



---

**Backbone Editing of Oxidized Polyethylene: Insertion of  
Oxygen and Nitrogen Atoms via Hydroxyalkyl Azide-  
Mediated Rearrangements**

Journal:	<i>Polymer Chemistry</i>
Manuscript ID	PY-ART-09-2024-000973.R1
Article Type:	Paper
Date Submitted by the Author:	19-Oct-2024
Complete List of Authors:	King, Andrew; The University of North Carolina at Chapel Hill, Chemistry Sherrier, Ryan; The University of North Carolina at Chapel Hill, Chemistry Aubé, Jeffrey; University of North Carolina at Chapel Hill, Chemical Biology and Medicinal Chemistry Zhukhovitskiy, Aleksandr; The University of North Carolina at Chapel Hill, Chemistry

## ARTICLE

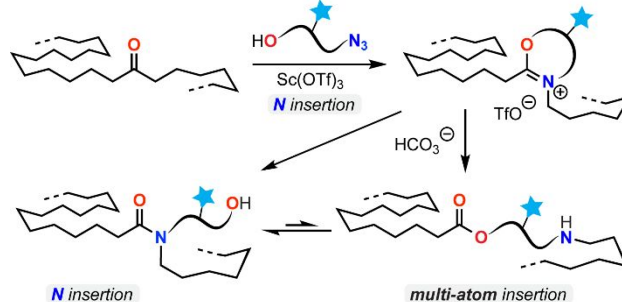
# Backbone Editing of Oxidized Polyethylene: Insertion of Oxygen and Nitrogen Atoms via Hydroxyalkyl Azide-Mediated Rearrangements

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Andrew J. King,<sup>‡a</sup> Ryan P. Sherrier,<sup>‡a</sup> Jeffrey Aubé,<sup>a</sup> and Aleksandr V. Zhukhovitskiy<sup>\*a</sup>

The properties, applications, and end-of-life considerations of plastics are fundamentally linked to the structure of the polymer backbones at the core of these materials. With that in mind, editing the polymer backbone composition offers exciting opportunities to transform the plastics economy; yet, few examples of such transformations utilize commodity plastics as starting materials. In this work, we describe the development of a tandem C–H oxidation/hydroxyalkyl azide mediated rearrangement strategy that converts polyethylene into “polyethylene-like” materials with iminium ethers, esters, amides, and other pendant chemical functionality. Control over formation of esters or amides is achieved by variation of the hydroxyalkyl azide reagent, as well as processing conditions. By targeting specific functionalities, a variety of thermal and



mechanical properties can be accessed. For example, incorporation of iminium ethers decreases the Young's modulus of post-consumer PE from 196 MPa to 69–83 MPa, but conversion of the iminium ethers to esters and amides produces materials with moduli of 212–287 MPa—values higher than the original material. Thus, the demonstration of a modular backbone editing methodology for polyethylene showcases the broader value of this emerging strategy for polymer modification.

## Introduction

Polyethylene (PE) is estimated to account for more than 25% of global plastic production (>100 Mt), which is forecasted to increase in coming years.<sup>1</sup> The massive scale of PE synthesis is tied to its many applications, which range from insulation for powerlines, to protective foams in helmets, to packaging of foods and drinks.<sup>2,3</sup> Although our society has benefited from PE use in numerous ways—including decreased food waste through packaging<sup>3</sup>—the limited approaches to end-of-life treatment for this plastic have led to a problematic accumulation of PE waste. This problem is exacerbated by the fact that much of the PE produced is applied in single-use

packaging.<sup>4</sup>

One approach to addressing the problem of PE waste accumulation is to upcycle the waste through C–H functionalization reactions.<sup>5</sup> By installing functional side chains *via* C–H functionalization, PE waste can be converted into a variety of new materials, such as hydroxylated PE, polyolefin ionomers, or thermosets.<sup>6–10</sup> Another approach is to develop alternatives to PE that maintain the properties of PE, but contain small quantities of an embedded functionality that can **Figure 1.** Utilization of hydroxyalkyl azide mediated rearrangement to convert ketones into esters and amides.

be leveraged for recycling or degradation. This class of materials is classified as “polyethylene-like” (“PE-like”) materials, and they can be sourced from a non-alternating copolymerization of CO and ethylene or from condensation reactions of monomers with long alkyl chains.<sup>11–15</sup> These approaches produce polymers with in-chain ketones or esters, and the latter, in particular, can be depolymerized and repolymerized, making them a closed-

<sup>a</sup> The University of North Carolina at Chapel Hill, Department of Chemistry, Chapel Hill, NC 27514. Email: alexzhuk@email.unc.edu

<sup>‡</sup> Authors contributed equally to work.

