



Selective, Catalytic Oxidation of Polyethylene Surfaces

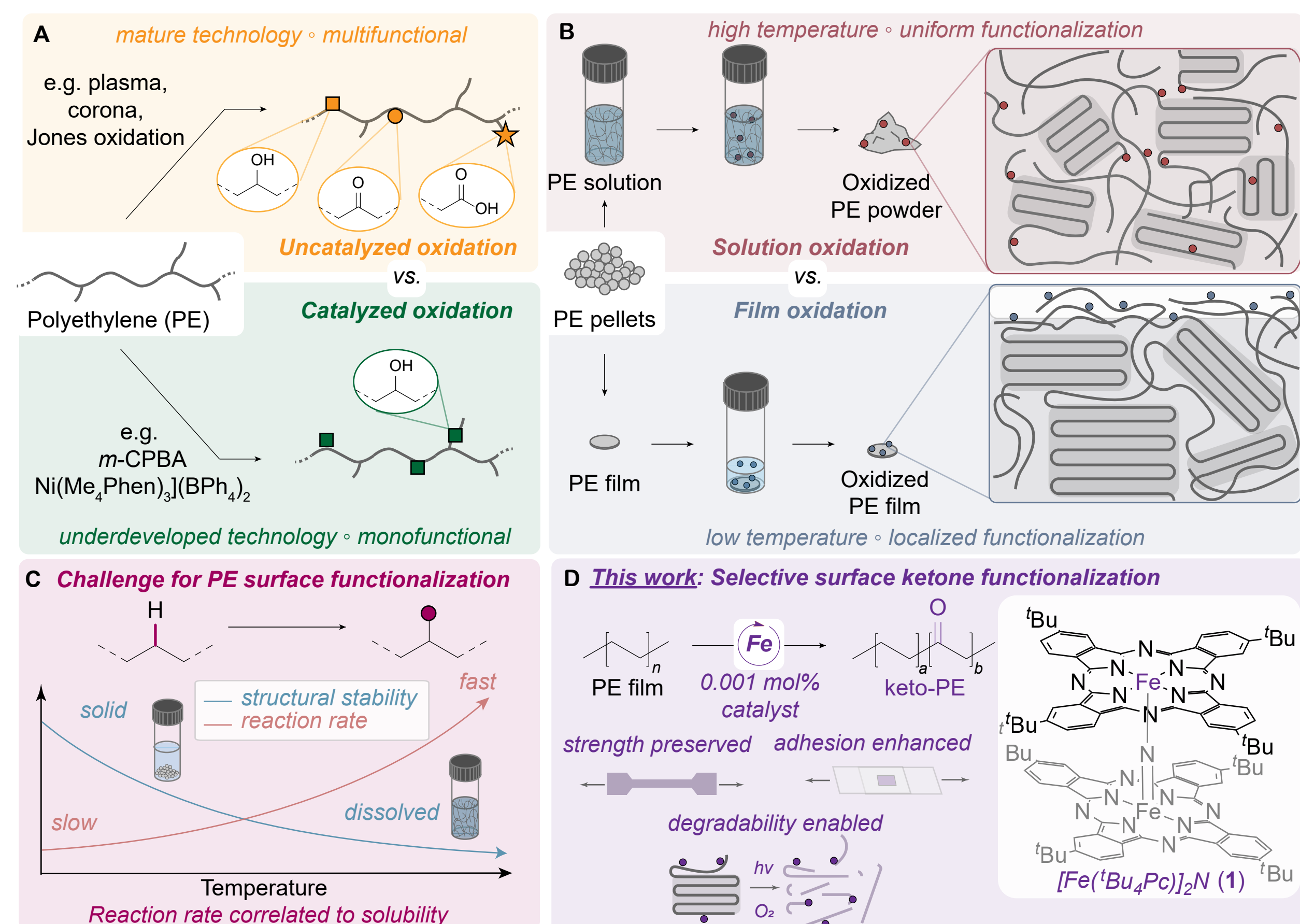
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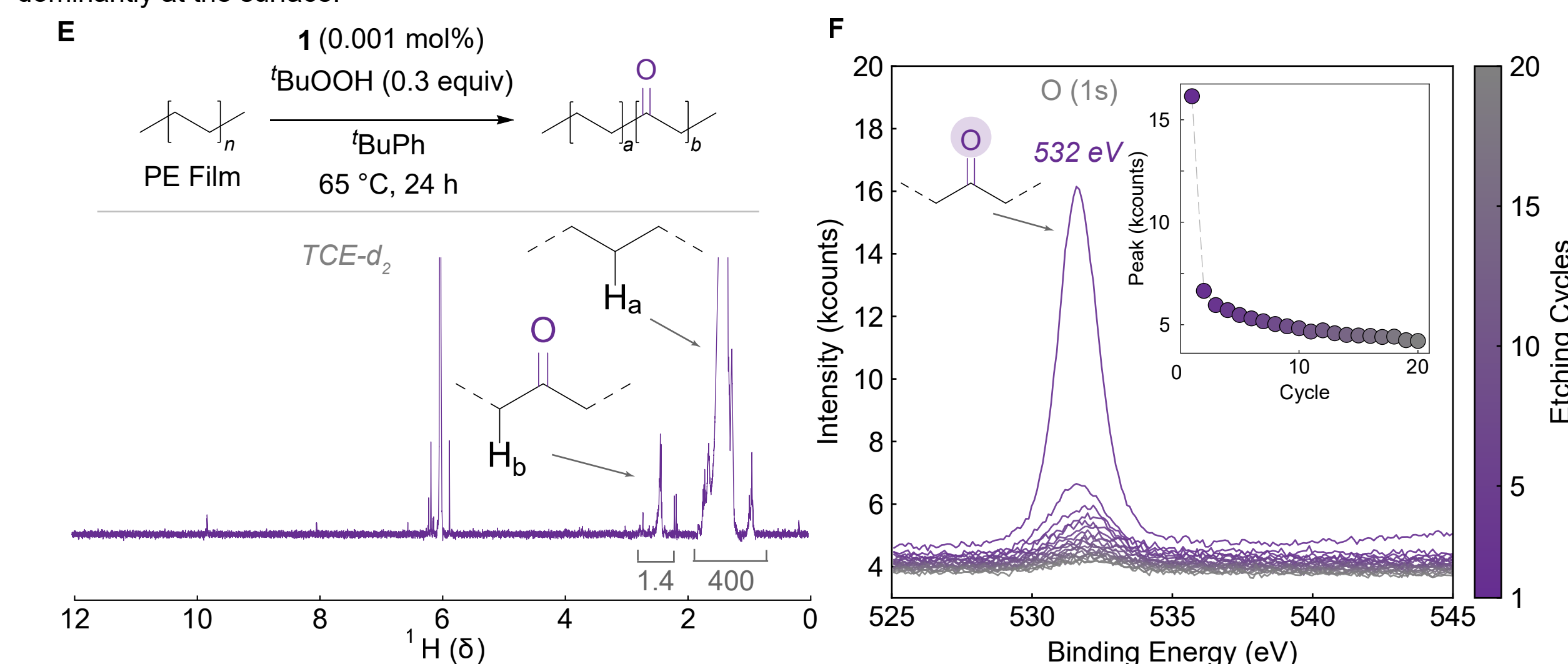
Introduction

