

Selective, Catalytic Oxidation of Polyethylene Surfaces

Corresponding Author: Professor John Hartwig

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

In this interesting paper, Hartwig and co-workers describe how selective, catalytic oxidation of polyethylene (PE) at a solid-liquid interface can yield materials with advantaged properties compared to virgin PE and PE oxidized in a homogenous solution. The PE film oxidation was performed by submerging it in a solution containing the iron-based catalyst $[\text{Fe}(\text{tBu}_4\text{Pc})]_2\text{N}$ and tert-butyl hydroperoxide oxidant at 65 °C for 24 h, resulting in selective PE surface functionalization with ~ 0.3 mol% ketone. A critical improvement in this work upon previous work is the selective amorphous functionalization of PE, which allows for maintenance of the crystalline domains thus maintaining a high Young's modulus and melting temperature in the ketone-functionalized PE. These samples were investigated via FTIR, uniaxial tensile testing, ^1H -NMR, DSC, and lap shear testing. Although surface functionalization of polyolefins including PE is common in literature, the current method and its reported results seem to solve the selectivity issues in PE surface functionalization. Below are suggested revision experiments and questions for the authors to consider.

- An important question is whether the PE selectively functionalized within its amorphous domain can maintain its melting temperature, degree of crystallinity, mechanical performance, and adhesion strength upon reprocessing (i.e., melt and reshape the oxidized films). To address this question, it requires multiple cycles of melt-reprocessing of the functionalized polymers. While there are DSC scans, thermomechanical reprocessing is likely to impart greater perturbation of PE crystallization, which can break up some shape or melt memory characteristics of PE. Two or more reprocessing experiments should be performed for a functionalized polymer, and DSC and/or SAXS/WAXS should be used to track these changes in crystallization. These findings would also give better insight into the practicality of their approach. That is, can oxidized material be pelletized and sold to converters to be shaped into a product? Can virgin pellets be oxidized and sold to converters? Or is it required that the product be preformed and then oxidized in order for this method to be used effectively? If the adhesion and tensile properties both diminish upon reprocessing, this would have implications for the recyclability of these materials.
- SAXS/WAXS is a very critical analytical technique for such a paper focused on amorphous functionalization of PEs. Thorough analysis of the functionalized samples with SAXS/WAXS and even PLOM would give critical insights into the crystallization of the various functionalized PE materials of this work and help the reader visualize changes in solution functionalized and film functionalized PEs.
- It would also be useful if the authors thermally fractionate the samples (i.e., pristine, solution, film, Figure 3C) via successive self-nucleation and annealing (SSA). This differential scanning calorimetry method is widely used to characterize PE and may give better insight into how the methylene sequence length distribution differs between localized (film-oxidized) versus homogenous (solution-oxidized) ketone incorporation, which can add value to the discussion.
- Although the catalyst loading is low, the amount of the oxidant used is rather high, i.e., 0.3 equiv. per PE repeating unit. Have the authors tried lower loadings of the oxidant to reduce waste. Is there any entrapment of the residual catalyst and the oxidant by the resulting products in the PE polymer matrix?
- As it seems, film thickness significantly impacts the mol% of ketone in the resulting polymer. A better control of pristine samples should be conducted on the basis of thickness thus exactly matching between film thicknesses of the same types of PEs. There is only one matched example in LDPE 30 μm . Thicknesses should be matched for HDPE and LLDPE.
- The statement "we did not observe a large difference between the efficiency of the oxidation of several common post-consumer PE items and the oxidation of pristine PE" is a blanket statement that can't be made given the presented data. A 0.1% mol difference between pristine and post-consumer LDPE is present at 30 μm . In this context, it amounts to a 25%

difference in efficiency, which is large.

- Heat of fusion values should be reported in the main text figures and within the main text. There is significance in showing those particular values to a reader in the main text. These are a greater indicator of changes in crystallinity as T_m typically does not change drastically unless significant changes in crystalline domains are made.
- There appears to be a significant variability in functionalized polymer films with respect to tensile properties, especially yield strength, can the authors comment on this? Is this purely a result of inhomogeneous ketone functionalization or some changes to the crystalline domains and crystallite packing?
- Figure 1A: The model oxidation studies of octadecane detailed in the SI show that alcohol and ketone functional groups are generated. Yet, the cartoon schematic describes the approach as being "monofunctional". Are the authors trying to suggest that only one type of functional group forms with their approach? This seems to disagree with the model studies.
- Line 70: Do the authors observe any evidence of hydroxy group formation? In their model studies (Table S1), they observe alcohol formation upwards of 25 mol%. If this does not occur for the polymer oxidation, why not?
- Line 91: The phrase "commercial plastics contain additives that are absent in pristine pellets" implies that pristine pellets do not contain additives. If this is what the authors indeed meant to imply, then this is incorrect. PE resin manufacturers regularly add additives such as antioxidants, UV stabilizers, processing aids, slip agents, and anti-blocking agents into the pellets they sell to converters (i.e., those that use pellets to shape a product). Sometimes, converters will choose to mix additional additives into their products. How do the authors know the additive packages used in the pellets they studied and the products they sampled are different? If they do not, then how is this comparison valuable?
- Line 114: If oxidation is localized to the surface, would the change in molar mass scale inversely with the sample thickness, assuming the mol% of ketone formation were held constant?
- Line 150: The authors should comment on observations related to adhesive and cohesive failure to help support this hypothesis. The failure modes are described in the SI, why not discuss them here?

Referee #2

(Remarks to the Author)

The manuscript by Woroch and co-workers, entitled "Selective, Catalytic Oxidation of Polyethylene Surfaces", represents an interesting and practically relevant study for the valorization of poorly adhesive PE commodity plastics and their post-consumable wastes. Considering the widespread presence of PE in post-consumable plastics and its enormous annual production volume yet relatively low recycling rate, this study attracts broad interests from readers in both chemistry and materials science. Notably, such interfacial modification can be performed with an extremely low catalyst loading of 10 ppm of porphyrin-chelated iron catalyst, under mild thermal conditions. There is one concern that a very similar paper was published a few weeks ago, but these data shows very systematic studies and most importantly, outperforms the previous one. Therefore, this reviewer believes that after several revisions, this should have enough conceptual novelty and broad interests for publication in Nature.

Main points

- 1) Authors need to do better job in citing other's work. A similar concept of the paper was just published a month ago using porphyrin-chelated vanadium catalysts (J. Am. Chem. Soc. 2026, 148, 22726–22738), so it is worthwhile to compare the work as well. Also, a related PE grafting method was published three months ago (J. Am. Chem. Soc. 2026, 148, 14, 14924–14933), again worth mentioning where PE-polar-graft is introduced.
- 2) In the recent J. Am. Chem. Soc. 2026, 148, 22726, comparable ketone ratios were attained in a single reaction cycle, albeit with a higher catalyst loading (0.03 mol%). As a comparison, the author's method requires 5 reaction cycles to reach a ketone incorporation ratio of 1.1 mol% while employing a much lower catalyst loading. In this regard, the reviewer is curious whether the ketone incorporation ratios could be further improved within a single reaction cycle by using a higher catalyst loading to enhance the overall reaction efficiency.
- 3) Page 7, line 118, "a lower melting temperature (T_m) or broader ... smaller or more imperfect crystallites". The reviewer agrees with this interpretation, and noted that relevant reference has been cited in support of this conclusion. Nevertheless, additional characterization, such as AFM analysis, may be helpful to further substantiate this claim. Such measurements could clarify whether the reduced T_m originates primarily from the formation of imperfect crystallites or alternatively increased surface roughness following oxidation, or a combination of both.
- 4) Page 8, line 139 to 142, "The lap-shear strength values... 5.9 MPa for LDPE and 6.9 MPa for HDPE". Could the author provide additional insight into why the interfacial oxidation with comparable ketone concentration resulted in much better mechanical properties and adhesion of LDPE and HDPE, compared to homogenous oxidations where are expected to have better ketone incorporation ratios. It is not clear yet. Would XRD give any other information?
- 5) For lap shear test, many metals such as Al and steel are used, but only glass is used here. Please test it on other surface to demonstrate the generality
- 6) Fig. 4E, purple bar of 4d. Incorporation of polar functional groups, such as ketones, is generally expected to enhance the wettability and thus reduce the WCA. However, functionalized HDPE 4d exhibited a higher WCA value compared to its pristine HDPE, any further clarification to this seemingly counter-intuitive observation?
- 7) Why is soxhlet extraction needed for the purification of solution process? What happens if one skips it, in terms of chemical structures, defects, and even adhesion? What are being removed by this process?

Minor point

- 1) In Fig. 2E, unit (cycles) could be added under "Oxidation Treatments" to improve clarity.

Reviewer comments:

Referee #1

(Remarks to the Author)

The responses from the authors are exemplary, thorough, and well written, which sufficiently addressed this reviewer's concerns and comments raised on the previous version. In the opinion of this reviewer, the currently revised version is ready for acceptance for publication in Nature.

The authors ought to be congratulated for this impressive accomplishment. Although the general idea of the selective functionalization of ideally only the amorphous region of PE was discussed at a conference about three years ago, the authors realized the idea and actually accomplished the feat. Congratulations!

Referee #2

(Remarks to the Author)

The revision looks great.

