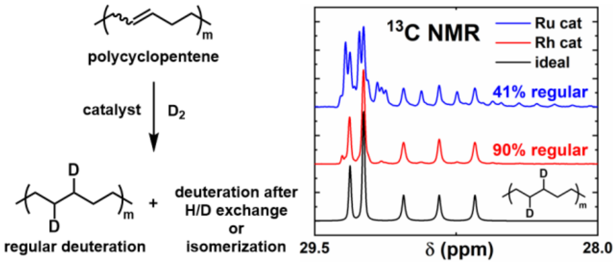
Regularity of Deuteration in Linear Polyethylene Prepared by Saturation of Polycyclopentene over Homogeneous Catalysts

Seong Hyuk Cho[†], *István Pelczer*[‡], *and Richard A. Register*[†]*

[†]Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544.

[‡]Department of Chemistry, Princeton University, Princeton, NJ 08544.

TABLE OF CONTENTS GRAPHIC



for Table of Contents use only

ABSTRACT

When isotopically labeling polymer chains for small-angle neutron scattering (SANS), it is highly desirable to achieve even intra- and inter-chain distributions of deuterium (D), such that scattering centers are uniformly placed along and among the chains. A common approach to introduce D is to catalytically saturate an unsaturated precursor polymer with D_2. Heterogeneous catalysts often induce net H/D exchange between the polymer and D_2 gas, yielding excess D on the polymer which is nonuniformly distributed; however, the homogeneous Wilkinson's catalyst (tris(triphenylphosphine)rhodium(I) chloride) has been shown to yield statistically uniform labeling. Here, ^{13}C NMR spectroscopy is employed to determine both the deuteration level and regularity of deuteration in partially deuterated polyethylene (dPE) synthesized by ring-opening metathesis polymerization (ROMP) of cyclopentene followed by deuteration over either Wilkinson's catalyst or an alternative homogeneous catalyst, carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) (Ru-H). Both catalysts produce deuterated methylenes other than the vicinal -CDH-CDH- pair expected from regular deuteration, as a consequence of β-elimination events prior to saturation; under typical saturation conditions, β-elimination is more prevalent with Ru-H. Compared with the deuteration level (DL) of 20% expected for ideal regular deuteration, DL values determined by ^{13}C NMR peak integration are 20.1% for Wilkinson's and 21.9% for Ru-H, indicating significant net H/D exchange over Ru-H. However, SANS from both dPEs shows no angular dependence in the q-range relevant to single-chain dimensions, demonstrating that the deuterium distribution is statistically uniform along and among polymer chains.

INTRODUCTION

Small-angle neutron scattering (SANS) allows measurement of the single-chain conformation[1–3] of polymers, and thermodynamic interactions in polymer blends.[4–7] Scattering contrast is achieved by blending isotopically labeled and unlabeled polymers, exploiting the large difference in neutron scattering length between hydrogen (H) and deuterium (D).[8] Labeled polymers can be directly synthesized if the deuterated monomers are available, allowing for direct control over the deuterium level and the distribution of deuterium along the chain.[9–16] Alternatively, the double bonds in unsaturated polymers may be saturated with D_2, over either heterogeneous or homogeneous catalysts, to prepare deuterated polymers. This approach is attractive as it allows the facile preparation of "matched pairs" of polymers – identical in all respects except for the D labelling – by simply using either H_2 or D_2 as the reducing gas.[4,6,17,18] While heterogeneous catalysts can achieve a higher level of deuteration, via H/D exchange between polymer and D_2 in addition to saturation of the double bonds, it has been repeatedly shown that the distribution of deuterium among the chains obtained with such catalysts is not uniform.[18–20] A uniformly deuterated polymer should not generate any coherent neutron scattering since there is no interchain contrast. However, Balsara et al. observed strong coherent scattering from an unblended saturated polybutadiene, which had been deuterated over a heterogeneous catalyst ($Pd/CaCO_3$).[18] The radius of gyration (R_g) obtained from this coherent scattering closely matched that obtained from data on an analogous matched pair prepared from the same unsaturated precursor polymer, indicating that the inhomogeneity in labelling at the whole-chain scale (i.e., among chains) was significant. More recently, Habersberger et al.[21] have shown that a $Pt\text{-}Re/SiO_2$ supported catalyst can deuterate high-density polyethylene (HDPE), isotactic polypropylene (iPP), and poly(ethylene-alt-propylene) (PEP) in various solvents solely by H/D exchange, with HDPE deuterated up to 68% in isooctane.

However, gel permeation chromatography (GPC) with infrared detection subsequently revealed that the deuteration level varied across the molecular weight distribution.[19,20,22]

In contrast to heterogeneous catalysts, the homogeneous catalyst tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst) is known to deuterate polybutadiene uniformly such that excess coherent scattering is avoided.[23] Accomplishing uniform deuteration is attractive as it ensures that the scattering is representative of the full chain, over the entire molecular weight distribution of the sample, and eliminates the need for an empirical correction for the excess scattering. The overall deuteration level of the saturated polymer, measured from its mass density, was also found to correspond to the concentration of double bonds in the polybutadiene precursor;[23] combined with the absence of coherent SANS from the neat deuterated product, one might infer that D_2 is simply added across the double bonds in the starting polybutadiene. However, a side reaction such as isomerization (double bond migration)[24] can alter the regularity of D position while still giving the same overall deuteration level as measured by density, and no substantial variation in D level along or between chains as observed by SANS.

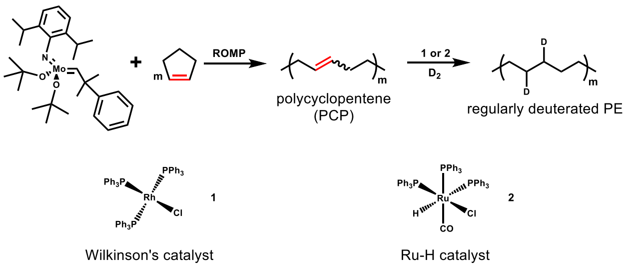
In fact, there is literature evidence of concurrent olefin isomerization during hydrogenation over Wilkinson's catalyst.[24] The active form of Wilkinson's catalyst, denoted Rh-H_2, forms by oxidative addition of H_2 to the Rh center; one of the hydrides on Rh-H_2 then adds to the olefin's double bond via 1,2-insertion, forming a σ-metalalkyl intermediate. This intermediate can either complete saturation by transferring the remaining hydride from the Rh center to the olefin substrate, or isomerize the double bond by β-hydride elimination. Experimentally, Bond and Hillyard have shown that *cis*-2-pentene isomerizes to 1-pentene and *trans*-2-pentene during hydrogenation over Wilkinson's catalyst at one-third of the hydrogenation rate.[24] Moreover, with polybutadiene saturated with D_2 over Wilkinson's catalyst, Zoller et al. showed via pyrolysis-photoionization mass spectrometry the presence of H/D interchange (“scrambling”) between mers, concluding that the deuteration is not entirely regular.[25] Analogous H/D scrambling during deuteration of cycloalkenes had been previously reported.[26,27] While these studies indicate that deuteration of double bonds over Wilkinson’s catalyst can involve isomerization and consequent H/D scrambling, there has been only limited investigation into the mechanism and extent of these side reactions.

The aforementioned hydrogenation mechanism would imply that Wilkinson’s catalyst cannot induce olefin isomerization in the absence of H_2, since the active form of the catalyst – needed to form the σ-metalalkyl intermediate – is not present. Experimentally, some olefin isomerization has been observed over Wilkinson’s catalyst in the absence of H_2, but only after a lengthy induction period.[28,29] The unidentified species which catalyzes this isomerization is thought to form slowly by loss of a PPh_3 ligand from Wilkinson’s catalyst, as adding excess PPh_3 extends the induction period, to beyond 6 months when 6 equivalents of excess PPh_3 are added.[29] Thus, under the conditions and times typically used for hydrogenations (including in the present work), Wilkinson’s catalyst does not induce significant isomerization in the absence of H_2.

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II), denoted Ru-H, is another homogeneous catalyst used for saturation of unsaturated polymers; like Wilkinson’s catalyst, it is also known to saturate double bonds without causing chain rearrangements such as scission or branching.[30–32] But in contrast to Wilkinson’s catalyst, Ru-H is known to isomerize olefins even in the absence of H_2, as it bears a hydride ligand that allows a 1,2-insertion to the olefin substrate *without* needing an oxidative H_2 addition to its metal center.[33–36] Consequently, the saturation mechanism is different from that over Wilkinson’s catalyst, where the reducing gas (H_2 or D_2) must be added to the metal center *prior* to forming the σ-metalalkyl intermediate. Gramlich and Hillmyer[37] have prepared polyisoprene containing conjugated double bonds by isomerizing polyisoprene over Ru-H. In addition to isomerization, it has been shown that Ru-H can facilitate H/D exchange between small-molecule olefins and D_2O.[38] Thus, as with Wilkinson's catalyst, deuteration of unsaturated polymers over Ru-H is expected to be non-regular, where the distribution of deuterium in the product does not precisely correspond to the positions of the double bonds in the precursor, while the labeling level is still expected to be statistically uniform along and among the chains. It is not clear *a priori* whether Ru-H will catalyze net H/D exchange between polymer and D_2, increasing the overall deuteration level, or if only H/D scrambling occurs.