<sup>†</sup> Electronic supplementary information (ESI) available: Detailed information on reagents, instrumentation, experimental and synthetic methods, spectral data, and supplementary text and figures. See DOI: 10.1039/x0xx00000x

loop alternative to polyethylene.<sup>11,13</sup>

We envisioned that polymer backbone editing could bridge the concepts of upcycling via C–H functionalization and “PE-like materials” by enabling the transformation of PE into more easily degradable/recyclable “PE-like” materials with esters or amides.<sup>16</sup> Notably, backbone editing in this context has several key precedents. In 1961, Michel and Murphey reported on the Schmidt rearrangement to convert ketones in CO/ethylene copolymers to amides or tetrazoles using hydrazoic acid; however, the harsh conditions, hazardous reagents, and potential for chain-scission have hampered wider application of this methodology.<sup>17</sup> In the same study, Michel and Murphey also report a two-step method to convert ketones to amides by first converting the ketone to an oxime with hydroxylamine, then performing the Beckmann rearrangement with  $\text{PCl}_5$ .<sup>17</sup> More recently, Nozaki applied the diethylaminosulfur trifluoride (DAST)-promoted Beckmann rearrangement in a similar non-alternating CO/ethylene copolymer substrate to achieve the same transformation;<sup>18</sup> this chemistry has the advantages of proceeding at room temperature and absence of chain scission, but it also requires 50 equivalents of DAST and produces stoichiometric HF as a byproduct. Lastly, Mecking and coworkers demonstrated the Baeyer-Villiger oxidation of ketones to esters in a non-alternating CO/ethylene copolymer,<sup>13</sup> a transformation analogous to an earlier report from Nozaki and coworkers.<sup>19</sup> Here, too, the reaction conditions are mild and chain scission is mitigated, but the use of 3 g of peroxide (*m*CPBA) per 0.5 g of polymer limits scalability of this chemistry. Notably, in all of these examples, the chemistry is not particularly modular: one transformation makes a maximum of two products. Lastly, the starting materials are CO/ethylene copolymers, rather than post-consumer plastic waste, which makes it challenging to extrapolate the potential impact of the of these methods in the context of polymer sustainability.

To address these challenges, we sought to develop an approach that would allow for on demand installation of both esters and amides with diverse substituents into the backbones of pristine and post-consumer waste PE. We identified the hydroxyalkyl azide mediated rearrangement of ketones as a promising candidate (**Figure 1**) because the ketones could be installed via established C–H oxidation methods,<sup>9</sup> and the rearrangement progresses through a cyclic iminium ether intermediate, which offers opportunities for product diversification. Specifically, the iminium ether can produce both esters and amides, and it features a modular fragment of the hydroxyalkyl azide that is ultimately incorporated into either the polymer backbone or the pendant *N*-substituted side chain in the cases of esters and amides, respectively (**Figure 1**).<sup>20–25</sup>

## Results and discussion

### Preliminary Studies and Reaction Optimization

Before we began our exploration of hydroxyalkyl azide rearrangement chemistry on an oxidized PE (**ox-PE**)<sup>9</sup> system, we

sought to investigate the reactivity on a small molecule model. To date, only a few examples of this chemistry have been published which applied to acyclic compounds, and in all cases, the reported reaction temperature, solvent, and concentration would be incompatible with **ox-PE**.<sup>20,25,26</sup> The latter is only soluble in a select few solvents—most commonly, 1,2-dichloroethane or chlorinated aromatics—and requires elevated temperatures and a large excess of solvent. Under these harsher conditions with low ketone concentrations, and in the presence of acids, the hydroxyalkyl azide can undergo acid-mediated thermal decomposition,<sup>27</sup> resulting in formation of low quantities of iminium ether and considerable amounts of side-products. Indeed, in reactions of 5-nonanone with 1.5 equivalents of 3-azido-1-propanol (**1-OH**) and 3 equivalents of either  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{BF}_3 \cdot \text{OEt}_2$  at 120 °C in 1,2-dichloroethane, **1-OH** is completely consumed within 2 h yielding 21–47% of the target product (**SI Table S1** and **SI Figures S1–S4**). To address this issue, we began an initial study of the reaction on a small molecule under the constraints required by **ox-PE** (namely solvent, temperature, and substrate concentration) to ultimately develop conditions that could be translated directly to **ox-PE**.

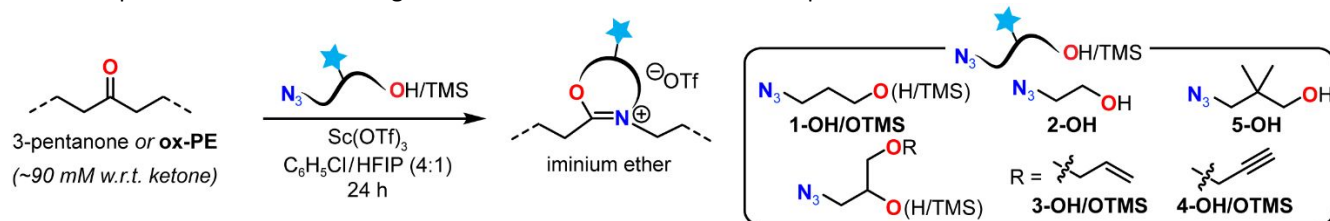
Given the side-reactivity observed with Brønsted-Lowry acids, we transitioned to Lewis acids. Similarly to Brønsted-Lowry acids, Lewis acids have been shown to facilitate decomposition of organic azides by binding to a nitrogen in the azide followed by loss of  $\text{N}_2$ .<sup>27</sup> Despite this precedent, we hypothesized that the reaction outcome could be improved with a Lewis acid that selectively activates the ketone without decomposing the azide. To this end, we screened main-group, transition-metal, and lanthanide Lewis acids in our reaction (**SI Table S1** and **SI Figures S5–S23**). Many of the Lewis acids gave poor results—low product formation and high consumption of **1-OH**; however,  $\text{Sc}(\text{OTf})_3$  gave 21% yield of the product with only 35% consumption of **1-OH**. Furthermore, the yield of iminium ether matched the consumption of ketone (23%), and the reaction progressed with virtually no side-products. Minimization of side-product formation is critical in polymer backbone editing because, in such a setting, separation of side-products from target products may not be feasible if they are embedded in the same polymer chain.