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Referee #1 (Remarks to the Author):

In this interesting paper, Hartwig and co-workers describe how selective, catalytic oxidation of polyethylene (PE) at a solid-liquid interface can yield materials with advantaged properties compared to virgin PE and PE oxidized in a homogenous solution. The PE film oxidation was performed by submerging it in a solution containing the iron-based catalyst [Fe(tBu4Pc)]₂N and tert-butyl hydroperoxide oxidant at 65 °C for 24 h, resulting in selective PE surface functionalization with ~ 0.3 mol% ketone. A critical improvement in this work upon previous work is the selective amorphous functionalization of PE, which allows for maintenance of the crystalline domains thus maintaining a high Young's modulus and melting temperature in the ketone-functionalized PE. These samples were investigated via FTIR, uniaxial tensile testing, ¹H-NMR, DSC, and lap shear testing. Although surface functionalization of polyolefins including PE is common in literature, the current method and its reported results seem to solve the selectivity issues in PE surface functionalization. Below are suggested revision experiments and questions for the authors to consider.

- An important question is whether the PE selectively functionalized within its amorphous domain can maintain its melting temperature, degree of crystallinity, mechanical performance, and adhesion strength upon reprocessing (i.e., melt and reshape the oxidized films). To address this question, it requires multiple cycles of melt-reprocessing of the functionalized polymers. While there are DSC scans, thermomechanical reprocessing is likely to impart greater perturbation of PE crystallization, which can break up some shape or melt memory characteristics of PE. Two or more reprocessing experiments should be performed for a functionalized polymer, and DSC and/or SAXS/WAXS should be used to track these changes in crystallization. These findings would also give better insight into the practicality of their approach. That is, can oxidized material be pelletized and sold to converters to be shaped into a product? Can virgin pellets be oxidized and sold to converters? Or is it required that the product be preformed and then oxidized in order for this method to be used effectively? If the adhesion and tensile properties both diminish upon reprocessing, this would have implications for the recyclability of these materials.

We appreciate the reviewer's suggestion and share their curiosity about how reprocessing might affect the thermomechanical properties of these materials. To address the reviewer's comment, we reprocessed PE that had been oxidized at the solid-liquid interface. Dogbones of this oxidized PE were melted and pressed between PTFE sheets to form new films. The reprocessed films were cut into dogbone geometries and subjected to thermal and mechanical measurements. Following this analysis of the reprocessed films, the materials were melted and pressed between PTFE sheets a second time. These twice-reprocessed films were cut into dogbone geometries and subjected to an additional round of thermal and mechanical measurements. We specifically investigated differences in elongation at break (ϵ_b), Young's modulus (E), lap shear strength (τ) to glass, melting temperature (T_m), and crystallinity (X_c). The results of these experiments are detailed in full in the supplementary discussion.

To summarize our findings, we did not observe statistically significant differences between the α_b , E , T_m , or X_c values of either LDPE or HDPE oxidized at the solid–liquid interface before or after two reprocessing cycles. We did, however, observe a statistically significant difference in the τ value of oxidized LDPE films before and after two reprocessing cycles. Before reprocessing, the τ value of LDPE that had been oxidized at the solid–liquid interface was 5.9 MPa. After two rounds of reprocessing, the τ value of this material was 3.2 MPa, which is closer to the 3.9 MPa τ value of LDPE oxidized in solution. We were surprised to find that a similar effect of reprocessing was not observed for oxidized HDPE. Instead, the τ value of HDPE that had been oxidized at the solid–liquid interface was 6.9 MPa and the τ value of twice-reprocessed HDPE that had been oxidized at the solid–liquid interface was 9.4 MPa. This value is greater but not statistically distinguishable from the sample before reprocessing. Previous studies of plasma-treated LDPE and HDPE showed that HDPE aged more slowly than LDPE.¹ We hypothesize that the greater chain mobility of LDPE than of HDPE allows polar functional groups to migrate from the surface more readily during reprocessing. In addition, we observed a slight increase in the crystallinity of HDPE after oxidation; we hypothesize that this increase results from annealing that occurs during the reaction conditions. Future work will study in more detail how polymer architecture affects the reprocessability of surface-functionalized polymers.

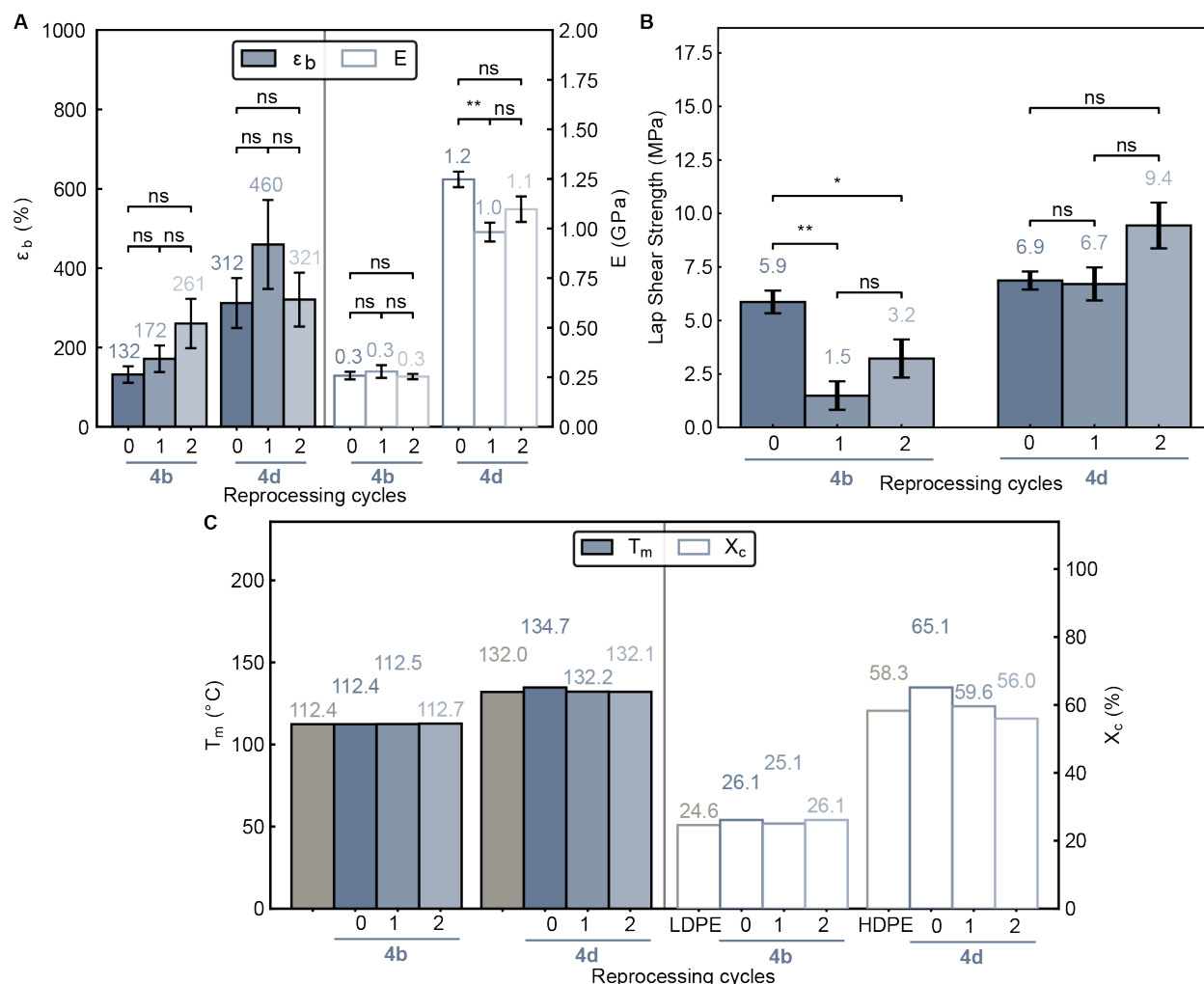


Fig. S11 | Thermomechanical properties of PE oxidized at the solid–liquid interface after reprocessing. **A)** Average elongation at break and Young’s modulus obtained from tensile tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2). **B)** Average glass lap-shear adhesion strengths obtained from glass lap-shear tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2). **C)** Melting temperature and crystallinity obtained from a first cycle of DSC (5 °C/min) of pristine PE and film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2).

The following section has been added to the supplemental discussion:

- 2.7. Reprocessing PE oxidized at the solid–liquid interface

The following figures have been added to the supplementary information:

- Fig. S8 | Thermomechanical properties of PE oxidized at the solid–liquid interface after reprocessing. **A)** Average elongation at break and Young’s modulus obtained from tensile tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1),

and after two reprocessing cycles (2). B) Average glass lap-shear adhesion strengths obtained from glass lap-shear tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2). C) Melting temperature and crystallinity obtained from a first cycle of DSC (5 °C/min) of pristine PE and film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2).

- Fig. S12 | Tensile data for reprocessed film-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).
- Fig. S13 | Tensile data for twice reprocessed film-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).
- Fig. S14 | Tensile data for reprocessed film-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).
- Fig. S15 | Tensile data for twice reprocessed film-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).
- Fig. S16 | Glass lap-shear adhesion data for reprocessed film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- Fig. S17 | Glass lap-shear adhesion data for twice reprocessed film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- Fig. S18 | Glass lap-shear adhesion data for reprocessed film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- Fig. S19 | Glass lap-shear adhesion data for twice reprocessed film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- Fig. S20 | Differential scanning calorimetry of reprocessed film-oxidized LDPE (0.3 mol%).
- Fig. S21 | Differential scanning calorimetry of twice-reprocessed film-oxidized LDPE (0.3 mol%).
- Fig. S22 | Differential scanning calorimetry of reprocessed film-oxidized HDPE (0.3 mol%).
- Fig. S23 | Differential scanning calorimetry of twice-reprocessed film-oxidized HDPE (0.3 mol%).