The present study aims to understand the mechanisms and extents of side reactions that accompany deuteration of unsaturated polymers over Wilkinson's and Ru-H catalysts, using polycyclopentene (PCP) as the precursor, which yields deuterated linear polyethylene (PE) upon saturation as shown in Scheme 1. As both catalysts can potentially induce both isomerization and H/D exchange between catalyst and D_2 during deuteration, the deuterated PE product is expected to show some irregularity in D distribution relative to the double bond positions prior to saturation. It is emphasized that the isomerization discussed in this study specifically refers to double bond migration – not to *cis-trans* stereoisomerization, which also occurs[24] – while H/D exchange between catalyst and polymer refers to a reaction where an H on a polymer chain is replaced by a D without concurrent double bond saturation. "Net H/D exchange", yielding deuteration levels higher than that corresponding to the precursor's double bond content, would require further exchange of D between catalyst and D_2. Quantitative ^{13}C NMR spectroscopy is used to assess the deuteration regularity at the monomer unit level as it enables a clear identification of CDH, CD_2, and CH_2 methylenes via their characteristic isotope shifts and the multiplicity of C-D coupling.[39] Recently, the isotope effect of deuterium in ^{13}C NMR has been employed to analyze deuterated poly(ϵ-caprolactone)[15,40] and to determine the deuteration level of methyl carbons in syndiotactic

PP following H/D exchange.[41] Any deviation from regular deuteration, i.e., any CD_2 resonances, or any CDH resonances other than the vicinal -CDH-CDH- pair expected from regular deuteration, can be easily identified. PCP is a particularly advantageous precursor for ^{13}C NMR analysis since the isotope effects are observed up to two carbons distance,[39] allowing the deuteration analysis to be done on the five-carbon PCP repeat unit. Furthermore, any complications to the spectra resulting from side branches – for example, from 1,2-addition when the precursor is polybutadiene[42] – are avoided by using PCP, which yields perfectly linear (high-density) PE upon saturation.[43]



Scheme 1. Scheme for regular deuteration of PCP. The PCP precursor is prepared by ring-opening metathesis polymerization (ROMP) of cyclopentene with Schrock's initiator and deuterated with D_2 gas over either Wilkinson's (1) or Ru-H (2) catalyst. The reaction product shown corresponds to perfectly regular deuteration, where deuterium is exclusively added across the PCP double bond.

We find that the deuteration of PCP over either Wilkinson's or Ru-H catalyst is accompanied by both isomerization and H/D exchange between catalyst and polymer prior to saturation; these reactions are more prevalent with Ru-H. Quantifying the types and extents of these isomerization and H/D exchange reactions illuminates the reaction mechanisms underlying their formation. Wilkinson's catalyst is found to induce minimal net H/D exchange, while under the reaction conditions employed here, Ru-H catalyzes modest but significant net H/D exchange. However, dPEs synthesized with both catalysts show no coherent SANS in the relevant angular range, confirming that labelling is statistically uniform along and among chains.

EXPERIMENTAL PROCEDURE

Materials.

Cyclopentene (CP) monomer (Sigma-Aldrich, 96%) was distilled through a 71 cm Hempel column filled with 8 mm ceramic Berl saddles to reduce the 1-pentene level to < 5 ppm (undetectable by ^1H NMR) to suppress chain transfer.[44] The distilled fractions were then dried over sec-butyllithium in the presence of 1,1-diphenylethylene until the red adduct formed; cyclopentene was then vacuum transferred into a storage flask. The Schrock initiator, 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(t-butoxide), was used as received (Strem Chemicals). Trimethylphosphine, PMe_3 (Sigma-Aldrich, 97%), was degassed, stirred overnight with sodium, and vacuum transferred. Propionaldehyde (Sigma-Aldrich, 97%) was degassed and stirred over 3 Å molecular sieves. Toluene was passed through an MBraun SPS solvent purification system connected to the glovebox used for polymerizations. Wilkinson's catalyst and Ru-H were used as received from Sigma-Aldrich. A heterogeneous catalyst, palladium (5 wt%) supported on calcium carbonate ($Pd/CaCO_3$), was purchased from Alfa Aesar and used as received. Cylinders of H_2 (99.999%) and D_2 (99.999% elemental purity; < 3000 ppm HD and < 100 ppm H_2 by volume) were purchased from Airgas and Praxair, respectively, and used as received.

Polymerization.

All degassed and dried ROMP reagents were moved into an MBraun UNIlab glovebox with an N_2 atmosphere (O_2, $H_2O < 0.1$ ppm). Polymerizations were done in 100 ml round bottom flasks (RBF) with magnetic stirring. The Schrock initiator was first dissolved in toluene in a scintillation vial and transferred into a 100 ml RBF. PMe_3 and CP were added sequentially such that the initial CP concentration was 10 mol/L. CP/Mo and PMe_3/Mo ratios were kept at 7500:1 and 15:1, respectively. PMe_3, a reversibly binding ligand, was added to slow propagation relative to initiation to decrease the dispersity of resulting polymer[43,44]. The polymerization was terminated at approximately 15% conversion[44] with propionaldehyde. After polymerization, PCP was precipitated into excess methanol and dried under vacuum overnight. Table 1 summarizes the molecular weights of the two PCP precursors employed, and the catalyst types that were used in the deuteration, where Rh and Ru indicate Wilkinson's and Ru-H catalysts, respectively.

Table 1. Molecular weights and dispersities of PCP precursors before deuteration.

Polymer[a]	M_w (g/mol)	Đ
PCP-Rh	105,300	1.17
PCP-Ru	87,900	1.16

[a]suffixes -Rh and -Ru indicate that Wilkinson's catalyst or Ru-H, respectively, was used for deuteration.

Hydrogenation and deuteration of PCP.

PCP was hydrogenated with H_2 over Pd/$CaCO_3$ and deuterated using D_2 over either Wilkinson's catalyst or Ru-H. For hydrogenation, PCP was dissolved in n-heptane at 5 g/L with 0.5 wt% of butylated hydroxytoluene (BHT) relative to polymer to prevent oxidative degradation. The polymer solution was transferred to a 2 L Parr stainless steel reactor and Pd/$CaCO_3$ was added at a 2:1 weight ratio of catalyst (including support) to polymer. The reactor was charged with 400 psi of H_2 at room temperature and stirred at 130 °C for 24 h, by which point saturation reached > 99.9% as determined by ^{1}H NMR. The hydrogenated PCP (hPE) was recovered by hot filtration, precipitated into methanol, and dried under vacuum overnight. The hPE served as a reference for density measurements and a check on the position of the ^{13}C NMR CH_2 resonance. Deuteration followed the analogous steps except that PCP was dissolved in toluene instead of n-heptane. Ru-H or Wilkinson's catalyst was dissolved in toluene in a separate vial and transferred to the reactor with the polymer solution. The molar ratio of double bonds to Ru-H was kept at 2250:1. Triphenylphosphine (PPh_3) was added with Wilkinson's catalyst to prevent deactivation by dimerization.[45] The molar ratios of double bonds to PPh_3 to Wilkinson's catalyst were kept at 450:20:1. The reactor was pressurized to 400 psi with D_2 and stirred for 24 h at 130 °C. After saturation, dPEs are designated by the identity of the catalyst used for saturation, i.e., dPE-Rh and dPE-Ru; their degrees of saturation determined by ^{1}H NMR were above 99.9%.

Molecular Characterization.

^{1}H and quantitative ^{13}C NMR spectra, using an inverse-gated decoupling scheme to avoid enhancement by the nuclear Overhauser effect, of PEs dissolved in deuterated 1,1,2,2-tetrachloroethane-d_2 were collected at 130 °C with a Bruker Avance III Nanobay 400 MHz spectrometer equipped with a BBO Prodigy nitrogen-cooled cryoprobe. For ^{13}C NMR, samples were prepared at approximately 50 mg/ml concentration and the spectra were collected at 100 MHz for at least 6000 scans with the overall recycle time set to 30 sec. For ^{1}H NMR, samples were prepared at 5 mg/ml and spectra were collected at 400 MHz on the same instrument. All NMR data processing and analysis was done using MestReNova (MNova) software (Mestrelab Research S.L., Santiago de Compostela, Spain). Molecular weights of the precursor PCPs were determined by GPC with tetrahydrofuran (THF) as the mobile phase (1 mL/min) with two 30 cm Agilent PLgel Mixed-C columns, and Wyatt Optilab T-rEX differential refractive index (DRI; 25 °C, 658 nm wavelength) and miniDAWN TREOS three-angle light scattering (ambient temperature, 658 nm) detectors. Dispersities (Đ) were determined from the DRI output with the elution time calibrated against narrow-distribution polystyrene standards. PCP M_w was determined from the light scattering results, using dn/dc = 0.1212 mL/g at 25 °C in THF at 658 nm.[44]

Small-angle Neutron Scattering (SANS).