Having identified a Lewis acid of choice for this transformation, we sought a solvent system that would both solubilize the polymer and improve the stability of the hydroxyalkyl azide. For PE solubility, we selected chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) because it is effective at solubilizing PE at elevated temperatures. Since incorporation of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) has previously been demonstrated to improve iminium ether formation,<sup>28</sup> we transitioned to a 4:1  $\text{C}_6\text{H}_5\text{Cl}$ :HFIP solvent mixture in our system. Notably, although **ox-PE** is insoluble in HFIP, we were able to solubilize **ox-PE** in chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) at 80 °C and then add HFIP to yield a homogenous solution with a 4:1 mixture of  $\text{C}_6\text{H}_5\text{Cl}$ /HFIP. Furthermore, after addition of HFIP, the solution could then be gradually cooled to 50 °C

without precipitation of low-molecular weight (MW)—derived from commercial 1.7 kg/mol PE—**ox-PE**.

With the solvent selected, we next explored the effect of  $\text{Sc}(\text{OTf})_3$  equivalents and reaction temperature using the small molecule model compound 3-pentanone (**Table 1**). Reaction

**Table 1.** Optimization of the rearrangement to form iminium ethers from 3-pentanone and **ox-PE**



Entry	Ketone	$\text{Sc}(\text{OTf})_3$ equiv	Hydroxyalkyl azide (equiv)	T (°C)	Yield (%)
1	3-pentanone	1.0	1-OH (1.5)	50	36 <sup>a</sup>
2	3-pentanone	3.0	1-OH (1.5)	50	100 <sup>a</sup>
3	3-pentanone	3.0	1-OH (1.5)	70	89 <sup>a</sup>
4	3-pentanone	3.0	1-OH (1.5)	90	74 <sup>a</sup>
5 <sup>c</sup>	<b>ox-PE</b>	1.0	1-OH (1.5)	50	5 <sup>b</sup>
6 <sup>c</sup>	<b>ox-PE</b>	3.0	1-OH (1.5)	50	41 <sup>b</sup>
7 <sup>c</sup>	<b>ox-PE</b>	3.0	1-OH (1.5)	70	42 <sup>b</sup>
8 <sup>c</sup>	<b>ox-PE</b>	3.0	1-OH (1.5)	90	26 <sup>b</sup>
9	<b>ox-PE</b>	3.0	1-OH (1.5)	50	67 <sup>b</sup>
10	3-pentanone	3.0	1-OTMS (1.5)	50	100 <sup>a</sup>
11	3-pentanone	3.0	2-OH (1.5)	50	80 <sup>a</sup>
12	3-pentanone	3.0	<i>rac</i> -3-OTMS (1.5)	50	50 <sup>a</sup>
13	3-pentanone	3.0	<i>rac</i> -4-OTMS (1.5)	50	51 <sup>a</sup>
14	<b>ox-PE</b>	3.0	2-OH (1.5)	50	51 <sup>b</sup>
15	<b>ox-PE</b>	3.0	3-(R)-OTMS (1.5)	50	29 <sup>b</sup>
16	<b>ox-PE</b>	3.0	<i>rac</i> -4-OTMS (1.5)	50	29 <sup>b</sup>
17	<b>ox-PE</b>	3.0	5-OH (1.5)	50	56 <sup>b</sup>
18	<b>ox-PE</b>	3.0	1-OTMS (1.5)	50	66 <sup>b</sup>

<sup>a</sup> Determined via  $^1\text{H}$  NMR spectroscopy of the reaction mixture using mesitylene as the internal standard. Yield is reported as an average of triplicate experiments

<sup>b</sup> Determined via  $^1\text{H}$  NMR spectroscopy of the isolated polymer

<sup>c</sup> Concentration of **ox-PE** was 20 mg/mL (~19 mM ketone)

yields decreased from 100% to 89% or to 74% when the temperature was raised to 70°C or to 90°C, respectively (**Table 1, entries 2–4** and **SI Figures S26–S28**). Reactions with **ox-PE** derived from commercial PE (1.7 kg/mol) confirmed the trends observed with 3-pentanone. Increasing equivalents of  $\text{Sc}(\text{OTf})_3$  from 1.0 to 3.0 substantially increases the yield of iminium ether (**Table 1, entries 5–6** and **SI Figure S29**); meanwhile increasing temperature from 50 to 70 °C had no effect on yield (41 vs. 42%), but a further increase to 90 °C lowered the yield to 26% (**Table 1, entries 6–8**) and **SI Figure S30**). Although the trends were the same, the yields in the reactions with **ox-PE** were typically much lower than reactions with 3-pentanone—41% vs 100%, respectively (**Table 1, entries 2** and **6**)—until we

outcome was substantially impacted by the stoichiometry of  $\text{Sc}(\text{OTf})_3$ : the yield of the iminium ether dramatically increased from 36% to 100% when 3.0 equivalents of  $\text{Sc}(\text{OTf})_3$  were added instead of 1.0 (**Table 1, entries 1–2** and **SI Table S2** and **SI Figures S24–S26**). Increases in temperature were poorly tolerated:

increased the polymer concentration to 100 mg/mL and achieved a similar concentration of ~90 mM w.r.t. ketone (**Table 1, entry 9** and **SI Figures S31–S32**). Further increase in the ketone concentration was limited by solubility of **ox-PE**.