- SAXS/WAXS is a very critical analytical technique for such a paper focused on amorphous functionalization of PEs. Thorough analysis of the functionalized samples with SAXS/WAXS and even PLOM would give critical insights into the crystallization of the various functionalized PE materials of this work and help the reader visualize changes in solution functionalized and film functionalized PEs.

We thank the reviewer for this valuable suggestion. To address this suggestion, we have worked with researchers at the Advanced Light Source and at Argonne National Laboratory to perform

and assist in the interpretation of the recommended wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) measurements. We have added a new section to the supplemental discussion detailing our findings.

To summarize the most prominent results, the general trends in crystallinity by WAXS match our findings by DSC. The WAXS spectrum of pristine PE contains two strong peaks for the (110) and (200) reflections. We do not observe a difference in the scattering vectors of those reflections for any of our oxidized samples, indicating that functionalization does not introduce a new crystalline phase. The crystallinity (X_c) of LDPE oxidized in solution was smaller (41.8%) than that of LDPE oxidized at the solid–liquid interface (42.1%). Similarly, we observe that the X_c value of HDPE oxidized in solution was 56.1% and that of HDPE oxidized as a film was 60.6%. Although the magnitude of the crystallinity from WAXS differed from what was observed by DSC, both measurements indicated that that PE oxidized as a film was more crystalline than PE oxidized in solution. The mesoscale morphology of pristine and oxidized PE assessed by SAXS yielded insights into how processing after functionalization impacts long-range order. We observed that the lamellar periodicity (L) values of PE oxidized in solution were smaller than those of PE oxidized as a film. Using the X_c values obtained from WAXS, we determined the contributions to L that were attributable to the average amorphous domain size (L_a) and the average crystalline lamellar size (L_c). We observed that the measurements of L_a and L_c for LDPE and HDPE samples oxidized in solution were lower than those of samples oxidized as films. For HDPE, the difference in L_c was particularly pronounced and constituted most of the overall change in the observed L .

The WAXS and SAXS data described here are consistent with our previous findings by DSC and hypotheses about the impact of oxidation of the film surface on polymer microstructure. We observed that the crystallinity and long-range order of PE oxidized in solution is lower than those of PE oxidized as a film. Future work will investigate impacts of surface and bulk functionalization on mesoscale morphology with more advanced spectroscopic and microscopic techniques.

The following authors have been added to the manuscript who contributed to collecting and interpreting the WAXS/SAXS measurements:

- Zachary P. Fink
- Xiaobing Zuo
- Cheng Wang

The following section has been added to the Supplemental Methods:

- 1.4. Small angle X-ray scattering (SAXS) and wide-angle X-ray scatter (WAXS) measurements and analysis.

The following section has been added to the Supplemental Discussion:

- 2.8. Analyzing crystalline microstructure of PE samples by WAXS and SAXS.

The following text has been added to the Acknowledgements section:

- This SAXS/WAXS research was performed at 12-ID-B on APS beam time award (DOI: <https://doi.org/10.46936/APS-195158/60017690>) from the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility at Argonne National Laboratory, and is based on research supported by the U.S. DOE Office of Science-Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

The following text in the Author contributions has been updated:

- **Original:** Conceptualization and methodology were performed by C.P.W., J.F.H., and B.A.H. Investigative synthesis and material analysis was performed by C.P.W. with assistance from D.P.M (XPS), L.K. (XPS), C.G. G. (DSC, TGA), and H.M. (FTIR).
- **Updated:** Conceptualization and methodology were performed by C.P.W., J.F.H., and B.A.H. Investigative synthesis and material analysis was performed by C.P.W. with assistance from D.P.M (XPS), L.K. (XPS), C.G. G. (DSC, TGA), H.M. (FTIR, adhesion, tensile), Z.F. (WAXS/SAXS), and X.Z. (WAXS/SAXS),

- It would also be useful if the authors thermally fractionate the samples (i.e., pristine, solution, film, Figure 3C) via successive self-nucleation and annealing (SSA). This differential scanning calorimetry method is widely used to characterize PE and may give better insight into how the methylene sequence length distribution differs between localized (film-oxidized) versus homogenous (solution-oxidized) ketone incorporation, which can add value to the discussion.

We thank the reviewer for this valuable suggestion. We have performed SSA experiments as recommended and have added a new section to the supplemental discussion detailing our findings.

To summarize, we fractionated pristine LDPE, LDPE functionalized in solution, and LDPE functionalized as a film by a DSC SSA experiment. We subsequently analyzed the final heating ramp to gain insight into the crystallite distribution in each sample. Each measurement was performed in triplicate using three separate sections of each sample. The distribution of melting enthalpies for pristine LDPE was similar to that for LDPE functionalized as a film; however, the normalized enthalpy of the endotherm at the highest melting temperature was lower for LDPE functionalized in solution than it was for either pristine LDPE or LDPE functionalized as a film. This result indicates that LDPE functionalized in solution contains fewer large crystallites than LDPE functionalized as a film.

The melting temperatures and melting enthalpies were further used to calculate the average lamellar thickness (L_c) and ethylene sequence length (n_{avg}). The L_c of 6.2 nm for LDPE oxidized as a film was equal to the L_c of 6.2 nm for pristine LDPE and greater than the L_c of 6.1 nm for LDPE oxidized in solution. Similarly, the n_{avg} of 41.9 for LDPE oxidized as a film was nearly

equal to the n_{avg} of 42.3 for pristine LDPE and greater than the n_{avg} of 41.0 for LDPE oxidized in solution. Together, these results further support our hypothesis that the functionalization of PE at the solid–liquid interface minimally affects the bulk crystalline microstructure, whereas functionalization of PE in solution leads to a decrease in crystallinity and average crystallite size, even at low degrees of functionalization.

The following section has been added to the supplemental discussion:

- 2.5. Analyzing by self-nucleation the impacts of functionalization on microstructure.

The following figures and tables have been added to the supplementary information:

- Fig. S5 | Self-nucleation DSC experiments on pristine PE. A) Example of the temperature program for self-nucleation of LDPE (ramp rate = 10 °C/min). B) The second cooling ramp for self-nucleation experiments of pristine LDPE at different T_s , showing the crystallization exotherm. C) The third heating ramp of pristine LDPE self-nucleation experiments at different T_s showing the melting endotherm D) Example of the self-nucleation temperature program for HDPE (ramp rate = 10 °C/min). E) The second cooling ramp of pristine HDPE self-nucleation experiments at different T_s showing the crystallization exotherm. F) The third heating ramp for self-nucleation experiments of pristine HDPE at different T_s , showing the melting endotherm.
- Fig. S6 | Self-seeding nucleation and annealing. A) The SSA temperature program for LDPE (ramp rate = 10 °C/min). B) The final heating ramp in an SSA measurement with pristine LDPE, LDPE oxidized in solution (4a) and LDPE oxidized as a film (4b). C) The SSA temperature program for HDPE (ramp rate = 10 °C/min). D) The final heating ramp in a SSA measurement for pristine HDPE, HDPE oxidized in solution (4c) and HDPE oxidized as a film (4d).
- Fig. S7 | Thermal fractionation by SSA of three samples from pristine LDPE.
- Fig. S8 | Thermal fractionation by SSA of three samples from LDPE oxidized in solution (4a).
- Fig. S9 | Thermal fractionation by SSA of three samples from LDPE oxidized as a film (4b).
- Fig S10 | Average lamellar thickness and ethylene sequence length of pristine LDPE, LDPE oxidized in solution (4a), and LDPE oxidized as a film (4b) from measurements performed in triplicate.
- Table S8. Enthalpy of melting from final heating ramp of SSA experiments of LDPE and oxidized LDPE.

- Although the catalyst loading is low, the amount of the oxidant used is rather high, i.e., 0.3 equiv. per PE repeating unit. Have the authors tried lower loadings of the oxidant to reduce

waste. Is there any entrapment of the residual catalyst and the oxidant by the resulting products in the PE polymer matrix?

We thank the reviewer for their comment and have conducted reactions with different amounts of oxidant. We have added these data to the supplementary information. For reactions with the lower amounts of 0.1 and 0.2 equivalents of *t*BuOOH, we observed total degrees of oxidation of 0.22 mol% and 0.26 mol%, respectively. Therefore, the total amount of oxidation does decrease with decreasing amount of oxidant, but it does not do so linearly. Surprisingly, increasing the oxidant loading did not increase the level of oxidation: an oxidant loading of 0.5 equivalents resulted in 0.22 mol% ketone groups with respect to ethylene units and an oxidant loading of 1.0 equivalents resulted in 0.17% ketone groups. We hypothesize that the decrease in total oxidation results from a reduced concentration of the catalyst. The oxidant solution is dispensed from a saturated solution of *t*BuOOH in *t*BuPh. As more oxidant is added, the concentration of the catalyst in the bulk solution decreases. We propose that the oxidation requires the catalyst and oxidant to be in proximity to the polymer surface for the generated radical to react with a C–H bond on the film before decomposing by another pathway. Therefore, the addition of more oxidant solution does not necessarily result in more oxidation at the surface.