SANS experiments were performed on the GP-SANS CG-2 beamline at the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. Films of dPE-Rh, dPE-Ru, and a completely hydrogenous HDPE (E4, Dow Chemical Company[46]), were prepared as described above for density measurement but at approximately 0.3 mm thickness. Circular disks of 19 mm diameter were punched from the films, and stacked to fill a 1 mm-thick brass spacer with inner diameter of 19 mm. The brass spacers and samples were assembled inside Peltier furnace cells by sandwiching them between fused silica windows (1 mm each) and PTFE O-rings. SANS measurements covered $0.004 \text{ Å}^{-1} < q < 0.08 \text{ Å}^{-1}$ using a wavelength (λ) of 4.75 Å with a sample-to-detector distance of 16 m. The Peltier furnace temperature was raised to 150 °C to melt the polymers, and before recording SANS data each polymer sample was visually inspected to ensure that it was completely melted. The scattered intensity was calibrated in absolute units (cm^{-1}) using a porous silica standard. The SANS data were reduced to account for empty cell scattering, sample transmission, thickness, and detector sensitivity, and were averaged azimuthally to generate one-dimensional plots of scattered intensity, I(q), versus the magnitude of the momentum transfer vector $q = \left(\frac{4\pi}{\lambda}\right)\sin(\theta)$, where 2θ is the angle between the incident and scattered neutron beams.

RESULTS AND DISCUSSION

Figure 1 shows the experimental ^{13}C NMR spectra of dPE-Ru and dPE-Rh, and the calculated spectrum of regularly deuterated PCP. Qualitatively, dPE-Ru and dPE-Rh show clear departures from regular deuteration. Cheng and Dziemianowicz[39] have shown through copolymerization of ethylene and ethylene-d_4 that replacement of CH_2 by CD_2 in polyethylene results in a 1:2:3:2:1 quintet with a coupling constant of 19 Hz. The isotope shift due to CD_2 was described by α = -0.84, β = -0.20, and γ = -0.05 ppm relative to the resonance position of runs of unlabeled CH_2 methylenes, where α indicates the shift for the carbon bearing two deuterons (CD_2), while β and γ indicate the shifts for the CH_2 methylenes which are one and two carbons distant from the α carbon (CD_2), respectively.[39] Given the additive nature of the isotope effect, the replacement of CH_2 by CDH is expected to give a 1:1:1 triplet with a coupling constant of 19 Hz, having isotope shifts of α' = -0.42, β' = -0.10, and γ' = -0.025 ppm relative to the CH_2 resonance of PE. The isotope shifts determined from our ^{13}C NMR spectra are in good agreement with Cheng's prior values, with slightly improved precision: α' = -0.424, β' = -0.099, and γ' = -0.023 ppm, with J_{CD} = 18.9 Hz (see Supporting Information). The magnitude of this isotope effect decreases by a factor of approximately 4.3 for each intervening carbon, so a CDH that is three carbons from the methylene of interest is expected to contribute an isotope shift of only δ' = 0.006 ppm, neglected during the following analysis. The chemical shift and multiplicity of the resonance for a carbon atom in the dPE chain is thus defined by the deuteration level of that carbon and its four neighboring carbons (two on either side), allowing the analysis to be based on a five-carbon repeat unit.

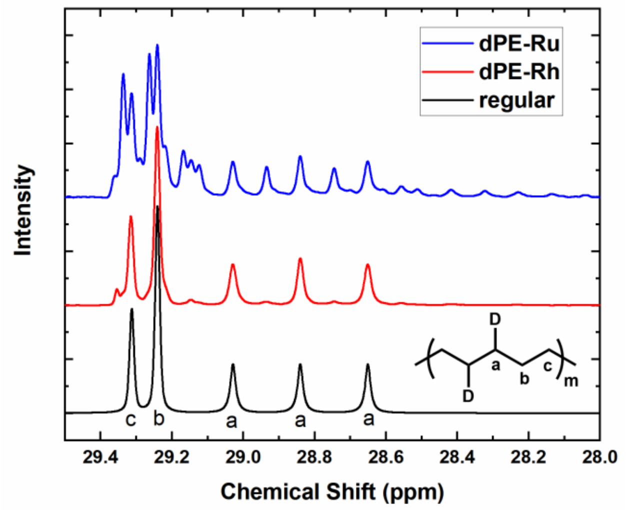


Figure 1. Experimental ^{13}C NMR spectra of dPE-Ru and dPE-Rh, and calculated spectrum for regularly deuterated dPE, shown with its carbons labeled. The triplet (“a”) position reflects the sum of the one-bond and two-bond isotope effects; longer-range couplings are not resolved.

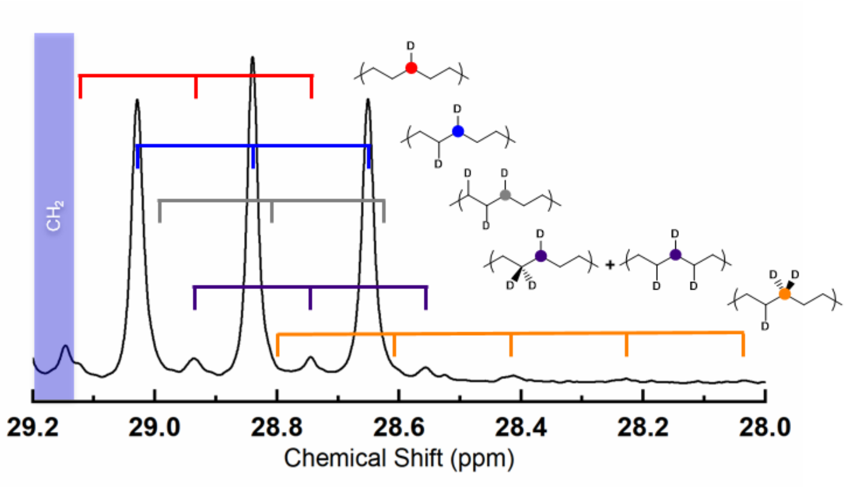
As the area (A) underneath each peak is proportional to the number of carbons in a particular chemical environment, the ratio A_{CDH}:A_{CH2} for regularly deuterated dPE is necessarily 2:3, reflecting the ideal deuteration level of exactly 20%. The general expression in Equation (1) calculates the deuteration level (DL) by counting the number of deuterons over the number of available bonding sites on the polyethylene backbone:

$$\mathrm{DL_{NMR}}\ (\%) = \frac{2\mathrm{A_{CD_2}}+\mathrm{A_{CDH}}}{2(\mathrm{A_{CD_2}}+\mathrm{A_{CDH}}+\mathrm{A_{CH_2}})} \times 100 \qquad \text{Eq. (1)}$$

The area of each methylene peak was determined using the “Line Fit” protocol in the MNova software (see Figures S1 and S2 for the fitting procedure and deconvoluted spectra), and following Equation (1), the DL values of dPE-Rh and dPE-Ru were determined to be 20.1% and 21.9%, respectively.

Analysis of dPE-Rh spectrum.

Figure 2 shows the peak assignments and a table of relative areas of CDH and CD_2 resonances for dPE-Rh. Each five-carbon repeat unit is numbered in descending order of chemical shift of its central carbon; the codes thus correspond specifically to the central deuterated methylene in each unit (indicated in color in Figure 2, with a distinct color for each unit), although many of the units contain multiple deuterated methylenes. The full set of peak assignments and corresponding deconvoluted areas is available in Table S2, while Figure S1 presents a graphical comparison of the spectrum and fit, including an expanded intensity scale for the weaker peaks in the 28.6 – 28.0 ppm region. The most intense triplet centered at 28.840 ppm corresponds to the CDH carbon (Rh-2) expected from the regularly deuterated dPE mer illustrated in Figure 1. The relative peak areas of the deuterated carbons in Figure 2 show that 90% of the deuterated carbons (Rh-2) derive from regular saturation, while the other 10% result from isomerization or H/D exchange prior to saturation.