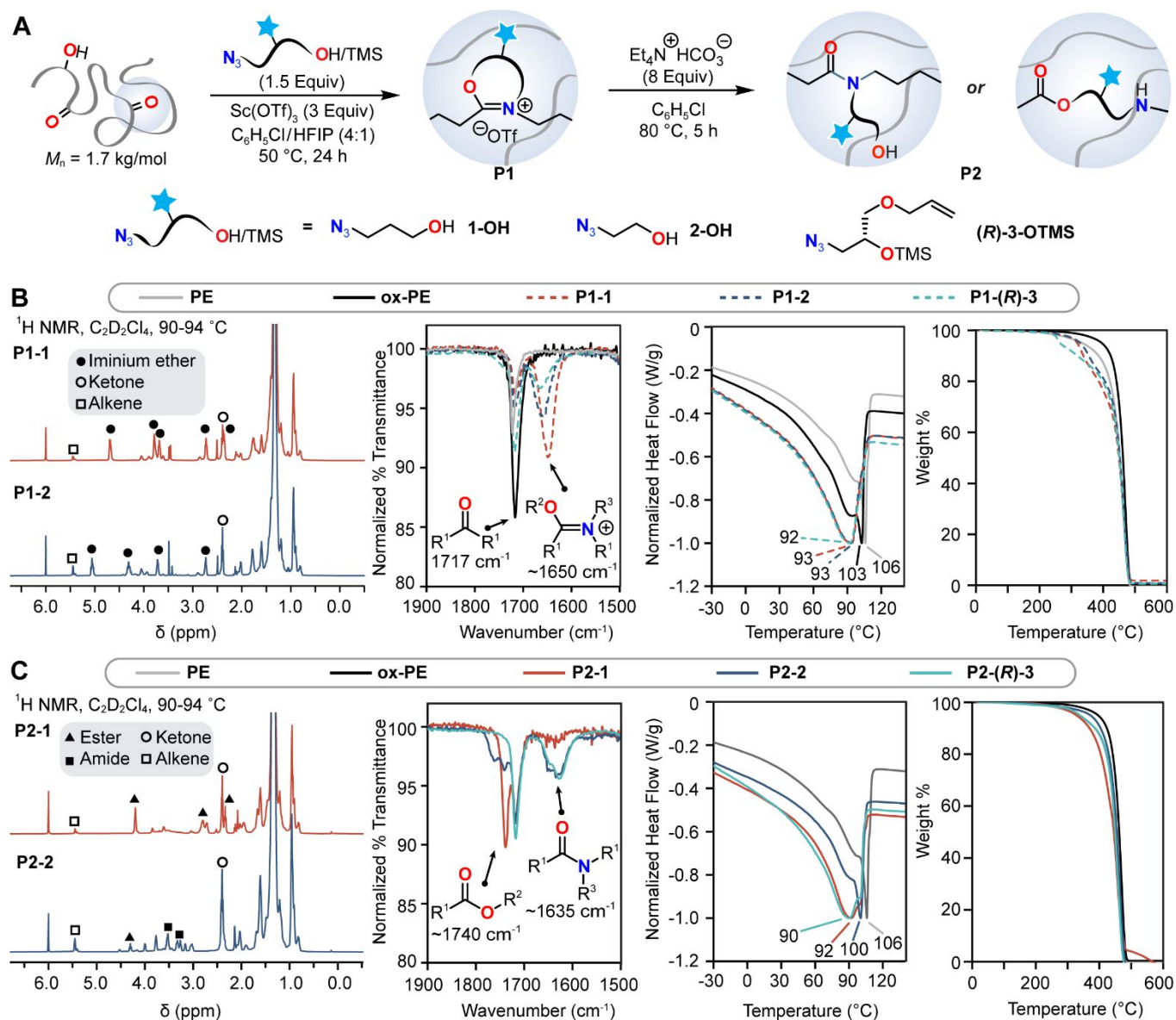
### Polymer Studies

With these results in hand, we transitioned to exploring the scope of reactivity of both 1,2- and 1,3-hydroxyalkyl azides and their trimethylsilyl (TMS) ether analogs in 3-pentanone and **ox-PE** using optimized reaction conditions (**Figure 2A** and **Table 1, entries 9–18** and **SI Figures S31–S45**). The trends for **ox-PE** and 3-pentanone were similar: both substrates reacted with both 1,2- and 1,3-hydroxyalkyl azides and the best yields are

observed when using unsubstituted and/or 1,3-hydroxyalkyl azides. In each case, for the iminium ether containing **P1** series (e.g. **P1-1** formed from reaction with **1-OH**), formation of the iminium ether is confirmed by the new vibration band at  $\sim 1650$   $\text{cm}^{-1}$  in Fourier transform infra-red (FTIR) spectroscopy and the downfield resonances in both  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic

resonance (NMR) spectroscopy (4.5–5.0 ppm and 170–180 ppm, respectively; **Figure 2B** and **SI Figures S31–S32, S41–S47**). Conversion to iminium ether was observed for all hydroxy- and trimethylsilyloxy-alkyl azides studied, with yields of iminium

**Figure 2.** A. Reaction scheme for conversion of **ox-PE** to **P1** (iminium ether) and **P2** (ester or amide) with scope of hydroxyalkyl azides reagents used. B-C. Representative  $^1\text{H}$  NMR, FTIR, DSC and TGA for **P1** series (B) and **P2** series (C). Legend denotes colors used for PE, **ox-PE**, and each variant of **P1** (dashed) and **P2** series.



ethers ranging from 29 to 67% (**Table 1, entries 9, 14–18**). In each case, we also observe formation of internal alkenes by  $^1\text{H}$  NMR, which result from elimination of water from the secondary alcohol units in **ox-PE**.