Entry	x (mol%)	y (equiv.)	Ketone (mol%)
1	0.001%	0.1	0.22%
2	0.001%	0.2	0.26%
3	0.001%	0.3	0.32%
4	0.001%	0.5	0.22%
5	0.001%	1	0.17%
6	0.002%	0.3	0.30%
7	0.010%	0.3	0.20%

We also thank the reviewer for inquiring about the residual catalyst or oxidant entrapped on the polymer surface. Residual oxidant or organic byproducts were not detected on films by ¹H NMR spectroscopy after the films were oxidized and washed by methanol Soxhlet extraction (Figure 2a). To investigate whether Fe remained on the surface, we performed X-ray photoelectron spectroscopy (XPS), focusing on the Fe 2p region. Pristine LDPE and LDPE were examined under a series of conditions, including our standard conditions for oxidation of the surface of LDPE (0.001 mol% **1**, 0.3 equiv *t*BuOOH, *t*BuPh, 65 °C, 24 h) oxidation without catalyst or oxidant (*t*BuPh, 65 °C, 24 h), without oxidant (0.001 mol% **1**, *t*BuPh, 65 °C, 24 h), and without

catalyst (0.3 equiv *t*BuOOH, *t*BuPh, 65 °C, 24 h). After these treatments, the films were washed by methanol Soxhlet extraction and dried in vacuo. Upon analysis with XPS, no Fe 2p peaks were observed for any of the samples examined. Therefore, we conclude that Fe is no longer present at the surface.

The following figures and tables have been added to the supplementary information:

- **Figure S89.** X-ray photoelectron spectroscopy (Fe 2p region) LDPE in pristine form and LDPE after reactions conducted under a series of conditions, including conditions without catalyst or oxidant (*t*BuPh, 65 °C, 24 h), without oxidant (0.001 mol% **1**, *t*BuPh, 65 °C, 24 h), without catalyst (0.3 equiv *t*BuOOH, *t*BuPh, 65 °C, 24 h), or under standard conditions for oxidation that form oxo-LDPE (0.001 mol% **1**, 0.3 equiv *t*BuOOH, *t*BuPh, 65 °C, 24 h).
- **Table S16.** Oxidation of LDPE with *t*BuOOH and **1** with varying catalyst and oxidant loadings.

- As it seems, film thickness significantly impacts the mol% of ketone in the resulting polymer. A better control of pristine samples should be conducted on the basis of thickness thus exactly matching between film thicknesses of the same types of PEs. There is only one matched example in LDPE 30 μm. Thicknesses should be matched for HDPE and LLDPE.

We appreciate the reviewer's attention to this issue and have extended our substrate scope to include samples of LDPE, HDPE, and LLDPE with thicknesses of 50-μm, 100-μm, and 200-μm. We observed an inverse relationship between film thickness and extent of oxidation for all samples, but the inverse relationship was more pronounced for more crystalline PE architectures, such as HDPE, than for less crystalline architectures, such as LLDPE.

We have updated Figure 2F to include results with the new samples.

In addition, we have updated the following lines in the main text:

- **Original:** Oxidation of LDPE films with thicknesses of 30-μm, 100-μm, and 200-μm revealed an inverse correlation between film thickness and extent of oxidation. The comparable extents of oxidation for films of LDPE, HDPE, and LLDPE imply that differences in bulk crystallinity do not significantly impact the extent of surface oxidation.
- **Updated:** Oxidation of LDPE, HDPE, and LLDPE films with thicknesses of 50-μm, 100-μm, and 200-μm, each, revealed an inverse correlation between film thickness and extent of oxidation.

- The statement “we did not observe a large difference between the efficiency of the oxidation of several common post-consumer PE items and the oxidation of pristine PE” is a blanket statement that can't be made given the presented data. A 0.1% mol difference between pristine and post-

consumer LDPE is present at 30 μm . In this context, it amounts to a 25% difference in efficiency, which is large.

We agree with the reviewer's assertion that our statement is too broad. Thus, have revised the language to reflect that post-consumer substrates undergo oxidation at the surface by our method without any modification to the procedure.

We have updated the following lines in the main text:

- **Original:** Commercial plastics contain additives that are absent in pristine pellets and that could interfere with chemical functionalization.²⁻⁴ However, we did not observe a large difference between the efficiency of the oxidation of several common post-consumer PE items and the oxidation of pristine PE (**Fig. 2G**).
- **Updated:** Oxidation also occurs on post-consumer PE samples without pretreatment (**Fig. 2I**).

- Heat of fusion values should be reported in the main text figures and within the main text.

There is significance in showing those particular values to a reader in the main text. These are a greater indicator of changes in crystallinity as T_m typically does not change drastically unless significant changes in crystalline domains are made.

We thank the reviewer for this suggestion and have implemented the recommended change. The heats of fusion have now been added to Figure 3C and have been referenced in the text. In a typical DSC measurement, we analyze 5.0 mg of polymer sample on a balance with mass accuracy of ± 0.1 mg. Thus, with a mass uncertainty of 2%, the melt enthalpies in the first melting endotherm of 166.5 J/g for **4c** are outside of the uncertainty of the melt enthalpy of HDPE (170.7 ± 3.4 J/g). Similarly, the melt enthalpy of **4d** is 195 J/g, and this value is larger than and outside the uncertainty of the melt enthalpy of pristine HDPE. We hypothesize that the HDPE crystallites anneal slightly during the 24 h at 65 $^{\circ}\text{C}$ time and temperature of the oxidation reaction. In addition, the melt enthalpy of **4a** (66.7 J/g) is lower than that of **4b** (76.5 J/g) and of LDPE (72.1 J/g) by a margin that cannot be explained by mass uncertainty. We initially focused on the small change in T_m because it is more easily visualized and is independent of the accuracy of the balance.

In addition, we note that we reproduced the synthesis and DSC analysis of pristine LDPE, LDPE oxidized in solution with 0.3 mol% ketones, LDPE oxidized as a film with 0.3 mol% ketones, pristine HDPE, HDPE oxidized in solution with 0.3 mol% ketones, and HDPE oxidized as a film with 0.3 mol% ketones to address other reviewer comments. In the year since our first measurements, we have recalibrated our DSC, and we consumed the batch of LDPE and HDPE pellets we used for the first experiments and purchased a new batch of these materials from the same vendor. We observed slight differences in the temperature and enthalpy of melting between the original and new batches of LDPE and HDPE we purchased. Therefore, we reproduced all the thermal measurements with the new starting materials. The updated values in Figure 3C and in the supplementary information were obtained with materials from this new batch of polymers.

We have updated the following line in the main text:

- **Original:** A lower melting temperature (T_m) or broader melting endotherm of the functionalized material than of the pristine material would indicate that the functionalization created smaller or more imperfect crystallites.⁵ Indeed, the T_m of both LDPE and HDPE samples functionalized in solution were lower and the melting endotherms were broader than those of the pristine LDPE and HDPE (**Fig. 3C**). In contrast, the T_m and melting endotherm of the PE functionalized at the solid–liquid interface were nearly identical to those of the pristine materials.
- **Updated:** A lower melting temperature (T_m) or enthalpy of melting (H_{fus}) of the functionalized material than of the pristine material would indicate that the functionalization created smaller or more imperfect crystallites.⁴⁶ Indeed, the T_m and H_{fus} values of both LDPE and HDPE samples functionalized in solution were slightly lower than those of the pristine LDPE and HDPE (**Fig. 3C**). In contrast, the T_m and H_{fus} values of the PE functionalized at the solid–liquid interface were identical or greater than those of the pristine materials.

- There appears to be a significant variability in functionalized polymer films with respect to tensile properties, especially yield strength, can the authors comment on this? Is this purely a result of inhomogeneous ketone functionalization or some changes to the crystalline domains and crystallite packing?

We appreciate the reviewer’s comment and share the concern about the variability in the tensile data. We did not observe large differences in the crystallinity of pristine PE, PE oxidized in solution, and PE oxidized as a film when calculated using the enthalpy of melting measured by DSC. We propose multiple potential sources of variability but cannot conclusively determine which is the major contributor to variability in these measurements.

We prepare films using a Carver benchtop lab press with heated plates. Oxidized or reprecipitated-pristine PE is compressed between PTFE sheets encased by stainless steel plates at 15 °C above the polymer melting point and a pressure of ~2000 psi for a duration of 10 minutes. To control the thickness of the resulting films, the polymer is encased in rectangular molds made from PTFE paper of the desired thickness. The resulting film is measured with calipers in at least 5 regions to ensure the average thickness matches the desired thickness. Although we observed good agreement between the thickness of the mold and the average thickness of the film, we observed regions of the film that differed by ± 10 -20 μm from the desired thickness. In previous studies from our laboratory in which 250 μm -thick PE films were tested,⁶ we observed less variability in tensile properties. In this work, we investigated thinner films to allow us to characterize more easily the functional groups introduced at the surface. Therefore, we hypothesize that some of the observed variability in the tensile samples cut from 100 μm -thick PE films can be explained by slight deviations in thickness across the film.

Another complementary explanation involves the formation of defects in tensile films from remaining solvent. Oxidized PE is prepared by reaction of the polymer with **1** and *t*-BuOOH in *t*-BuPh. The *t*-BuPh solvent is nonpolar, and its boiling point is 169 °C at atmospheric pressure. We observe that *t*-BuPh swells PE at 65 °C. After the reaction, oxidized PE is precipitated in methanol if oxidized in solution or washed with methanol if oxidized on the solid–liquid interface. The resulting films are subsequently dried in vacuo at 80 °C. The PE that was oxidized in solution is then pressed into a film at 125 °C or 150 °C for LDPE or HDPE, respectively. At no point in the process is the sample heated near the boiling point of *t*-BuPh because such a temperature would damage the polymer. Although we did not detect solvent by ¹H NMR spectroscopy, trace quantities of remaining solvent could lead to defects that might cause variability in the measurements of mechanical properties.