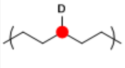
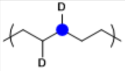
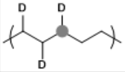
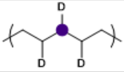
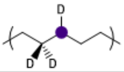
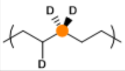
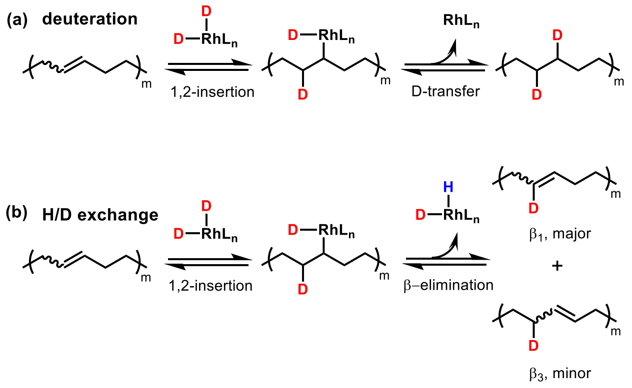
deuterated carbon	code	relative peak area
	Rh-1	0.018
	Rh-2	0.90
	Rh-3	0.028
	Rh-4(a)	0.036
	Rh-4(b)	
	Rh-5	0.019

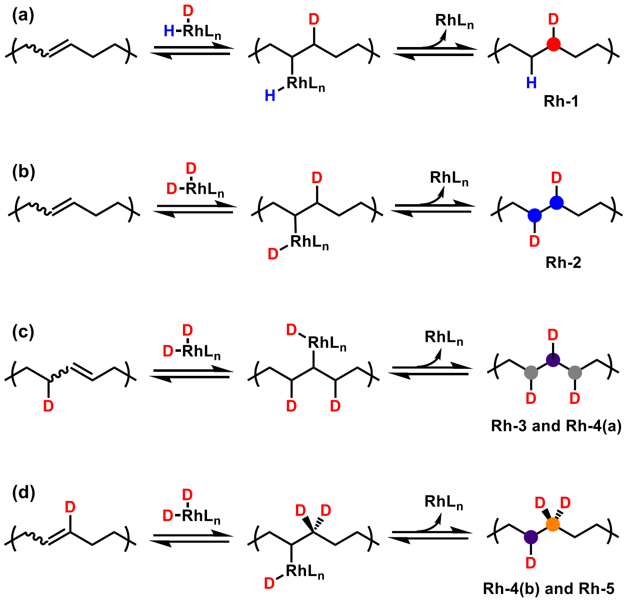
Figure 2. (Left) ^{13}C NMR peak assignments for dPE-Rh and (right) relative peak areas of deuterated methylenes, corresponding to the central carbon in each five-carbon unit (color coded). Rh-4(a) and Rh-4(b) correspond to carbons with different D substitution patterns, but having the same isotope shift.

The identification of each deuterated methylene resonance provides an opportunity to examine the reaction mechanisms. The hydrogenation process begins with Wilkinson's catalyst losing one PPh_3 ligand and adding H_2 to form a rhodium dihydride complex (Rh-H_2), the active form of the catalyst. Then the σ-metalalkyl intermediate is formed via 1,2-insertion of Rh-H_2 to the olefin substrate, and the remaining H on the Rh center is transferred to complete the hydrogenation and regenerate the inactive form of the catalyst.[45,47,48] Scheme 2(a) shows the analogous deuteration mechanism, where H_2 is replaced with D_2, and with the PCP repeat unit as the substrate. H/D exchange between catalyst and polymer then becomes possible, as shown in Scheme 2(b), where Rh-D_2 first coordinates with the PCP double bond and forms a σ-metalalkyl intermediate by 1,2-insertion. Instead of transferring the remaining deuteron onto the polymer, a hydrogen is abstracted from the polymer backbone to generate Rh-HD in solution and H/D-exchanged PCP. Depending on the site of β-hydride elimination, H/D exchange can occur either exclusively (β_1) or simultaneously with isomerization (β_3). While regenerated Rh-HD can potentially release HD, the D_2 contained just in the reactor headspace (not considering the additional D_2 dissolved in solution) is ~20 times more abundant than all HD that could potentially be released from all olefinic H on the polymer (a limit which is not approached over either catalyst). Thus, coordination of the "inactive" form of Wilkinson's catalyst with "free" HD is not considered as a significant pathway to form Rh-HD. All possible permutations of catalyst complex, hydrogen transfer, and β-hydride elimination are provided in Figure S3.



Scheme 2. Reaction mechanisms for (a) deuteration and (b) H/D exchange of PCP over Wilkinson's catalyst under deuteration conditions.

Based on the reaction mechanisms outlined above, deuteration over Wilkinson's catalyst can be described by three reaction parameters: the fraction of D out of all H and D atoms bound to Rh (f_D), the probability of elimination prior to saturation (p_E), and the fraction of β_3 vs. β_1 elimination ($\beta \equiv \frac{\beta_3}{\beta_3+\beta_1}$). Since the fraction of regularly deuterated carbons (Rh-2) is high, it is reasonable to assume that most double bonds are deuterated either prior to any elimination reaction, or following at most one elimination reaction, i.e., p_E is small. Based on this assumption, the most probable reaction pathways for each deuterated carbon identified in Figure 2 are provided in Scheme 3. Note that these may not be exclusive mechanisms, but they are intended to represent the shortest (most favored) reaction paths that generate the observed structures. Schemes 3(a) and 3(b) begin with the original PCP repeat structure, whereas Schemes 3(c) and 3(d) begin with PCP that has already undergone β_3 or β_1 elimination, respectively, as described in Scheme 2(b). Following these reaction pathways, the probabilities of formation of each deuterated carbon are expressed in terms of f_D, p_E, and β and provided in Table 2 (see Supporting Information for example derivations of probability expressions and reaction parameter calculations). With f_D = 0.98, p_E = 0.07, and β = 0.42, respectively, the calculated probabilities and experimental results are in good agreement, and the small value of p_E confirms the internal consistency of this analysis, i.e., the probability of two or more elimination reactions prior to saturation is negligible.



Scheme 3. Suggested mechanisms for formation of the deuterated methylenes detected in the ^{13}C NMR spectrum of dPE-Rh.

Table 2. Reaction parameter estimation for dPE-Rh deuteration with $f_D = 0.98$, $p_E = 0.07$, and $\beta = 0.42$.

deuterated carbon	probability	calculated[a]	experimental[a]	exp/calc
Rh-1	$2(1-p_E)f_D(1-f_D)$	20	20	0.98
Rh-2	$2(1-p_E)f_D^2$	1000	1000	1
Rh-3	$2f_D^2p_E\beta$	32	32	1.01
Rh-4(a) + Rh-4 (b)	$f_D^2p_E\beta + p_E(1-\beta)f_D^2$ $= f_D^2p_E$	38	40	1.06
Rh-5	$p_E(1-\beta)f_D^2$	22	21	0.96

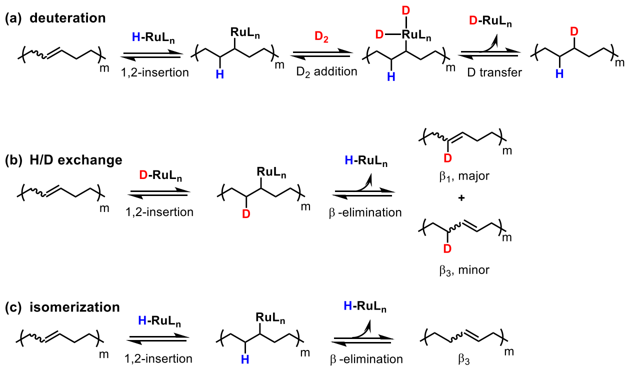
[a] normalized to Rh-2 probability or area (=1000)

From Scheme 2(b), the ratio of β_1 to β_3 elimination might be expected to be 1:2 (β = 0.67), simply based on the number of hydrides available for elimination on each carbon. However, the value of β = 0.42 indicates that β_1 is slightly favored over β_3 elimination. The relative frequency of β_1 and β_3 elimination is influenced by the proximity of the hydride that is being eliminated, which depends on relative ease of bond rotations in the metalalkyl intermediate. In the case of *cis*-2-pentene, once the metalalkyl intermediate is formed, bond rotation about the rhodium-carbon bond (σ-bond in σ-metalalkyl intermediate) is less hindered compared to rotation about the C_2-C_3 bond (C=C of *cis*-2-pentene prior to 1,2-insertion), leading to higher β_3 elimination, i.e., higher 1-pentene content compared to *trans*-2-pentene.[24] However, in the case of the PCP metalalkyl intermediate (center structure in Scheme 2(b)), the steric hindrance against rotation about the Rh-C bond should be enhanced because the alkyl units flanking the carbon bonded to the Rh center are polymeric, whereas they are methyl and propyl groups in the case of *cis*-2-pentene.

For every elimination event, a molecule of Rh-HD complex is formed as shown in Scheme 2(b). The rate of unbinding between Rh and HD determines whether there will be net H/D exchange between polymer and D_2 or not. If unbinding of HD from Rh is slow, i.e., if Rh-HD does not equilibrate with D_2 to release HD and form Rh-D_2 (from free D_2 in solution) prior to the Rh-HD complex's next reaction with PCP, the H abstracted via β elimination will be redeposited onto another polymer unit. In this limit, the H/D exchange reactions indicated in Scheme 2(b) simply result in H/D scrambling, as only two deuterons are placed on polymer chains per saturation event – although the two deuterons are, in general, not deposited on adjacent carbons in this two-stage process. On the other hand, if the unbinding rate is high and Rh-HD equilibrates with D_2 to release HD and form Rh-D_2, a net positive H/D exchange and a deuteration level above 20% would result. The DL of 20.1% for dPE-Rh suggests that Rh-HD unbinding is slow and that elimination reactions mostly lead to H/D scrambling, consistent with what has been found by pyrolysis-photoionization mass spectrometry.[25] Of course, low levels of exchange between hydrides bound to the catalyst and reducing gases dissolved in solution (D_2, HD, or H_2) are not ruled out by this analysis. In the limit of no exchange, $f_D = 1-p_E/2$; the value of $p_E = 0.07$ would thus yield $f_D = 0.965$ in the no-exchange limit, vs. the best-fit value of $f_D = 0.98$. If both $f_D = 0.98$ and $p_E = 0.07$ are taken to be precise (indicating some exchange between catalyst and gas), this would yield, on average, an additional 0.03 D added per double bond, or DL = 20.6%, within uncertainty of the 20.1% measured by summation of the fitted ^{13}C NMR peak areas.