We attribute diminished yields for reactions with **ox-PE** to inhibition of the reaction by neighboring iminium ethers on the same polymer chain, which highlights some of the unique challenges in polymer functionalization. Despite moderate yields, this editing transformation has utility in the polymer

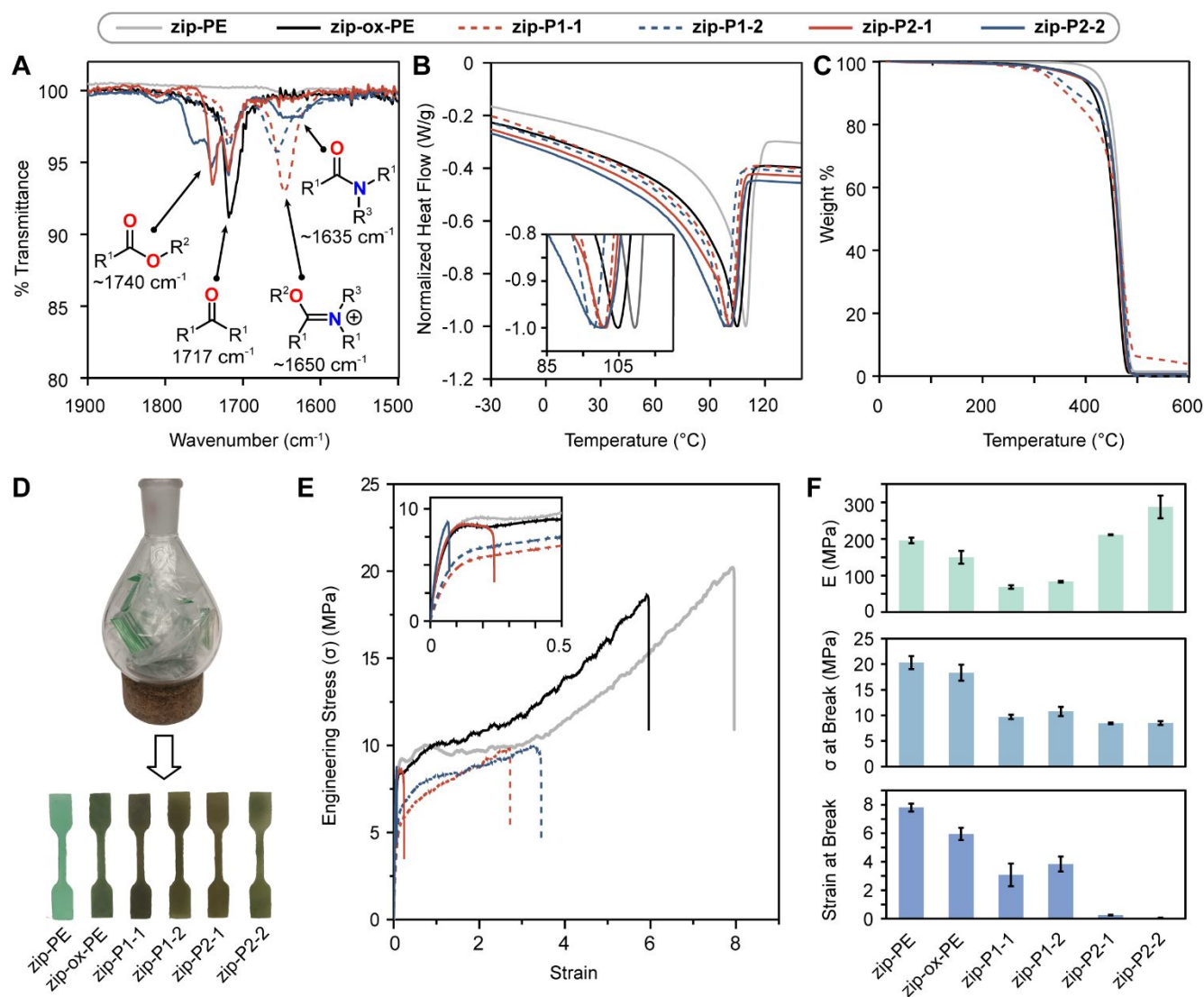
context because it selectively transforms the ketone to iminium ether with minimal side product formation. For example, the sum of product and unreacted ketone accounts for 94% of the starting ketone in **P1-5** (**SI Figure S31**).

To understand the impact of the iminium ether on the crystallinity and thermal stability of the polymer samples, we characterized **P1** using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (**Figure 2B** and **SI Table S3** and **SI Figures S48–S49**). For the whole **P1** series, the melting

transition of the crystalline regions is preserved, with a decrease in the melting temperature from 103 °C (**ox-PE**) to 90–93 °C (**P1** series). The enthalpy of melting is also reduced from 140 J/g (**ox-PE**) to 101–108 J/g (**P1** series). Together, these data indicate decreased crystalline domain size<sup>29</sup> and reduced crystallinity in the iminium ether containing material, which we hypothesize results from the introduction of functional groups that can disrupt chain packing. TGA shows mass loss at lower temperatures for **P1** polymers compared to commercial PE and **ox-PE**, which we hypothesize is due to decomposition of the iminium ether moiety *via* C–O or C–N bond cleavage and dealkylation (**Figure 2B** and **SI Figure S50**).