Future work will investigate strategies to decrease the variability of tensile measurements on polymers functionalized at the solid–liquid interface. To highlight the variability in the film thickness, however, we have added additional detail to the methods section.

- **Original:** Dogbones for mechanical testing were cut from polymer films using a Print-a-Punch 3D printed dogbone die.
- **Updated:** Dogbones for mechanical testing were cut from polymer films with an average thickness of 100 μm but local variations in thickness of 10-20 μm using a Print-a-Punch 3D printed dogbone die.

- Figure 1A: The model oxidation studies of octadecane detailed in the SI show that alcohol and ketone functional groups are generated. Yet, the cartoon schematic describes the approach as being “monofunctional”. Are the authors trying to suggest that only one type of functional group forms with their approach? This seems to disagree with the model studies.

We thank the reviewer for their comment and apologize for any confusion. While we observe the formation of alcohol during the model studies on light alkanes, we do not observe any formation of alcohol from our polymeric substrates. We address this comment more fully in the next response.

- Line 70: Do the authors observe any evidence of hydroxy group formation? In their model studies (Table S1), they observe alcohol formation upwards of 25 mol%. If this does not occur for the polymer oxidation, why not?

We share the reviewer’s curiosity about the mechanistic origin for the difference in selectivity. To address their question, we have added an additional section to the Supplemental Discussion reporting additional experiments we have performed and our current mechanistic hypothesis.

Model studies on the oxidation of octadecane with **1** suggest that a substantial quantity of alcohols form, even though ketones are the major product (**Table S1**). Free-radical oxidation of alkanes typically produces both alcohols and ketones. However, the oxidation of PE with **1** under the conditions reported here does not produce observable quantities of alcohol (**Fig. 1A-C**). To

investigate the difference between the oxidation of light alkanes and the PE studied here, we oxidized alkanes and polyethylene of varying molar mass by our method. We determined the quantities of hydroxyl and oxo groups by ^1H NMR spectroscopy (**Table S7**). Small quantities of hydroxyl groups were observed for all substrates except the LDPE film. The selectivity for the ketone product correlated with the molar mass of the substrate.

We hypothesize that selectivity under the reaction conditions is dictated by diffusion. In a free-radical oxidation mechanism, ketones are formed by oxidation of the alcohol. Because the bond dissociation energy of a C–H bond α to an alcohol is lower than that of a C–H bond in an alkane, the oxidation of an alcohol to a ketone by a mechanism involving hydrogen-atom abstraction is typically faster than the oxidation of an alkane to an alcohol by a similar mechanism. Under the reaction conditions, light alkanes diffuse more rapidly than polymer chains. When alcohols form from light alkanes, they diffuse from the catalyst, and the large concentration of alkane can compete with the small concentration of alcohol. Because the polymer chains diffuse more slowly, the alcohol diffuses from the catalyst slowly, and the catalyst reacts with the alcohol to form ketone prior to diffusion. Ongoing work seeks to test this hypothesis further and to determine how differences in diffusion between small molecules and macromolecules affect this selectivity.

Table S7. Oxidation of alkanes and polyethylene of different molar masses catalyzed by **1**.

Entry	Substrate	Ketone (mol%)	Alcohol (mol%)	Selectivity (%)
1	Cyclohexane	0.84%	0.32%	72%
2	Octadecane	1.07%	0.35%	75%
3	Paraffin Wax	1.34%	0.30%	82%
4	Low MW PE ($M_{n,SEC} = 2.4$ kDa, $M_{w,SEC} = 7.9$ kDa, Powder)	1.06%	0.15%	88%
5	LDPE film (50 μm) ($M_{n,SEC} = 7.2$ kDa, $M_{w,SEC} = 57.4$ kDa,	0.37%	0.00%	>99%

The following section has been added to the supplemental discussion:

- 2.4. Understanding ketone selectivity in the oxidation of PE with **1**.

The following figures and tables have been added to the supplementary information:

- **Table S7.** Oxidation of alkanes and polyethylene of different molar masses catalyzed by 1.

- Line 91: The phrase “commercial plastics contain additives that are absent in pristine pellets” implies that pristine pellets do not contain additives. If this is what the authors indeed meant to imply, then this is incorrect. PE resin manufacturers regularly add additives such as antioxidants, UV stabilizers, processing aids, slip agents, and anti-blocking agents into the pellets they sell to converters (i.e., those that use pellets to shape a product). Sometimes, converters will choose to mix additional additives into their products. How do the authors know the additive packages used in the pellets they studied and the products they sampled are different? If they do not, then how is this comparison valuable?

We appreciate and agree with the reviewer’s comment. We acknowledge that commercial polyethylene pellets contain additives and have reworded the sentence in the manuscript to avoid confusion. To limit the number of additives that might interfere with our study, we conducted all transformations described as using pristine polymer on material that had been purified by precipitation: PE pellets were dissolved in xylenes, precipitated in methanol, and dried in vacuo before they were melt-pressed. We have corrected the wording in the methods section to make clear that we purified the starting polymer. The post-consumer samples, by contrast, were not pre-processed in any way. This difference highlights that oxidation occurs with commercial samples of PE, even though they contain these additives.

We have updated the following lines in the main text:

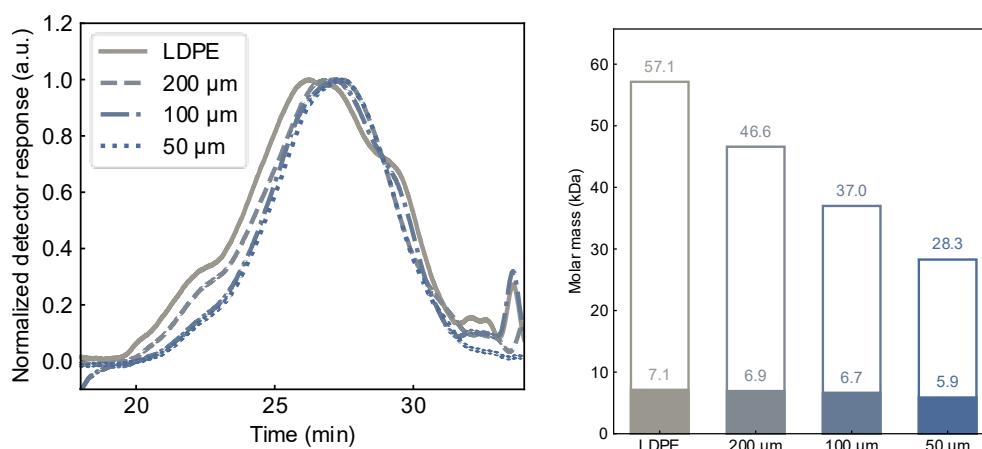
- **Original:** Commercial plastics contain additives that are absent in pristine pellets and that could interfere with chemical functionalization.^{2–4} However, we did not observe a large difference between the efficiency of the oxidation of several common post-consumer PE items and the oxidation of pristine PE (**Fig. 2G**).
- **Updated:** “Oxidation also occurs on post-consumer PE samples without pretreatment (**Fig. 2I**).”

We have updated the following lines in methods sections:

- **Original:** Polymer substrates were compressed between PTFE sheets encased by stainless steel plates at 15 °C above their melting point (e.g. 125 °C for LDPE, 150 °C for HDPE), a pressure >2000 psi, and a duration of 10 min.
- **Updated:** Pristine polymer pellets were dissolved in xylenes, precipitated in methanol, and dried in a vacuum oven at 80 °C before use. Polymer films were fabricated using a Carver benchtop lab press with heated plates (model 4386). Pristine polymer, which was precipitated from xylenes and dried, was pressed between PTFE sheets encased by stainless steel plates at 15 °C above its melting point (e.g. 125 °C for LDPE, 150 °C for HDPE) at a pressure >2000 psi for a duration of 10 min.

- Line 114: If oxidation is localized to the surface, would the change in molar mass scale inversely with the sample thickness, assuming the mol% of ketone formation were held constant?

The reviewer's question is well-founded. We investigated whether the thickness of the sample correlated with the change in molar mass by subjecting LDPE films with thicknesses of 50 μm , 100 μm and 200 μm to the standard oxidation conditions (0.3 equiv. tBuOOH, 0.001 mol% **1**, 24 h, 65 $^{\circ}\text{C}$). Indeed, we observed that both the number-average molar mass and the weight-average molar mass correlated with film thickness. We have added the following figures to the supplemental information and included a reference in the main text to this observation.



Name	M_n (kDa)	M_w (kDa)	$\bar{D}$
Pristine LDPE	7.2	57.1	8.0
Film-oxidized LDPE (200 μm)	7.2	40.8	5.7
Film-oxidized LDPE (100 μm)	6.7	37.0	5.6
Film-oxidized LDPE (50 μm)	5.9	28.3	4.8

We have updated the following lines in the main text:

- **Original:** “Oxidation of LDPE and HDPE solutions led to a 42% and 34% reduction in the number-average molar mass ($M_{n,SEC}$), respectively, whereas oxidation of LDPE and HDPE films led to smaller 7% and 11% reductions in $M_{n,SEC}$, respectively.”
- **Updated:** “Oxidation of LDPE and HDPE in solutions with $t\text{BuPh}$ as solvent led to a 42% and 34% reduction in the number-average molar mass ($M_{n,SEC}$), respectively, whereas oxidation of LDPE and HDPE films led to smaller 7% and 11% reductions in $M_{n,SEC}$, respectively. Further, chain scission after oxidation of the films was inversely correlated with film thickness (**Fig. S33-Fig. S34**).”