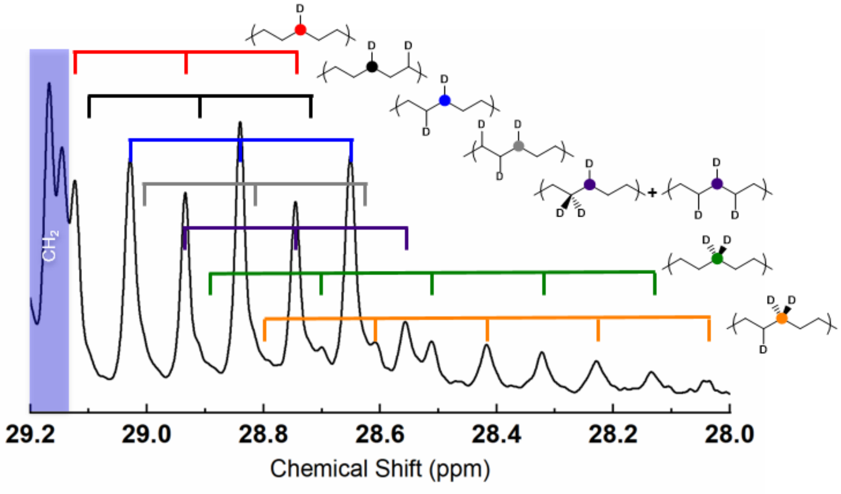
Analysis of dPE-Ru spectrum.

While the mechanisms of saturation over Ru-H are analogous to those over Wilkinson's catalyst – oxidative addition of D_2 to the metal center, formation of a σ-metalalkyl intermediate by metal-hydride insertion, and transfer of a hydride – there is one important difference: Ru-H adds to the double bond *before* D_2 adds to the metal center.[31,32] This difference has two major consequences. First, the precursor double bond is reduced by receiving one H or D from the ligand borne by the catalyst prior to the catalyst's binding to the polymer; the other H or D comes from the reducing gas (D_2, HD, or H_2), but in the present case, D_2 overwhelmingly dominates the free reducing gas species and is the only possibility considered. The regenerated catalyst complex carries a D or H ligand remaining from the reducing gas, as illustrated in Scheme 4(a). A more detailed discussion of the Ru-H saturation mechanism is provided in the Supporting Information. Second, Ru-H can facilitate isomerization by β-hydride elimination even in the complete absence of H_2, HD, and D_2, as shown in Scheme 4(c), and several studies have used the Ru-H catalyst for olefin isomerization via this mechanism.[34–36,49–52] In addition to isomerization, Tse et al.[38] have shown that Ru-H can mediate H/D exchange between styrene or its derivatives and D_2O; 85% of the olefinic protons on styrene are replaced by deuterons within an hour at 100 °C. Tse et al. explain that H/D exchange occurs by addition of Ru-D to the double bond and subsequent elimination of Ru-H, analogous to the reaction shown in Scheme 4(b) with PCP as the substrate. Under similar conditions, *trans*-β-methylstyrene was shown to undergo H/D exchange and isomerization simultaneously, resulting in a mixture of isomers of deuterated *trans*-β-methylstyrene.[38] Analogous to the behavior over Wilkinson's catalyst, H/D exchange over Ru-H can either occur exclusively (β_1) or simultaneously with isomerization (β_3) as shown in Scheme 4(b). In the presence of D_2, the Ru-D complex necessary for H/D exchange could form either as the byproduct of a saturation event, as illustrated in Scheme 4(a), or by direct H/D exchange between Ru-H and D_2.[53]



Scheme 4. Reaction mechanisms for (a) deuteration, (b) H/D exchange, and (c) isomerization of PCP over the Ru-H catalyst under deuteration conditions.

Figure 3 shows the ^{13}C NMR spectrum peak assignments and a table of relative areas of CDH and CD_2 resonances for dPE-Ru. The full spectrum and fit (including the CH_2 region) are provided in Figure S2, and the full table of peak assignments and deconvoluted areas is provided in Table S3. The complexity of the dPE-Ru spectrum (Figure 3) over the dPE-Rh spectrum (Figure 2) reflects a much greater proclivity for β-hydride elimination (isomerization, with or without H/D exchange, as shown in Schemes 4(b) and 4(c); only 41% (Ru-3) of the deuterated methylenes correspond to those formed by regular deuteration.



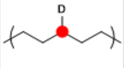
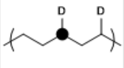
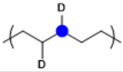
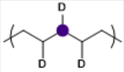
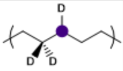
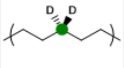
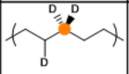
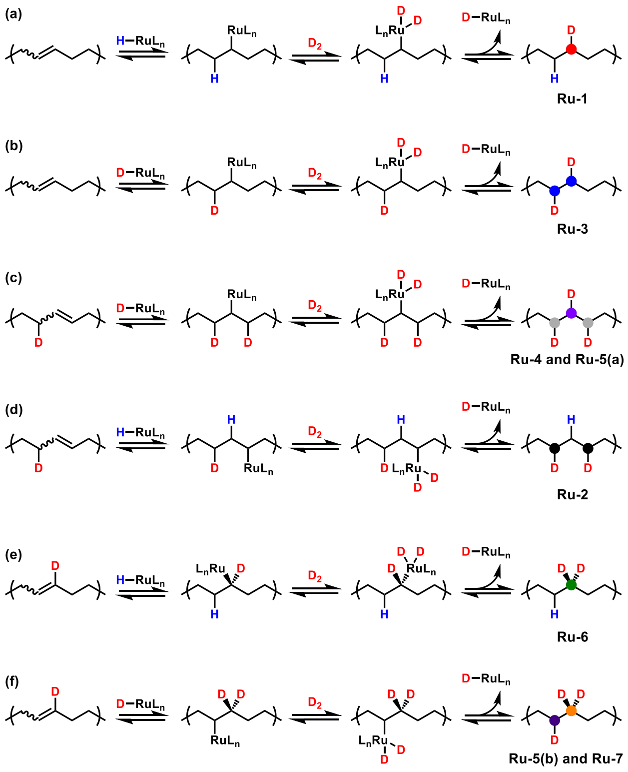
deuterated carbon	code	relative peak area
	Ru-1	0.17
	Ru-2	0.028
	Ru-3	0.41
	Ru-4	0.020
	Ru-5(a)	0.15
	Ru-5(b)	
	Ru-6	0.11
	Ru-7	0.11

Figure 3. (Left) ^{13}C NMR peak assignments for dPE-Ru and (right) relative peak areas of deuterated methylenes, corresponding to the central carbon in each five-carbon unit (color coded). Ru-5(a) and Ru-5(b) correspond to carbons with different D substitution patterns, but having the same isotope shift.

This enhanced elimination generates additional types of deuterated methylenes that were not detectable in dPE-Rh, such as Ru-2 and Ru-6. It also means that the probability of elimination prior to saturation (p_E) is not small in the dPE-Ru case; a double bond can undergo multiple elimination events prior to saturation. All of the structures shown in Figure 3 can be generated by pathways requiring at most one elimination event as shown in Scheme 5. Analogous to Scheme 3, these mechanisms may not be exclusive, but they are intended to represent the shortest (most favored) reaction paths that generate the observed structures.



Scheme 5. Suggested mechanisms for formation of the deuterated methylenes detected in the ^{13}C NMR spectrum of dPE-Ru.

If p_E is not small, pathways involving more than one elimination event become significant contributors to the levels of these structures. Moreover, new structures which require at least two elimination events to form – and which are not considered in Figure 3 – can become significant. However, since the resonances for all deuterated methylenes (CDH and CD_2) appear in the same limited spectral region shown in Figure 2 and Figure 3, peak overlap becomes severe as the diversity of deuterium substitution patterns increases. Some additional discussion on this point is provided in the Supporting Information, but in brief, a "small p_E" quantitative analysis like that outlined above for dPE-Rh is of limited utility for dPE-Ru. Nonetheless, some conclusions about the catalytic species present (f_D) and the relative rates of β_1 and β_3 elimination (β) can still be drawn from such an analysis as summarized in Table 3.

