguing set of results was reported by Zeng et al.[9] with respect to degradation of the 1,4PI-1,4PB samples. Six 1,4PB homopolymers (with the same microstructure as 1,4PB in the diblock copolymer), ranging in molecular weight from 4 kg/mol to 610 kg/mol were hydrogenated using PtRe/SiO_2 and the same conditions used to produce the PEP-PE shown in Fig. S1: cyclohexane, 1:5 catalyst:polymer, 170 °C, and 17 h. None of these polymers showed evidence of degradation based on high temperature SEC. We do not know with certainty which block in the 1,4PI-1,4PB samples degraded during saturation, nor do we know whether chain cleavage occurred prior to, during, or after the addition of hydrogen to the unsaturated bonds. The data of Zeng et al. suggests that the PI/PEP block was affected, which seems plausible given the susceptibility of PEP to some chain breaking as reported in Table 1. Another possibility is that the 1,4PB/PE block increases the overall adsorption of the diblock copolymer onto the catalyst surface, which enhances hydrogenolysis of the PEP block. This explanation would be consistent with the generation of pristine PEP-$\mathrm{PEE_E}$ under conditions that led to degradation with PEP-PE.

Yet more perplexing is the behavior of LLDPE versus hydrogenated 1,4PB. Zeng et al.[9] performed deuterium exchange reactions with a series of hydrogenated polybutadienes with branch fractions ranging from 2.6 to 50 per 100 backbone carbon atoms. Here we focus on the 2.6/100 case, i.e. hydrogenated 1,4PB, which is similar to the 1.8/100 branch content of the LLDPE. Both polymers were subjected to deuterium exchange under the same harsh conditions: 1:1 $\mathrm{PtRe/SiO_2}$:polymer in isooctane, at 170 °C for 17 h. Remarkably, the hydrogenated 1,4PB exhibited no chain degradation as shown by high temperature SEC, while LLDPE undergoes extensive hydrogenolysis resulting in a 10-fold or greater reduction in molecular weight as shown in this report. The only difference between these two polymers is the length of the side chains, C_2H_5 for hydrogenated 1,4PB versus C_4H_9 with LLDPE. As indicated above, we speculate that the longer pendant group enhances adsorption of the LLDPE chains to the catalyst surface, thus facilitating hydrogenolysis.

Finally, we note that our first report of deuterium exchange on polyolefins in 2012 was conducted using several different saturated hydrocarbon solvents with the following reactions conditions: 2:5 $\mathrm{PtRe/SiO_2}$:polymer, at 170 °C for 16 h.[6] A polymer identified as Dow high density polyethylene (HDPE) (M_w = 52 kg/mol, $Đ$ = 2.5) exchanged deuterium for hydrogen without chain degradation based on SEC analysis. The microstructure of the HDPE was not reported, but presumably this polymer contained few side chains based on the lack of degradation, similar to the limited hydrogenolysis obtained with the linear PE (Table 1) at a higher catalyst loading.

This reexamination of past work with the PtRe/SiO_2 catalyst reveals no case where hydrogenolysis appears to have compromised the integrity of the saturated polymers. However, the results presented here lead to several guiding principles in applying the wide-bore catalysts to hydrogenation and deuterium exchange. Firstly, the use of PtRe/SiO_2 for the saturation of polydienes, and deuterium exchange on polyolefins, should be restricted to $T \leq 130$ °C and reduced catalyst loadings. Secondly, there seems to be no disadvantage for deuterium exchange using Pt/SiO_2, while the absence of Re virtually eliminates hydrogenolysis, even at 170 °C and high catalyst loading. The advantages of PtRe/SiO_2, reportedly robustness against poisoning by certain impurities, should be carefully weighed against the hazards associated with polymer degradation. Finally, any publication that makes use of these catalysts should provide a detailed summary of the experimental conditions, including the ratio of catalyst-to-polymer employed.

Conclusions

We have presented a systematic study of isotope exchange and the associated chain degradation of polyolefins using the heterogenous catalysts Pt/SiO_2 and PtRe/SiO_2, and showed that the latter promotes hydrogenolysis under certain reaction conditions. Hydrogenolysis was measured with three saturated hydrocarbon polymers: perfectly linear poly(ethylene) (PE), low dispersity poly(ethylene-*alt*-propylene) (PEP), and a commercial linear low-density poly(ethylene) (LLDPE). The results reveal that the perfectly linear PE underwent the least chain degradation while LLDPE degraded severely. This outcome is interpreted in conjunction with the absence of tertiary carbon centers and short chain branches in a perfectly linear PE. However, PEP underwent much less degradation compared to LLDPE, even though it contains 10 times as many tertiary carbon centers per 100 backbone carbon atoms. Moreover, a narrow-dispersity PS, which has a tertiary carbon center on every other carbon, maintained perfect molecular integrity upon saturation, evidenced by a dispersity of 1.02 before and after the reaction. These findings implicate the butyl side chains and/or tertiary carbon centers in hydrogenolysis. Microstructural analyses of the LLDPE degradation products indicated that degradation occurs through breaking of methylene bonds along the polymer backbone. Thus, the side chains, local chain configurations on the catalyst surface, and perhaps steric hindrance and the distance between tertiary carbon centers, all may play a role in the hydrogenolysis process.

Time-resolved studies showed that hydrogenolysis of LLDPE during H/D exchange at 170 °C on PtRe/SiO_2 is accompanied by a reverse isotope exchange reaction. This finding indicates that the catalyst activates the solvent molecules, which are then involved in H/D exchange. Significantly, deuterium exchange using the Pt/SiO_2 catalyst did not result in chain degradation under any of the conditions examined with any of the polymers investigated. While the conditions for H/D exchange onto LLDPE without compromising macromolecular chain integrity have been identified, our findings of hydrogenolysis of LLDPE paves the way for enticing new utilization of the PtRe/SiO_2 catalyst, such as upcycling of waste plastics,[50] in addition to its recent use in biomass derived fuels and chemicals, and hydrogenolysis of glycerol.[37,51–53]

Associated Content

Supporting Information

^1H NMR and FTIR spectra of PCHE, linear PE, and PEP. FTIR spectra of LLDPE before and after H/D exchange. SEC traces of LLDPE during time resolved and mechanistic analysis studies. FTIR spectra of all the time-resolved experiments. ^1H and ^{13}C NMR spectra of the mechanistic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

S.P.E. contributed to all aspects of the experimental work and drafted the manuscript. She was supervised by F.S.B, T.P.L, and T.M.R. C.E.O. performed deuterium exchange reactions and various characterization experiments and was supervised by F.S.B. and T.P.L. H.W., who was supervised by M.A.H., provided the perfectly linear PE. All authors reviewed the manuscript.

Notes

The authors declare no competing financial interest.

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