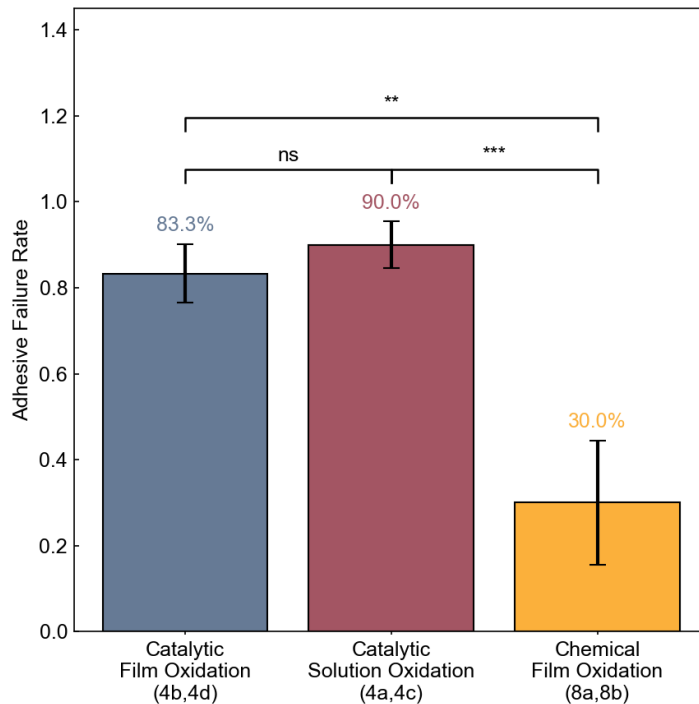
We have added the following figures to the supplemental information:

- Figure S36 - HT SEC data for pristine LDPE (gray) and LDPE oxidized as films (blue) with thicknesses of 200 μm , 100 μm , and 50 μm (1 mg/mL in 1,2,4-trichlorobenzene, 1 mL/min, PE standards)
- Figure S37 – Summarized M_n ,SEC and M_w ,SEC results for pristine LDPE (gray) and LDPE oxidized as films with thicknesses of 200 μm , 100 μm , and 50 μm

- Line 150: The authors should comment on observations related to adhesive and cohesive failure to help support this hypothesis. The failure modes are described in the SI, why not discuss them here?

We thank the reviewer for this suggestion. Although we observed some differences in failure mode for lap shear adhesion tests between PE oxidized in solution and PE oxidized at the solid–liquid interface in individual samples, we cannot draw strong conclusions from the observed differences in failure mode between PE oxidized as a film and PE oxidized in solution because of a lack of statistical significance.

We investigated whether the failure mode depended on the oxidation method during lap shear tests of polymers **4a**, **4b**, **4c**, and **4d** on substrates of nylon, glass, and aluminum. The samples that were oxidized in solution (**4a** and **4c**) were compared to the samples that were oxidized at the solid–liquid interface (**4b** and **4d**) using a Fisher Exact Test. The samples oxidized in solution underwent adhesive failure in 90.0% of tests, whereas the samples oxidized at the solid–liquid interface underwent adhesive failure in 83.3% of tests, but this observed difference was not statistically significant. We next compared the catalytically oxidized samples to samples chemically oxidized with chromic acid and sulfuric acid (**8a** and **8b**). We observed that chemically oxidized samples underwent adhesive failure in 30% of tests, and this value is statistically different from the values for samples oxidized catalytically in solution and samples oxidized catalytically as films.



Referee #2 (Remarks to the Author):

The manuscript by Woroch and co-workers, entitled “Selective, Catalytic Oxidation of Polyethylene Surfaces”, represents an interesting and practically relevant study for the valorization of poorly adhesive PE commodity plastics and their post-consumable wastes. Considering the widespread presence of PE in post-consumable plastics and its enormous annual production volume yet relatively low recycling rate, this study attracts broad interests from readers in both chemistry and materials science. Notably, such interfacial modification can be performed with an extremely low catalyst loading of 10 ppm of porphyrin-chelated iron catalyst, under mild thermal conditions. There is one concern that a very similar paper was published a few weeks ago, but these data shows very systematic studies and most importantly, outperforms the previous one. Therefore, this reviewer believes that after several revisions, this should have enough conceptual novelty and broad interests for publication in Nature.

Main points

1) Authors need to do better job in citing other’s work. A similar concept of the paper was just published a month ago using porphyrin-chelated vanadium catalysts (J. Am. Chem. Soc. 2026,

148, 22726–22738), so it is worthwhile to compare the work as well. Also, a related PE grafting method was published three months ago (J. Am. Chem. Soc. 2026, 148, 14, 14924–14933), again worth mentioning where PE-polar-graft is introduced.

We thank the reviewer for noting these complementary publications. The first work by Zhao et al. describes another method for the surface oxidation of polyethylene using a vanadium porphyrin complex. The paper by Zhao et al. was published on May 27, 2026, which is after the initial submission of our manuscript on May 4, 2026. The text has been updated to cite this work. We thank the reviewer for noting the advantages of the method and depth of analysis presented in our manuscript. As the reviewer notes, our work meets the high standards of *Nature* because our report uniquely demonstrates functionalization at the surface by depth-profiling X-ray photoelectron spectroscopy measurements, reports differences between the microstructure and thermomechanical properties of PE functionalized in solution and those properties of PE functionalized at its surface, describes additional surface modulation by derivatization of the ketone, and shows how the long-term stability of materials from selective surface oxidation is greater than the that of materials produced from conventional oxidation methods. Further, our method is complementary to the recently disclosed method and has notable benefits, including a 30-fold lower catalyst loading, a ligand scaffold that can be made more readily at scale, a significantly reduced operating temperature (65 °C vs. 105 °C), a greater retention of film molecular weight, thermal properties, and mechanical properties, a greater enhancement in adhesion, and negligible discoloration or deformation of the solid substrate.

The second work by Kim et al. describes a photochemical strategy for grafting vinyl monomers and polymers onto polyethylene substrates and shows that greater retention of crystallinity correlates with greater adhesion. As a result, we have added a citation to this work and thank the reviewer for their comment.

We have updated the following lines in the main text:

- **Original:** Polar polymer grafts have been grown on polyolefin surfaces through the photochemical activation of C-H bonds, but selective thermocatalytic installation of a functional group on PE has not been reported.
- **Updated:** Photochemical activation of C–H bonds has previously been used to grow polar polymer grafts onto polyolefin surfaces,^{7–11} but, until recently, selective thermocatalytic functionalization of C–H bonds on PE remained unreported.¹² (2 citations updated)

2) In the recent J. Am. Chem. Soc. 2026, 148, 22726, comparable ketone ratios were attained in a single reaction cycle, albeit with a higher catalyst loading (0.03 mol%). As a comparison, the author’s method requires 5 reaction cycles to reach a ketone incorporation ratio of 1.1 mol% while employing a much lower catalyst loading. In this regard, the reviewer is curious whether the ketone incorporation ratios could be further improved within a single reaction cycle by using a higher catalyst loading to enhance the overall reaction efficiency.

The reviewer is correct that the total amount of ketone introduced by our method in a single pass is lower than that introduced by the recently reported method (J. Am. Chem. Soc. 2026, 148, 22726) and that we obtained materials with higher degrees of ketone incorporation by conducting additional cycles of oxidation. To address the reviewer's comment, we oxidized an LDPE film with 0.002 mol% and 0.01 mol% of the catalyst **1** and 0.3 equivalents of *t*BuOOH. We observed that the yield of ketones was lower when 0.002 mol% of **1** was used and when 0.01 mol% of **1** was used than the yield of ketones when 0.001 mol% **1** was used. For example, we observed 0.3 mol% ketone when 0.001 mol% catalyst **1** was used, but only 0.2 mol% ketone when 0.01 mol% of catalyst **1** was used. We propose that this result is related to the similar counterintuitive observation made about effect of the quantity of oxidant. When greater than 0.3 equivalents of oxidant were used, a reduced yield of ketone was observed. We hypothesize that this lower yield results from faster activation of the radical chain process farther from the surface of the polymer.

Entry	x (mol%)	y (equiv.)	Ketone (mol%)
1	0.001%	0.1	0.22%
2	0.001%	0.2	0.26%
3	0.001%	0.3	0.32%
4	0.001%	0.5	0.22%
5	0.001%	1	0.17%
6	0.002%	0.3	0.30%
7	0.010%	0.3	0.20%

These data imply that our oxidation occurs by a radical chain mechanism, and these data and the conclusions we draw from them are detailed in the supplementary discussion. The tert-butoxy radical generated in our proposed mechanism is known to undergo unproductive decomposition readily;¹³ therefore, for the desired oxidation chemistry to occur, the radical must be generated near the polymer surface. We conclude that the lower yield with higher catalyst loading results from greater, unproductive consumption of the oxidant in the bulk solution before it reaches the

polymer surface. Similarly, a higher oxidant loading dilutes the catalyst, thereby reducing the catalyst concentration at the solid–liquid interface and limiting the productive oxidation.

We have added the following figure to the supplemental information to show these results:

- **Table S16.** Oxidation of LDPE with t BuOOH and **1** with varying catalyst and oxidant loadings.