Table 3. Reaction parameter estimation for dPE-Ru deuteration with $f_D = 0.26$, $p_E = 0.90$, and $\beta = 0.085$.

structure	probability	calculated[a]	experimental[a]	exp/calc
Ru-1	$(1-f_D)(1-p_E)$	329	402	1.22
Ru-2	$f_D(1-f_D)\beta p_E$	65	68	1.04
Ru-3	$2(1-p_E)f_D + f_D(1-f_D)\beta p_E +$ $f_D p_E(1-\beta)(1-f_D)$ $= 2(1-p_E)f_D + f_D(1-f_D)p_E$	1000	1000	1
Ru-4	$2f_D^2\beta p_E$	46	49	1.08
Ru-5(a) + Ru-5(b)	$f_D^2\beta p_E + f_D^2 p_E(1-\beta) = f_D^2 P_E$	270	374	1.38
Ru-6	$\frac{1}{2}f_D p_E(1-\beta)(1-f_D)$	352	273	0.78
Ru-7	$f_D^2 p_E(1-\beta)$	247	264	1.07

[a] normalized to Ru-3 probability or area (=1000)

An approximate value of $\beta = 0.085$ can be extracted from the observed levels of structures whose shortest generating pathways differ only by one β_3 vs. β_1 elimination (Ru-4 vs. Ru-7, shown in Scheme 5(c) and Scheme 5(f)). The small value of β indicates that β_1 elimination is much preferred over β_3 elimination, presumably due to a larger steric hindrance to bond rotation about Ru-C relative to rotation about C-C (vicinal carbons of PCP) in the σ-metalalkyl intermediate, even more pronounced than in the Wilkinson's catalyst case. Furthermore, an approximate value of $f_D = 0.26$ can be extracted from the structures whose shortest generating pathways differ only by whether saturation was initiated by Ru-D vs. Ru-H (Ru-4 vs. Ru-2, shown in Schemes 5(c) and 5(d)). With $\beta = 0.085$ and $f_D = 0.26$, an approximate fit to the experimental peak areas is achieved with $p_E = 0.90$, where the largest discrepancy is within a factor of 1.4. However, the large value of p_E refutes the premise of the "small p_E" analysis by which it was obtained, and should be interpreted with caution.

Ru-H can undergo H/D exchange with D_2 in toluene,[53] so it is useful to consider this possibility and its impact here as well. In the limit of complete equilibrium, where all Ru-H is converted to Ru-D by exchange with the large excess of D_2 prior to saturation, $f_D \rightarrow 1$ and the deuterated carbons that require Ru-H to form – Ru-1, Ru-2, and Ru-6 – would not be present (see Scheme 5 for relevant reaction mechanisms), though all of these are observed with significant intensity. On the other hand, if there were zero exchange between Ru-H and D_2, f_D would be set by the balance between saturation (which always generates Ru-D) and H/D exchange with the PCP (which regenerates Ru-H), and the final deuteration level would be maintained at 20%. In the absence of direct exchange between Ru-H and D_2, $f_D = 1-p_E$ when p_E is small. However, as p_E becomes larger, the probability of having multiple elimination events prior to saturation becomes significant, and some eliminations will regenerate Ru-D instead of Ru-H, raising f_D above $1-p_E$. The values of $f_D = 0.26$ and DL = 21.9% obtained from analysis of the ^{13}C NMR spectrum suggest that there is nonzero but limited H/D exchange between Ru-H and D_2, closer to the "zero exchange" limit than the "complete exchange" limit under the conditions employed.

In the case of Wilkinson's catalyst, $p_{E,Rh}$ represents the relative rates of elimination vs. saturation since these reactions both proceed from the same intermediate –the σ-metalalkyl, as shown in Schemes 2(a) and 2(b). Thus, $p_{E,Rh}$ is controlled solely by the structure of this intermediate: the ligands on Wilkinson's catalyst and the polymer backbone structure. On the other hand, $p_{E,Ru}$ is expected to vary with the pressure of D_2 in the reactor, because the saturation and elimination reactions proceed through different intermediates: as shown in Schemes 4(a) and 4(c), saturation requires oxidative addition of D_2 to the Ru center, while elimination does not. Hence, the ratio of rates of elimination vs. saturation (deuteration) must decrease with an increase in D_2 concentration in the solution (or D_2 pressure in the reactor). This provides an extra experimental handle to adjust the extent of elimination (hence isomerization and H/D exchange) that occurs during deuteration when employing the Ru-H catalyst. Similarly, since the analysis above indicates some direct exchange between Ru-H and D_2, this mechanistic distinction should also provide a handle to adjust the overall deuteration level: higher D_2 pressure should produce structures more closely resembling regular deuteration (with DL = 20%), while lower D_2 pressures (but still a large ratio of D_2:double bonds) should produce more isomerization, and DL > 20%.

Complementary density and FTIR measurements were carried out to corroborate the ^{13}C NMR analyses (see the Supporting Information for details). Deuteration levels determined by FTIR were 20.6% and 21.4% for dPE-Rh and dPE-Ru, respectively, which satisfactorily match the values of 20.1% and 21.9% measured by ^{13}C NMR. The deuteration levels determined by density measurement were 20.2% and 24.3% for dPE-Rh and dPE-Ru, respectively; the former is in good agreement with the value from ^{13}C NMR, while the latter is 2% higher. We attribute this apparent difference to the difficulty in correcting the density result for small mismatches in the degree of crystallinity between members of the dPE/hPE matched pair, a mismatch which was larger in the case of PE-Ru vs. PE-Rh. In addition, the CD_2:CDH ratio calculated by FTIR and ^{13}C NMR showed good agreement: 0.05:0.95 vs. 0.02:0.98 (FTIR vs. ^{13}C NMR) for dPE-Rh and 0.25:0.75 vs. 0.22:0.78 for dPE-Ru.

SANS analysis.

As outlined above, the mechanisms involving isomerization and H/D exchange over these homogeneous catalysts are intermolecular, i.e., H and D can move from chain to chain. Thus, the deuteration level will vary slightly among the chains when these processes are concurrent with deuteration. However, these reactions are expected to occur at random positions along and among the many ($> 10^3$) mers per chain, so it is unlikely that the deuteration level will show a significant molecular weight dependence as it does for heterogeneous catalysts, i.e., the deuteration level among chains should be statistically uniform. Thus, despite having non-regular labeling, the dPEs presented here are not expected to show significant coherent scattering in SANS, as confirmed below.

To probe the uniformity of dPEs at the polymer chain level, SANS data were collected for both dPEs, as well as a broad-distribution linear PE (E4, Dow Chemical Company[46]), in the melt state at 150 °C. If the dPEs are uniformly deuterated, the SANS profile is expected show only flat incoherent scattering similar to that of unlabeled PE, whereas non-uniform deuteration will cause scattering that reflects the radius of gyration (R_g) of the labelled sections (chains or subchains).[18,23] The experimental SANS data as well as the calculated scattering from non-uniform deuteration[18] with an R_g equal to that of the entire polymer chain are plotted in Figure 4 (see Supporting Information for scattering calculation).

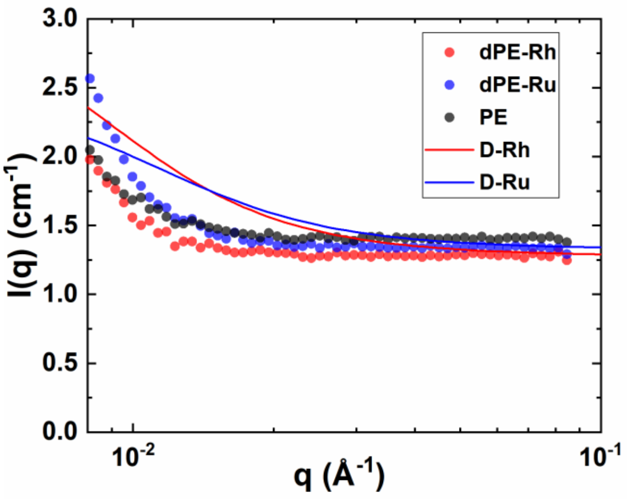


Figure 4. Experimental SANS data for dPE-Ru, dPE-Rh, and unlabelled PE in the melt at 150 °C (symbols). Solid curves show calculated Debye functions for dPE-Rh (D-Rh) and dPE-Ru (D-Ru), respectively, assuming a level of labeling heterogeneity comparable to that obtained by deuteration of polybutadiene over Pd/$CaCO_3$.[18]

The scattering profiles for all three PEs are featureless, except for an upturn at $q < 0.015$ Å^{-1}, observed in all three cases. Considering the similarity between the low-q scattering in the unlabeled PE and the two dPEs, this feature is not believed to reflect non-uniform labeling in the dPEs. Such excess scattering in this q-range in the melt state has been observed for completely hydrogenous poly(ethylene oxide) and attributed to voids in the sample.[54] Indeed, the calculated curves in Figure 4 (D-Rh and D-Ru) show that, for a polymer of R_g similar to our two dPEs, the onset of Debye scattering would be near $q = 0.04$ Å^{-1}, considerably higher in q than the observed onset of the upturn. Note that nonuniformity of labelling at a scale smaller than the whole chain (e.g., from "blocky" exchange) would lead to scattering at even higher q (smaller R_g) than in calculated D-Rh and D-Ru profiles in Figure 4, contrary to what is observed. Similarly, Reichart et al. have observed that SANS from polybutadiene deuterated over Wilkinson's catalyst showed a flat intensity profile for $q > 0.015$ Å^{-1}, whereas polybutadiene ($M_w = 62.5$ kg/mol) deuterated over $Pd/CaCO_3$ showed significant coherent scattering at $q < 0.04$ Å^{-1}.[23] The absence of coherent scattering from dPE-Rh and dPE-Ru in the relevant q-range proves that the labeling provided by both homogeneous catalysts is effectively uniform – even for Ru-H, despite the substantial irregularity in D position, and the modest net H/D exchange. As noted above, it could be interesting in future work to conduct saturations over Ru-H at lower D_2 pressures, to see whether a higher DL can be obtained – for enhanced contrast in SANS experiments – while maintaining the expected statistical uniformity of labelling.