Opening the iminium ethers in the **P1** series in weakly basic conditions with tetraethylammonium bicarbonate in C<sub>6</sub>H<sub>5</sub>Cl for 5 h at 80 °C completely consumes the iminium ether, as evidenced by <sup>1</sup>H NMR and FTIR, and generates the **P2** series (e.g. **P2-1** formed from **P1-1**), which contain esters and amides (**Figure 2C** and **SI Figures S51–S58**). For **P1-1** and **P1-5**, exclusive formation of the ester is observed by FTIR and <sup>1</sup>H NMR spectroscopy. Conversely, **P2-2** contains a 2.2:1 ratio of amide and ester products and **P2-3** and **P2-4** both contain exclusively amide products. The divergent reactivity of 5- and 6-membered

iminium ether intermediates highlights the capability of the hydroxyalkyl azide-mediated rearrangement to diversify the scope of edited products from a single polymer feedstock. Furthermore, the ability to incorporate allyl and propargyl groups using **3-OTMS** and **4-OTMS**, respectively, and chiral moieties, using (**R**)-**3-OTMS** (**SI Figures S59–S60**), demonstrates the ability of the transformation to install chemically useful handles into a commodity polymer through backbone editing. Similarly to the **P1** series, all the **P2** polymers retain a melting transition with  $T_m = 85$ –102 °C (**Figure 2C** and **SI Table S3** and **SI Figure S61**). However, the enthalpy of melting increases for **P2** polymers (118–132 J/g) compared to **P1** polymers (101–108 J/g), which suggests that the installed functional groups contribute additional interchain interactions (e.g. hydrogen bonding of OH or NH groups) that facilitates crystallization; it is also possible that cyclic iminium ethers disrupt the crystallinity more than their ring-opened products. Lastly, TGA of the **P2** series closely resembles the starting polyethylene which demonstrates that the esters and amide linkages present in **P2** materials are more thermally stable than the iminium ethers in **P1** materials (**Figure 2C** and **SI Figure S62**). In total, the hydroxyalkyl azide mediated rearrangement offers access to



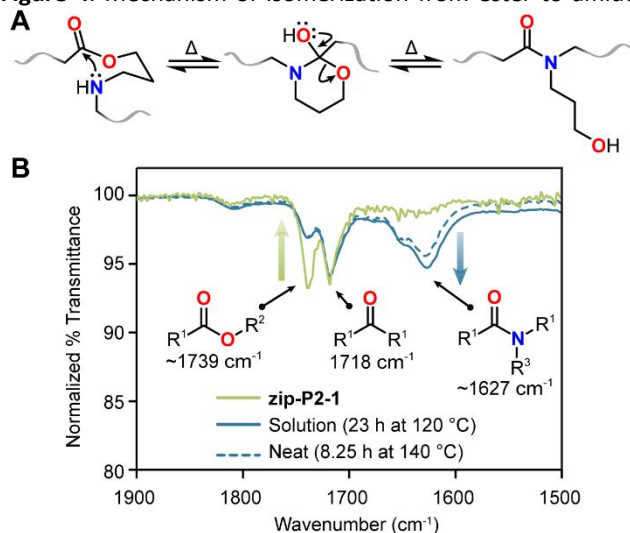
variable thermal properties by accessing either iminium ether or ester/amide containing “PE-like” materials. Melting temperature, degree of crystallinity, and degradation temperature can be controlled by selection of the hydroxyalkyl azide reagent and the terminal functionality (e.g. iminium ether, ester, or amide).

With a greater understanding of the strengths and limitations of the transformation in “PE-like” substrates, we next wanted to explore our editing approach in commercial PE substrates. Oxidation of commercial LDPE from ziplock bags (**zip-PE**) using established conditions yielded **zip-ox-PE** with 2.0% ketone and 1.9% alcohol.<sup>9</sup> Reactions to form **zip-P1** were performed using optimized reaction conditions, except the reaction temperature was 70 °C to assist with polymer solubility. Formation of iminium ether was observed for both **zip-P1-1** and **zip-P1-2** with 54% and 29% yields of iminium ether, respectively (Figure 3A and SI Figures S63–S64). Similarly to reactions on lower-MW PE, **zip-P2-1** contained exclusively esters and **zip-P2-2** contained a mixture of ester and amide groups, as evidenced by NMR and FTIR spectroscopies (SI Figures S63–S68). Of note, there was a smaller ratio of amides to esters compared to lower-MW PE, which we hypothesized was due to higher reaction temperature of 100 °C used for **zip-PE**, compared to 80 °C for lower MW PE. DSC shows preservation of the melting transition in all polymers, with a slight decrease in  $T_m$  from 109 °C for the starting PE to 104 °C for **zip-ox-PE**, and 98–101 °C for the **zip-P1** and **zip-P2** series (Figure 3B and SI Table S4). These results are consistent with the observations for lower-MW PE, and similarly suggest a decrease in the average size of the crystalline domains after oxidation and backbone editing. Changes in the degree of crystallinity in edited **zip-PE** derived samples also mirrored the trends in lower-MW PE. The enthalpy of melting decreases from 142 to 128 J/g from **zip-PE** to **zip-ox-PE** and further decreases to 98–99 J/g for **zip-P1-1** and **zip-P1-2**. However, opening of the iminium ether to form **zip-P2-1** and **zip-P2-2** restores the enthalpy of melting to 130–133 J/g, which is similar to **zip-PE** and **zip-ox-PE**. TGA of both **zip-P1-1** and **zip-P1-2** reveals the characteristic mass loss of the iminium ether—a feature that is no longer present once opening the iminium ether intermediate to **zip-P2-1** and **zip-P2-2** (Figure 3C).