3) Page 7, line 118, “a lower melting temperature (T_m) or broader ... smaller or more imperfect crystallites”. The reviewer agrees with this interpretation, and noted that relevant reference has been cited in support of this conclusion. Nevertheless, additional characterization, such as AFM analysis, may be helpful to further substantiate this claim. Such measurements could clarify whether the reduced T_m originates primarily from the formation of imperfect crystallites or alternatively increased surface roughness following oxidation, or a combination of both.

We appreciate the reviewer’s request for additional characterization. First, we performed the requested surface roughness characterization by atomic force microscopy (AFM). Pristine PE films, PE oxidized in a solution that was melt-pressed into a film, and PE oxidized as a film were adhered to a glass slide. Three $10\ \mu\text{m} \times 10\ \mu\text{m}$ regions on each film that were picked randomly were analyzed by AFM. The surface roughness was calculated using the root-mean squared roughness (R_q). We report the average R_q of three measurements. The differences in average R_q of LDPE and the two oxidized LDPE samples were not statistically significant. Likewise, the differences in the average R_q of HDPE and the two oxidized HDPE samples were not statistically significant. Therefore, we conclude that surface roughness is not a key contributor to the differences in observed adhesion or melting temperature. We have added to the supplementary information the raw data on AFM height and a bar graph showing the average surface roughness.

The following section has been added to the supplementary methods:

- **1.3. Atomic force microscopy for surface roughness determination.**

The following figures have been added to the supplementary information:

- **Figure S74.** Atomic force microscopy height maps of pristine LDPE film (3 regions).
- **Figure S75.** Atomic force microscopy height maps of LDPE oxidized in solution before melt-pressing into a film (**4a**) (3 regions).
- **Figure S76.** Atomic force microscopy height maps of LDPE oxidized as a film (**4b**) (3 regions).
- **Figure S77.** Atomic force microscopy height maps of pristine HDPE film (3 regions).
- **Figure S78.** Atomic force microscopy height maps of HDPE oxidized in solution before melt-pressing into a film (**4c**) (3 regions).
- **Figure S79.** Atomic force microscopy height maps of HDPE oxidized as a film (**4d**) (3 regions).

- **Figure S80.** Root-mean squared surface roughness of pristine and oxidized PE samples as measured by atomic force microscopy.

4) Page 8, line 139 to 142, “The lap-shear strength values... 5.9 MPa for LDPE and 6.9 MPa for HDPE”. Could the author provide additional insight into why the interfacial oxidation with comparable ketone concentration resulted in much better mechanical properties and adhesion of LDPE and HDPE, compared to homogenous oxidations where are expected to have better ketone incorporation ratios. It is not clear yet. Would XRD give any other information?

We thank the reviewer for this comment and provide additional explanation below to clarify our hypothesis. We propose that the greater adhesive and tensile properties of PE functionalized at the solid–liquid interface than of PE functionalized in solution are related to both the localization of the polar functional groups and the preservation of the bulk polymer properties during functionalization.

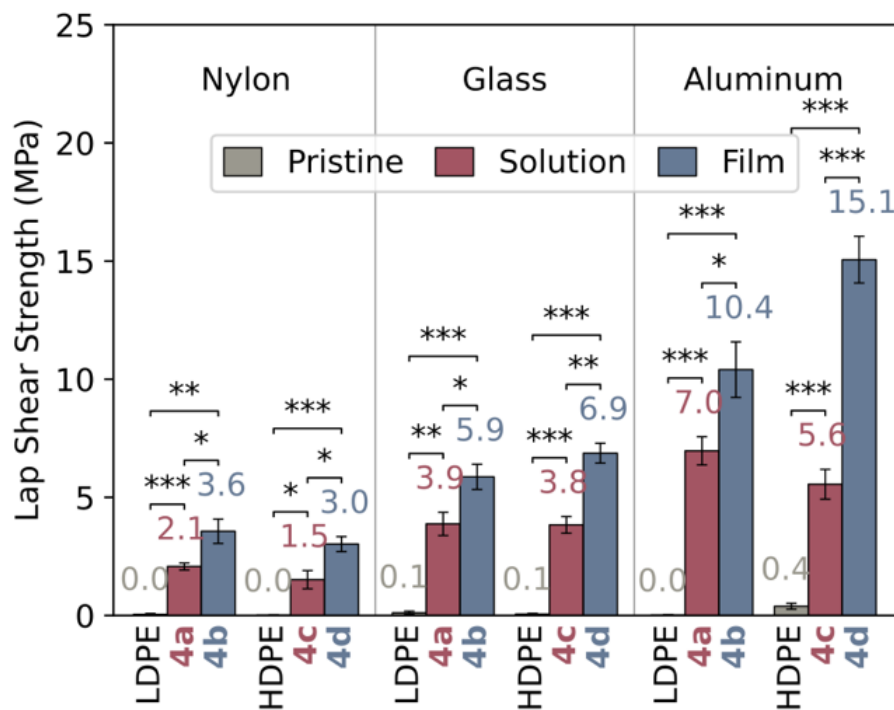
We hypothesized that the introduction of functional groups at the solid–liquid interface will yield stronger adhesive contacts than those introduced in the bulk of the material because the functional groups will be more accessible to interact with a polar substrate. To test this hypothesis, we synthesized PE functionalized at the solid–liquid interface and PE functionalized in solution with a range of total ketone content ranging from 0.1-0.8 mol% (Figure 3G). We observed that the lap-shear adhesive strength of PE functionalized at the solid–liquid interface is greater than that of PE functionalized in solution at comparable degrees of functionalization for all degrees of functionalization tested. In addition, the enhancement in lap shear strength per ketone incorporation (the slope) was greater for PE functionalized at the solid–liquid interface than it was for PE functionalized in the bulk. We concluded from these data that polar groups introduced directly at the surface lead to more adhesive materials.

We also propose that an additional difference between oxidation in solution and oxidation at the solid–liquid interface is retention of polymer molecular weight. Radical chain reactions can cause chain scission that reduces polymer chain length and degrade material properties. We observed that oxidation of LDPE and HDPE solutions led to a 42% and 34% reduction in the number-average molar mass ($M_{n,SEC}$), respectively, whereas oxidation of LDPE and HDPE films led to smaller 7% and 11% reductions in $M_{n,SEC}$, respectively. This smaller loss in molar mass contributes to tensile properties in the PE samples oxidized at the solid–liquid interface that are superior to those oxidized in solution.

In response to other reviewer comments, we also added experiments that measure crystallinity and microstructure (SSA, WAXS, and SAXS). We further observe from these measurements that the crystallinity of PE oxidized at the solid–liquid interface is higher than that of PE oxidized in solution. We assert that the increased crystallinity further contributes to both the greater tensile strength and adhesive strength of PE oxidized at the solid–liquid interface than of PE oxidized in solution.

5) For lap shear test, many metals such as Al and steel are used, but only glass is used here. Please test it on other surface to demonstrate the generality.

We appreciate the reviewer's suggestion. In response, we performed additional lap shear adhesion with pristine LDPE, LDPE oxidized in solution to generate 0.3 mol% ketones, LDPE oxidized as a film to generate 0.3 mol% ketones, pristine HDPE, HDPE oxidized in solution to generate 0.3 mol% ketones, and HDPE oxidized as a film to generate 0.3 mol% ketones on both aluminum and nylon substrates. The raw data have been added to the supplementary information, and the summarized results have been added to the main text in Figure 3F. We observed that the adhesion of PE functionalized as a film to the polar substrates was greater than that of PE functionalized in solution for all three materials.



We have updated the following lines in the main text:

- Original:** We investigated surface adhesion through lap-shear tests on glass substrates. Pristine PE did not adhere measurably to glass (Fig. 3F, Fig. S21-Fig. S26). The lap-shear strength (τ) values for adhesion of films from PE oxidized in solution were higher: 3.9 MPa for LDPE and 3.6 MPa for HDPE. However, the τ values of PE films oxidized at the solid-liquid interface to the same total ketone concentration as PE oxidized in solution were even higher: 5.9 MPa for LDPE and 6.9 MPa for HDPE.
- Updated:** We investigated surface adhesion through lap-shear tests on nylon, glass, and aluminum substrates (Fig. 3F, Fig. S47-Fig. S64). Pristine PE did not adhere strongly to

any of the substrates. PE oxidized in solution adhered to all substrates, and the average lap-shear strengths (τ) of these samples were between 2–7 MPa. PE oxidized at the solid–liquid interface adhered more strongly to the same substrates. The τ values were 50–270% greater than those of PE oxidized in solution, even though the total ketone concentration of the film-functionalized materials were the same as the solution-functionalized materials.

We have updated the caption to Figure 3 with the following text:

- **Original:** **F)** Average lap-shear strength to glass over 5 replicate trials of pristine PE versus PE oxidized with 0.3 mol% ketones and **G)** PE oxidized with 0.1-0.8 mol% ketone as a film versus in solution.
- **Updated:** “**F)** Average lap-shear strength to nylon, glass, and aluminum over 5 replicate trials of pristine PE versus PE oxidized to generate 0.3 mol% ketone. **G)** Average lap-shear strength to glass of PE oxidized as a film to generate 0.1-0.8 mol% ketone versus PE oxidized in solution to generate the same amount of ketone.”

We have added the following figures to the supplemental information:

- **Fig. S50** | Nylon lap-shear adhesion data for pristine LDPE (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S51** | Nylon lap-shear adhesion data for solution-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S52** | Nylon lap-shear adhesion data for film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S53** | Nylon lap-shear adhesion data for pristine HDPE (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S54** | Nylon lap-shear adhesion data for solution-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S55** | Nylon lap-shear adhesion data for film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S56** | Aluminum lap-shear adhesion data for pristine LDPE (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S63** | Aluminum lap-shear adhesion data for solution-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S64** | Aluminum lap-shear adhesion data for film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S65** | Aluminum lap-shear adhesion data for pristine HDPE (1.5 mm/min). (* = failed during pre-strain step).
- **Fig. S66** | Aluminum lap-shear adhesion data for solution-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).