SUMMARY AND CONCLUSION

Narrowly-distributed, partially-deuterated linear polyethylenes were synthesized by ROMP of cyclopentene followed by deuteration over either Wilkinson's or Ru-H catalyst. The ^{13}C NMR spectra of these dPEs indicate that both isomerization and H/D exchange between polymer and catalyst occur concomitantly with deuteration; under typical saturation conditions, Ru-H induces more extensive isomerization and exchange compared with Wilkinson's catalyst, yielding a greater diversity of deuterated methylene types. Wilkinson's catalyst undergoes minimal H/D exchange with the reducing gas (D_2), yielding deuteration levels (20 – 21%) close to the stoichiometric value (20%), while Ru-H undergoes significant direct exchange with D_2 and yields a higher deuteration level ($\approx 22\%$). From the underlying mechanisms revealed by analysis of the ^{13}C NMR spectrum, the DL for dPE-Ru is expected to depend on the D_2 pressure during saturation, with lower pressures leading to higher DL. Nonetheless, both catalysts produce statistically uniform labelling at the polymer chain-length level, as confirmed by SANS experiments, where dPEs from both catalysts show only incoherent scattering in the q-range corresponding to R_g. Since PCP is synthesized by living ROMP, the synthetic route described in Scheme 1 provides a facile route to uniformly-labelled dPEs, and precisely matched hPE/dPE pairs, having a wide range of molecular weights and narrow dispersities.

ASSOCIATED CONTENT

Supporting Information

^{13}C NMR peak assignments and areas, reaction mechanisms, example probability calculations for the formation of different deuterated methylenes, density measurements and deuteration levels determined therefrom, deuteration analysis by FTIR, and calculated SANS from nonuniform labelling. (PDF)

Corresponding Author

*Tel +1 609 258 4691; fax +1 609 258 0211; e-mail register@princeton.edu

Notes

The authors declare no competing financial interest.

Acknowledgements

This research was generously supported by the National Science Foundation, Polymers Program (DMR-2002991), and used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. The authors gratefully acknowledge Dr. Lilin He (ORNL) for running the SANS measurements and for helpful discussions.

REFERENCES

(1) Stamm, M.; Fischer, E. W.; Dettenmaier, M.; Convert, P. Chain Conformation in the Crystalline State by Means of Neutron Scattering Methods. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 263–278.

(2) Crist, B.; Nicholson, J. C. Small-Angle Neutron-Scattering Studies of Partially Labelled Crystalline Polyethylene. *Polymer* **1994**, *35*, 1846–1854.

(3) Ballard, D. G. H.; Cheshire, P.; Longman, G. W.; Schelten, J. Small-Angle Neutron Scattering Studies of Isotropic Polypropylene. *Polymer* **1978**, *19*, 379–385.

(4) Krishnamoorti, R.; Graessley, W. W.; Dee, G. T.; Walsh, D. J.; Fetters, L. J.; Lohse, D. J. Pure Component Properties and Mixing Behavior in Polyolefin Blends. *Macromolecules* **1996**, *29*, 367–376.

(5) Rhee, J.; Crist, B. Isotope and Microstructure Interactions in Blends of Random Copolymers. *J. Chem. Phys.* **1993**, *98*, 4174–4182.

(6) Reichart, G. C.; Graessley, W. W.; Register, R. A.; Lohse, D. J. Thermodynamics of Mixing for Statistical Copolymers of Ethylene and α-Olefins. *Macromolecules* **1998**, *31*, 7886–7894.

(7) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. Thermodynamic Interactions in Model Polyolefin Blends Obtained by Small-Angle Neutron Scattering. *Macromolecules* **1992**, *25*, 6137–6147.

(8) Higgins, J. S.; Benoît, H. C. *Polymers and Neutron Scattering*; Clarendon Press, 1994.

(9) Cotton, J. P.; Farnoux, B.; Jannink, G.; Decker, D.; Benoît, H.; Picot, C.; Higgins, J.; Ober, R.; des Cloizeaux, J. Conformation of Polymer Chain in the Bulk. *Macromolecules* **1974**, *7*, 863–872.

(10) Kirste, R. G.; Kruse, W. A.; Ibel, K. Determination of the Conformation of Polymers in the Amorphous Solid State and in Concentrated Solution by Neutron Diffraction. *Polymer* **1975**, *16*, 120–124.

(11) Schelten, J.; Ballard, D. G. H.; Wignall, G. D.; Longman, G.; Schmatz, W. Small-Angle Neutron Scattering Studies of Molten and Crystalline Polyethylene. *Polymer* **1976**, *17*, 751–757.

(12) Schelten, J.; Wignall, G. D.; Ballard, D. G. H.; Longman, G. W. Small-Angle Neutron Scattering Studies of Molecular Clustering in Mixtures of Polyethylene and Deuterated Polyethylene. *Polymer* **1977**, *18*, 1111–1120.

(13) Bates, F. S.; Bair, H. E.; Hartney, M. A. Block Copolymers near the Microphase Separation Transition. 1. Preparation and Physical Characterization of a Model System. *Macromolecules* **1984**, *17*, 1987–1993.

(14) Li, L.; Arras, M. M. L.; Li, T.; Li, W.; Chang, D.; Keum, J. K.; Bonnesen, P. V.; Qian, S.; Peng, X.; Lee, B.; Hong, K. Alternating Crystalline Lamellar Structures from Thermodynamically Miscible Poly(ε-Caprolactone) H/D Blends. *Polymer* **2019**, *175*, 320–328.

(15) Li, L.; Chang, D.; Arras, M. M. L.; Li, W.; Li, T.; Keum, J. K.; Bonnesen, P. V.; Peng, X.; Hong, K. Isotope Effects on the Crystallization Kinetics of Selectively Deuterated Poly(ε-Caprolactone). *J. Polym. Sci. Part B Polym. Phys.* **2019**, *57*, 771–779.

(16) Chang, D.; Li, T.; Li, L.; Jakowski, J.; Huang, J.; Keum, J. K.; Lee, B.; Bonnesen, P. V.; Zhou, M.; Garashchuk, S.; Sumpter, B. G.; Hong, K. Selectively Deuterated Poly(ϵ-Caprolactone)s: Synthesis and Isotope Effects on the Crystal Structures and Properties. *Macromolecules* **2018**, *51*, 9393–9404.

(17) Tanzer, J. D.; Bartels, C. R.; Crist, B.; Graessley, W. W. Dimensions of Polymer Chains in the Semicrystalline Solid State. *Macromolecules* **1984**, *17*, 2708–2714.

(18) Balsara, N. P.; Lohse, D. J.; Graessley, W. W.; Krishnamoorti, R. Small-Angle Neutron Scattering by Partially Deuterated Polymers and Their Blends. *J. Chem. Phys.* **1994**, *100*, 3905–3910.

(19) Kang, S.; Zeng, Y.; Lodge, T. P.; Bates, F. S.; Brant, P.; López-Barrón, C. R. Impact of Molecular Weight and Comonomer Content on Catalytic Hydrogen-Deuterium Exchange in Polyolefins. *Polymer* **2016**, *102*, 99–105.

(20) Habersberger, B. M.; Hart, K. E.; Gillespie, D.; Huang, T. Molecular Weight Dependence of Deuterium Exchange on Polyethylene: Direct Measurement and SANS Model. *Macromolecules* **2015**, *48*, 5951–5958.

(21) Habersberger, B. M.; Lodge, T. P.; Bates, F. S. Solvent Selective Hydrogen-Deuterium Exchange on Saturated Polyolefins. *Macromolecules* **2012**, *45*, 7778–7782.

(22) Zeng, Y.; López-Barrón, C. R.; Kang, S.; Eberle, A. P. R.; Lodge, T. P.; Bates, F. S. Effect of Branching and Molecular Weight on Heterogeneous Catalytic Deuterium Exchange in Polyolefins. *Macromolecules* **2017**, *50*, 6849–6860.

(23) Reichart, G. C.; Register, R. A.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J. Effect of Nonuniform Deuterium Labeling on Small-Angle Neutron Scattering Results for Polymer Blends. *Macromolecules* **1995**, *28*, 8862–8864.