We next wanted to investigate the mechanical properties of polymer materials throughout the editing process using uniaxial tensile testing. After thermal testing was complete, films of each material were made *via* melt pressing, and dogbones were punched out of the films for triplicate pulls (Figure 3D–F and SI Figure S69 and SI Table S5). Compared to the starting **zip-PE**, which has a Young’s modulus ( $E$ ) of  $196 \pm 8$  MPa, **zip-ox-PE** has a slightly lower  $E$  of  $150 \pm 18$  MPa, but similar strain at break. Incorporation of iminium ether moieties produces polymers with diminished  $E$  of  $69 \pm 5$  and  $83 \pm 2$  MPa and strains at break

of  $3.1 \pm 0.8$  and  $3.8 \pm 0.5$ , for **zip-P1-1** and **zip-P2-2**, respectively. Interestingly, opening of the iminium ether elevates  $E$  to values of  $212 \pm 1$  and  $287 \pm 31$  MPa for **zip-P2-1** and **zip-P2-2**, respectively, which is greater than that of the starting **zip-PE**. We hypothesize that the decreased modulus of **zip-ox-PE** and **zip-P1** is due to decreased average crystalline domain size—evidenced by decreasing  $T_m$ —and the increase in modulus for **zip-P2** is a result of the presence of hydrogen bonding. Decreased strain at break for **zip-P2** suggests either (1) the presence of chain-cleavage, which could occur from hydrolysis of esters or amides in **zip-P2-1** and **zip-P2-2**, or (2) reduction in tie chains connecting crystalline domains, which affects the plastic deformation of the materials. Gel permeation chromatography of non-melt pressed materials shows an increased retention time for **zip-P1-1** and **zip-P2-1** compared to **zip-PE** and **zip-ox-PE**. We hypothesize the increase in retention time is the result of either chain-cleavage or a reduced radius of gyration in functionalized polymers (SI Figure S70). Irrespective of the potential for chain-cleavage, we believe the stiffening of **zip-P2-1** and **zip-P2-2** compared to their **zip-P1** counterparts demonstrates an unusual structure-property relationship for these materials and offers another opportunity to control mechanical properties using the modular hydroxyalkyl azide-mediated rearrangement.

Lastly, because the ester and amide products formed from opening of an iminium ether with hydroxide are constitutional isomers, we envisioned that the more thermodynamically stable amide could be accessed through a thermal isomerization of the ester product. Specifically, isomerization can proceed through intramolecular nucleophilic attack of the proximate secondary amine on the ester carbonyl (Figure 4A). Isomerization could also theoretically proceed through an intermolecular reaction, although this is expected to be exceeding slow compared to the intramolecular reaction due to the low concentration of esters and amines. To test this hypothesis, we heated **zip-P2-1** both in solution and solvent-free (Figure 4B and SI Figure S71). In both instances, we observed decreased intensity of the ester vibrational band in FTIR spectroscopy and an increase in the amide vibrational band. As expected, the ketone functionalities in **zip-P1-1**—present from unreacted ketones in **zip-ox-PE**—are unaffected by the isomerization reaction (Figure 4B). Formation of the amide is further supported by <sup>1</sup>H NMR spectroscopy of the

**Figure 4.** Mechanism of isomerization from ester to amide in

**zip-P2-1** (A) and FTIR of starting and isomerized polymer (B). material isomerized in solution, which shows a 4:1 ratio of amide to ester (SI Figure S72).

## Conclusions

This work presents a new approach for converting PE into “PE-like” materials through a tandem C-H oxidation/hydroxyalkyl azide-mediated rearrangement sequence. We demonstrate the ability to access backbone iminium ethers, esters, and amides from the same ketone-containing polymer feedstock, thereby enabling synthesis of “PE-like” materials with variable thermal and mechanical properties—*e.g.*, crystallinity, enthalpy of melting, and Young’s modulus. Furthermore, control over esters vs. amides selectivity in the ring-opening of the iminium ether intermediate can be influenced by selection of the hydroxyalkyl azide reagent or *via* subsequent thermal isomerization from ester to amide. Installation of esters and amides is limited by the non-quantitative conversion of ketones to iminium ethers in polymer substrates, which we attribute to the unique challenges with functionalizing multiple positions on a single polymer chain. In addition to accessing both esters and amides, our modular synthesis enables installation of chemical moieties that add new features to a material—*e.g.* introduction of chirality—or offer opportunities for further reactivity or degradation—*e.g.* addition of allyl or propargyl groups for click reactions or hydrolysis of esters or amides. In total, this work demonstrates the viability of polymer backbone editing to insert new functionality or degradable linkages in commodity materials and paves the way for future editing strategies that are targeted at upcycling/recycling/degradation of commodity materials.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Electronic Supplementary Information.