- **Fig. S67** | Aluminum lap-shear adhesion data for film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).

6) Fig. 4E, purple bar of 4d. Incorporation of polar functional groups, such as ketones, is generally expected to enhance the wettability and thus reduce the WCA. However, functionalized HDPE 4d exhibited a higher WCA value compared to its pristine HDPE, any further clarification to this seemingly counter-intuitive observation?

We share the reviewer's initial surprise about this unintuitive observation. The difference between the wettability of HDPE and oxidized HDPE **4d** was found not to be statistically significant by a Welch's 2-sided t-test, and so we did not evaluate it further. The impact of ketone groups on the water contact angle (θ_w) of polyethylene (e.g. $\Delta\theta_w < 5^\circ$) is typically small, so we hypothesized that the observed difference was not caused by our treatment but is from statistical variation.

Previous studies have shown that the effect of ketone functionalization on the contact angle of polyethylene is smaller than the effect of other oxidized functional groups. Whitesides and colleagues found that the contact angle of polyethylene functionalized with ketones and esters was closer to that of unfunctionalized polyethylene than was the contact angle of polyethylene functionalized with carboxylic acids or alcohols.¹⁴ In a mild oxidation of polyethylene by Gif chemistry that introduced predominantly ketone groups, only a minor difference in the contact angle was observed, although the degree of functionalization was low.¹⁵ The water contact angle of polyethylene containing approximately 0.5 mol% ketone groups also was found to be within approximately 3° of commercial polyethylene.¹⁶ Our observations of the contact angle of LDPE agree well with these previous studies. Nevertheless, the slight increase in θ_w observed for HDPE was unexpected.

To determine whether the small increase in θ_w observed for HDPE than for the oxidized HDPE was simply from statistical variation, we prepared two new samples for analysis using the same conditions as were used to prepare the sample for the original oxidized material **4d**. Each sample was cut into three sections, and each section was subjected to a water contact angle measurement, recording the left and right angle of the water droplet for a total of six measured angles. The results of the test are as follows:

Sample #	Angle 1	Angle 2	Angle 3	Angle 4	Angle 5	Angle 6	Avg.	+/-
4d (#2)	96.9	98.2	96.3	97.6	96.1	97.4	97.1	0.1
4d (#3)	104.1	103.3	97.6	98.9	98.1	95.1	99.5	0.5

Our previously collected data were the following:

Sample #	Angle 1	Angle 2	Angle 3	Angle 4	Angle 5	Angle 6	Avg.	+/-
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HDPE	102.3	102.5	100.2	100.6	98.1	98.5	100.4	0.8
4d (#1)	104.5	102.5	102.7	101.2	102.5	101.1	102.4	0.5

(Note: An error in the average calculation was corrected in Table S16)

A Tukey Honestly Significant Difference (HSD) test after an Analysis of Variance (ANOVA) of the four samples revealed no statistically significant difference between the mean for HDPE and the means for the three independent trials of HDPE oxidized at the solid–liquid interface. To address the reviewer’s comment, we have included in the supplementary information the average water contact angle from six angle measurements on the three independent syntheses of oxidized HDPE. In addition, we have replaced the contact angle data for **4d** (#1) with the contact angle data for **4d** (#3) and added statistical significance markers to demonstrate that there is no systematic difference between HDPE and **4d**.

We have updated the following lines in the methods:

- **Original:** Water contact angle was measured using a Ramé–Hart goniometer. Droplets of 2 μ L were dispensed on the surface of the film. Reported values are the average of six independent trials.
- **Updated:** Water contact angle was measured using a Ramé–Hart goniometer. Droplets of 2 μ L were dispensed on the surface of the film. Reported values are the average of six angle measurements on three regions of the film.

We have updated the following tables in the supplementary information:

Original: Table S16. Water contact angle measurements for pristine LDPE and oxidized PE immediately after treatment

Sample	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Average	+/-
LDPE	100.7	100.5	97.8	97.7	95.5	95.7	98.0	0.8
HDPE	102.3	102.5	100.2	100.6	98.1	98.5	102.4	0.5
4b	97.5	94.3	94.4	97.0	97.1	90.7	95.2	1.0
4d	104.5	102.5	102.7	101.2	102.5	101.1	100.4	0.8
8a	26.5	33.3	59.2	39.5	48.3	60.9	44.6	5.2
8b	67.3	66.7	46.4	46.4	93.5	92.4	68.8	8.5

Updated: Table S20. Water contact angle measurements for pristine LDPE and oxidized PE immediately after treatment.

Sample	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Average	+/-
LDPE	100.7	100.5	97.8	97.7	95.5	95.7	98.0	0.8
HDPE	102.3	102.5	100.2	100.6	98.1	98.5	100.4	0.8
4b	97.5	94.3	94.4	97.0	97.1	90.7	95.2	1.0
4d	104.1	103.3	97.6	98.9	98.1	95.1	99.5	0.5
8a	26.5	33.3	59.2	39.5	48.3	60.9	44.6	5.2

8b	67.3	66.7	46.4	46.4	93.5	92.4	68.8	8.5
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We have added the following figures in the supplementary information:

- **Fig. S101** | Representative water contact angle measurement of **4d**.
- **Fig. S104** | Average water contact angle from pristine HDPE and from three different experiments with HDPE oxidized as a film to incorporate 0.3 mol% ketones (each bar is the average of six angle measurements per sample).

7) Why is soxhlet extraction needed for the purification of solution process? What happens if one skips it, in terms of chemical structures, defects, and even adhesion? What are being removed by this process?

We appreciate the reviewer's curiosity about the use of Soxhlet extraction. We used Soxhlet extraction to remove adventitious non-covalently bound impurities on the polyethylene surface. Initial oxidation experiments were performed by washing the oxidized material three times at room-temperature with methanol. We observed no significant difference in ^1H NMR spectroscopy, FTIR spectroscopy, DSC, lap shear tests, or tensile tests between the films washed by this treatment and those washed by Soxhlet extraction. The Soxhlet extraction was employed, however, after characterization of the oxidized material by X-ray photoelectron spectroscopy (XPS). XPS revealed signals in the N(1s) and O(1s) region after room temperature methanol washes, indicating the presence of chemical species at the material surface. Some unexpected peaks in these regions also were observed in pristine polyethylene. XPS is a surface-sensitive technique that can detect small quantities of adventitious species adsorbed to the surface. We found that Soxhlet extraction with methanol removed most of the surface impurities. The bulk thermomechanical properties measured by lap shear testing, tensile testing, and DSC in PE samples purified without Soxhlet extraction, however, did not differ from those of samples purified with Soxhlet extraction.

Minor point

1) In Fig. 2E, unit (cycles) could be added under "Oxidation Treatments" to improve clarity.

We thank the reviewer for this feedback and have made the requested change to the x-axis of figure 2E.

In addition to the comments made by the reviewers, we have made the following changes to aid in the clarity of the work, provide the reader with additional information, and credit additional contributions made to address the reviewer comments.

- 1) Earlier drafts of the manuscript included comments on the ability of our method to preserve the shape of oxidized films and to be used for region-specific oxidation. We have added figures showing this type of oxidation to Figure 2G,H and adding a line of text.
 - **Added text:** “Further, oxidation at the solid–liquid interface retained film shape, and we showed that oxidation can functionalize selected regions of the film exclusively (**Fig. 2G,H**).”
- 2) We have updated the following line in the main text to give context for exploring phthalocyanine-based catalysts:
 - **Original:** To identify a method to functionalize of PE films selectively, we first conducted the oxidation of C–H bonds at moderate temperatures (< 80 °C) with octadecane as a model compound (see SI).
 - **Updated:** To identify a method to functionalize of PE films selectively, we first conducted the oxidation of C–H bonds at moderate temperatures (< 80 °C) with octadecane as a model compound (see SI).^{17–20} We targeted phthalocyanine-based catalysts for their activity at mild temperatures, synthetic accessibility, and commercial prevalence.^{41,44} A screen of phthalocyanine-based catalysts, showed that nitride dimer **1** led to the highest yield of ketones and was soluble in organic solvents (**Table S4**).
- 3) While revising the manuscript, we detected a small Si impurity in the XPS reported in Figure 2. We have determined that the Si impurity originated from silicone oil used for heating baths and was likely placed on the surface by contaminated gloves. Therefore, we reproduced the depth profiling measurements in Figure 2B with a clean sample and with additional etching cycles. The same trend is observed, but the magnitude of the initial O(1s) peak is smaller than previously observed.

Citations in this response letter:

- (1) Encinas, N.; Díaz-Benito, B.; Abenojar, J.; Martínez, M. A. Extreme Durability of Wettability Changes on Polyolefin Surfaces by Atmospheric Pressure Plasma Torch. *Surf. Coat. Technol.* **2010**, 205 (2), 396–402. <https://doi.org/10.1016/j.surfcoat.2010.06.069>.
- (2) Wiesinger, H.; Wang, Z.; Hellweg, S. Deep Dive into Plastic Monomers, Additives, and Processing Aids. *Environ. Sci. Technol.* **2021**, 55 (13), 9339–9351. <https://doi.org/10.1021/acs.est.1c00976>.
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