(24) Bond, G. C.; Hillyard, R. A. Hydroisomerization of Olefins Catalyzed by Tris(triphenylphosphine)Rhodium (I) Halides. *Discuss. Faraday Soc.* **1968**, *46*, 20–30.

(25) Zoller, D. L.; Johnston, M. V.; Qian, K.; Lohse, D. J. A Study of Deuterium Distribution in Deuterated Polyolefins by Pyrolysis-Photoionization Mass Spectrometry.

Macromolecules **2000**, *33*, 5388–5394.

(26) Atkinson, J. G.; Luke, M. O. Hydrogen–Deuterium Exchange of Medium Ring Cycloalkenes during Deuterogenation with Tris(triphenylphosphine)Chlororhodium(I). *Can. J. Chem.* **1970**, *48*, 3580–3582.

(27) Bayerl, B.; Wahren, M.; Graefe, J. Isotopenaustauschvorgänge bei Homogen Katalysierten Reaktionen-II. H/D-Austausch bei der Deuterierung von Cycloalkenen in Gegenwart von Tris-(Triphenylphosphin-)Rhodium(I)-Chlorid. *Tetrahedron* **1973**, *29*, 1837–1842.

(28) Tuner, M.; Jouanne, J. V.; Brauer, H. D.; Kelm, H. The Isomerization of n-Butenes Catalyzed by $RhCl(PPh_3)_3$ I. The Isomerization of 2-Butenes. *J. Mol. Catal.* **1979**, *5*, 425–431.

(29) Tuner, M.; Jouanne, J. V.; Brauer, H. D.; Kelm, H. The Isomerization of n-Butenes Catalyzed by $RhCl(PPh_3)_3$ II. The Isomerization of 1-Butene. *J. Mol. Catal.* **1979**, *5*, 433–445.

(30) Jangareddy, S.; Register, R. A. Incorporation of Styrene into a Model Polyolefin for Enhanced Compatibility with Polyisoprene. *Macromolecules* **2020**, *53*, 9142–9151.

(31) Otsuki, T.; Goto, K.; Zen, K.; Komiya, Z. Development of Hydrogenated Ring-Opening Metathesis Polymers. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 4661–4668.

(32) Yoshida, Y.; Yoshinari, M.; Iio, A.; Komiya, Z. Hydrogenation of Ring-Opening Metathesis Polymer with Ruthenium Catalysts. *Polym. J.* **1998**, *30*, 819–823.

(33) Yue, C. J.; Liu, Y.; He, R. Olefins Isomerization by Hydride-Complexes of Ruthenium. *J. Mol. Catal. A Chem.* **2006**, *259*, 17–23.

(34) Wakamatsu, H.; Nishida, M.; Adachi, N.; Mori, M. Isomerization Reaction of Olefin

Using RuClH(CO)(PPh_3)$_3$. *J. Org. Chem.* **2000**, *65*, 3966–3970.

(35) Krompiec, S.; Penczek, R.; Krompiec, M.; Pluta, T.; Ignasiak, H.; Kita, A.; Michalik, S.; Matlengiewicz, M.; Filapek, M. Transition Metals for Conjugation of Polyunsaturated Acids and Their Esters. *Curr. Org. Chem.* **2009**, *13*, 896–913.

(36) Krompiec, S.; Kuźnik, N.; Krompiec, M.; Penczek, R.; Mrzigod, J.; Tórz, A. The Role of the Functional Group in Double Bond Migration in Allylic Systems Catalysed by Ruthenium Hydride Complexes. *J. Mol. Catal. A Chem.* **2006**, *253*, 132–146.

(37) Gramlich, W. M.; Hillmyer, M. A. Catalytic Synthesis and Post-Polymerization Functionalization of Conjugated Polyisoprene. *Polym. Chem.* **2011**, *2*, 2062–2067.

(38) Tse, S. K. S.; Xue, P.; Lin, Z.; Jia, G. Hydrogen/Deuterium Exchange Reactions of Olefins with Deuterium Oxide Mediated by the Carbonylchlorohydridotris(triphenylphosphine)Ruthenium(II) Complex. *Adv. Synth. Catal.* **2010**, *352*, 1512–1522.

(39) Cheng, H. N.; Dziemianowicz, T. S. ^{13}C NMR Characterization of Copolymers of Ethylene and Perdeuteroethylene. *Makromol. Chem.* **1988**, *189*, 845–849.

(40) Li, L.; Li, T.; Arras, M. M. L.; Bonnesen, P. V.; Peng, X.; Li, W.; Hong, K. Chain Arrangements of Selectively Deuterated Poly(ε-Caprolactone) Copolymers as Revealed by Neutron Scattering. *Polymer* **2020**, *193*, 122375.

(41) Habersberger, B. M.; Baugh, D. W. Solvent and Polymer Stereochemistry Play Key Roles in Deuterium Exchange and Partial Racemization of Polypropylenes. *Macromolecules* **2018**, *51*, 1290–1295.

(42) Van Der Velden; P.M., G.; Fetters, L. J. Microstructure Determination of Nondeuterated, Partially Deuterated, and Perdeuterated Polybutadienes with Cis-1,4, Trans-1,4, and

Vinyl-1,2 Units by ^{13}C NMR. *Macromolecules* **1990**, *23*, 2470–2473.

(43) Trzaska, S. T.; Lee, L. B. W.; Register, R. A. Synthesis of Narrow-Distribution "Perfect" Polyethylene and Its Block Copolymers by Polymerization of Cyclopentene. *Macromolecules* **2000**, *33*, 9215–9221.

(44) Mulhearn, W. D.; Register, R. A. Synthesis of Narrow-Distribution, High-Molecular-Weight ROMP Polycyclopentene via Suppression of Acyclic Metathesis Side Reactions. *ACS Macro Lett.* **2017**, *6*, 112–116.

(45) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. The Preparation and Properties of Tris(triphenylphosphine) Halogenorhodium(I) and Some Reactions Thereof Including Catalytic Homogeneous Hydrogenation of Olefins and Acetylenes and Their Derivatives. *J. Chem. Soc. A* **1966**, *1*, 1711–1732.

(46) Wasserman, S. H.; Graessley, W. W. Prediction of Linear Viscoelastic Response for Entangled Polyolefin Melts from Molecular Weight Distribution. *Polym. Eng. Sci.* **1996**, *36*, 852–861.

(47) Birch, A. J.; Williamson, D. H. Homogeneous Hydrogenation Catalysts in Organic Synthesis. In *Organic Reactions*; John Wiley & Sons, Inc.: Hoboken, 2011; pp 1–186.

(48) Duckett, S. B.; Newell, C. L.; Eisenberg, R. Observation of New Intermediates in Hydrogenation Catalyzed by Wilkinson's Catalyst, $RhCl(PPh_3)_3$, Using Parahydrogen-Induced Polarization. *J. Am. Chem. Soc.* **1994**, *116*, 10548–10556.

(49) Krompiec, S.; Pigulla, M.; Krompiec, M.; Baj, S.; Mrowiec-Białoń, J.; Kasperczyk, J. Highly Selective Isomerization of N-Allylamides and N-Allylamines. *Tetrahedron Lett.* **2004**, *45*, 5257–5261.

(50) Larock, R. C.; Dong, X.; Chung, S.; Reddy, C. K.; Ehlers, L. E. Preparation of Conjugated

Soybean Oil and Other Natural Oils and Fatty Acids by Homogeneous Transition Metal Catalysis. *J. Am. Oil Chem. Soc.* **2001**, *78*, 447–453.

(51) Krompiec, S.; Pigulla, M.; Szczepankiewicz, W.; Bieg, T.; Kuznik, N.; Leszczynska-Sejda, K.; Kubicki, M.; Borowiak, T. Highly Selective Synthesis of (E)-N-Aryl-N-(1-Propenyl) Ethanamides via Isomerization of N-Allyl Ethanamides Catalyzed by Ruthenium Complexes. *Tetrahedron Lett.* **2001**, *42*, 7095–7098.

(52) Bingham, D.; Webster, D. E.; Wells, P. B. Homogeneous Catalysis of Olefin Isomerisation. Part V. Pent-1-Ene Isomerisation Catalysed by Solutions of $RuHCl(PPh_3)_3$ and of $RuHCl(CO)(PPh_3)_3$; Variation of the Isomeric Composition of Pent-2-Ene and Its Attribution to Steric Factors. *J. Chem. Soc. Dalt. Trans.* **1974**, *14*, 1519–1521.

(53) Vaska, L. Homogeneous Activation of Molecular Hydrogen by Four-, Five-, and Six-Coordinate Transition Metal Complexes. In *Proceedings of the 8th International Conference on Coordination Chemistry*; Gutmann, V., Ed.; Springer Science & Business Media: Vienna, 1964; pp 99–101.

(54) Xie, S.; Zhang, B.; Mao, Y.; He, L.; Hong, K.; Bates, F. S.; Lodge, T. P. Influence of Added Salt on Chain Conformations in Poly(ethylene Oxide) Melts: SANS Analysis with Complications. *Macromolecules* **2020**, *53*, 7141–7149.