## Acknowledgements

This material is based off work supported by the National Science Foundation under Grant No. CHE-0922858 and CHE-1828183 (NMR Instrument Grants). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. Funding for this work was also provided by the Army Research Office Young Investigator Program (Award No. W911NF-23-1-0265). A.J.K. is supported by the Department of Chemistry at UNC Chapel Hill through the Venable Fellowship. The authors thank the University of North Carolina’s Department of Chemistry NMR Core Laboratory for the use of their NMR spectrometers. The authors also thank the Leibfarth group for use of their Instron, DSC, IR, and high temp GPC instruments, the Dingemans group for use of their melt-press, and the You group for use of their TGA instrument.

## References

- S. Gerassimidou, B. Geueke, K. J. Groh, J. Muncke, J. N. Hahladakis, O. V. Martin and E. Iacovidou, *J. Hazard. Mater.*, 2023, **454**, 131422.
- M. Demirors, in *100+ Years of Plastics. Leo Baekeland and Beyond*, American Chemical Society, 2011, vol. 1080, pp. 115–145.
- S. Billiet and S. R. Trenor, *ACS Macro Lett.*, 2020, **9**, 1376–1390.
- H. Mangold and B. von Vacano, *Macromol. Chem. Phys.*, 2022, **223**, 2100488.
- J. B. Williamson, S. E. Lewis, R. R. Johnson III, I. M. Manning and F. A. Leibfarth, *Angew. Chem., Int. Ed.*, 2019, **58**, 8654–8668.
- E. K. Neidhart, M. Hua, Z. Peng, L. T. Kearney, V. Bhat, F. Vashahi, E. J. Alexanian, S. S. Sheiko, C. Wang, B. A. Helms and F. A. Leibfarth, *J. Am. Chem. Soc.*, 2023, **145**, 27450–27458.
- T. J. Fazekas, J. W. Alty, E. K. Neidhart, A. S. Miller, F. A. Leibfarth and E. J. Alexanian, *Science*, 2022, **375**, 545–550.
- Y. Kondo, D. García-Cuadrado, J. F. Hartwig, N. K. Boen, N. L. Wagner and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2002, **124**, 1164–1165.
- L. Chen, K. G. Malollari, A. Uliana, D. Sanchez, P. B. Messersmith and J. F. Hartwig, *Chem*, 2021, **7**, 137–145.
- J. X. Shi, N. R. Ciccio, S. Pal, D. D. Kim, J. N. Brun, C. Lizandara-Pueyo, M. Ernst, A. M. Haydl, P. B. Messersmith, B. A. Helms and J. F. Hartwig, *J. Am. Chem. Soc.*, 2023, **145**, 21527–21537.
- M. Häußler, M. Eck, D. Rothauer and S. Mecking, *Nature*, 2021, **590**, 423–427.
- H. Mutlu, R. Hofstätter, R. E. Montenegro and M. A. R. Meier, *RSC Adv.*, 2013, **3**, 4927–4934.
- M. Baur, N. K. Mast, J. P. Brahm, R. Habé, T. O. Morgen and S. Mecking, *Angew. Chem., Int. Ed.*, 2023, **62**, e202310990.



- 14 M. Baur, F. Lin, T. O. Morgen, L. Odenwald and S. Mecking, *Science*, 2021, **374**, 604–607.
- 15 S. Tang, F. W. Seidel and K. Nozaki, *Angew. Chem., Int. Ed.*, 2021, **60**, 26506–26510.
- 16 R. A. J. Ditzler, A. J. King, S. E. Towell, M. Ratushnyy and A. V. Zhukhovitskiy, *Nat. Rev. Chem.*, 2023, **7**, 600–615.
- 17 R. H. Michel and W. A. Murphey, *J. Polym. Sci.*, 1961, **55**, 741–751.
- 18 Y. Lu, K. Takahashi, J. Zhou, R. Nontarin, S. Nakagawa, N. Yoshie and K. Nozaki, *Angew. Chem., Int. Ed.*, 2024, **63**, e202410849.
- 19 N. Kosaka, T. Hiyama and K. Nozaki, *Macromolecules*, 2004, **37**, 4484–4487.
- 20 V. Gracias, G. L. Milligan and J. Aube, *J. Am. Chem. Soc.*, 1995, **117**, 8047–8048.
- 21 V. Gracias, G. L. Milligan and J. Aubé, *J. Org. Chem.*, 1996, **61**, 10–11.
- 22 V. Gracias, K. E. Frank, G. L. Milligan and J. Aubé, *Tetrahedron*, 1997, **53**, 16241–16252.
- 23 J. E. Forsee, B. T. Smith, K. E. Frank and J. Aubé, *Synlett*, 1998, **1998**, 1258–1260.
- 24 J. E. Forsee and J. Aubé, *J. Org. Chem.*, 1999, **64**, 4381–4385.
- 25 E. Fenster, B. T. Smith, V. Gracias, G. L. Milligan and J. Aubé, *J. Org. Chem.*, 2008, **73**, 201–205.
- 26 G. L. Milligan, C. J. Mossman and J. Aube, *J. Am. Chem. Soc.*, 1995, **117**, 10449–10459.
- 27 R. A. Abramovitch and E. P. Kyba, in *The Chemistry of the Azido Group*, John Wiley & Sons, Ltd, 1971, pp. 221–329.
- 28 H. F. Motiwala, M. Charaschanya, V. W. Day and J. Aubé, *J. Org. Chem.*, 2016, **81**, 1593–1609.
- 29 J. J. Weeks, *J. Res. Natl. Bur. Stand. A Phys. Chem.*, 1963, **67A**, 441.

The data supporting this article have been included as part of the Electronic Supplementary Information.