Oxidation of polyethylene (PE) using mature methods (e.g. plasma treatment) enhances desirable surface properties but produces a complex mixture of functional groups (A). Catalytic oxidation has recently emerged as a selective way to functionalize PE but primarily operates in homogeneous media (B). Functionalization of the PE surface is challenging because it must occur at temperatures low enough to avoid melting or dissolving the material but high enough to functionalize typically unreactive alkyl C-H bonds (C). Herein, we report the selective, catalytic oxidation of a PE surface using 0.001 mol% of an iron complex and demonstrate how catalytic surface functionalization leads to fundamentally distinct materials compared to functionalization in solution (D).

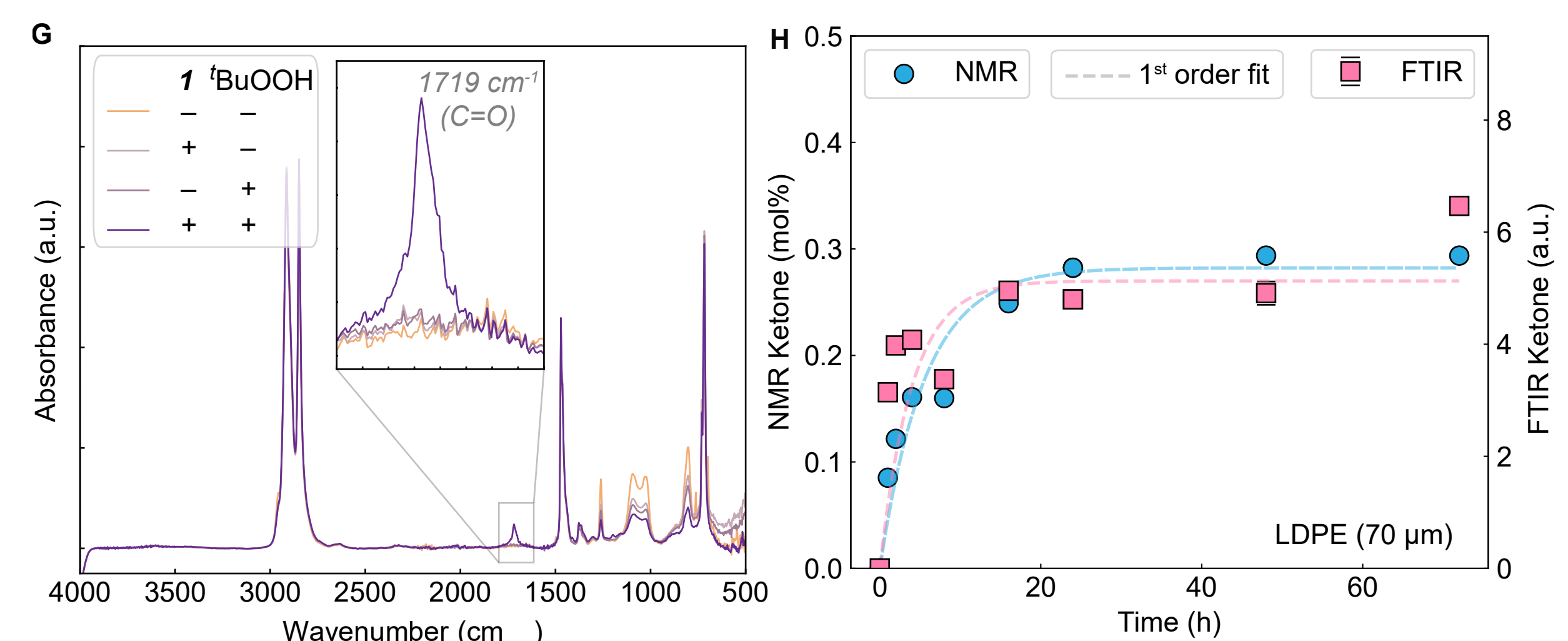


Oxidation of PE Substrates

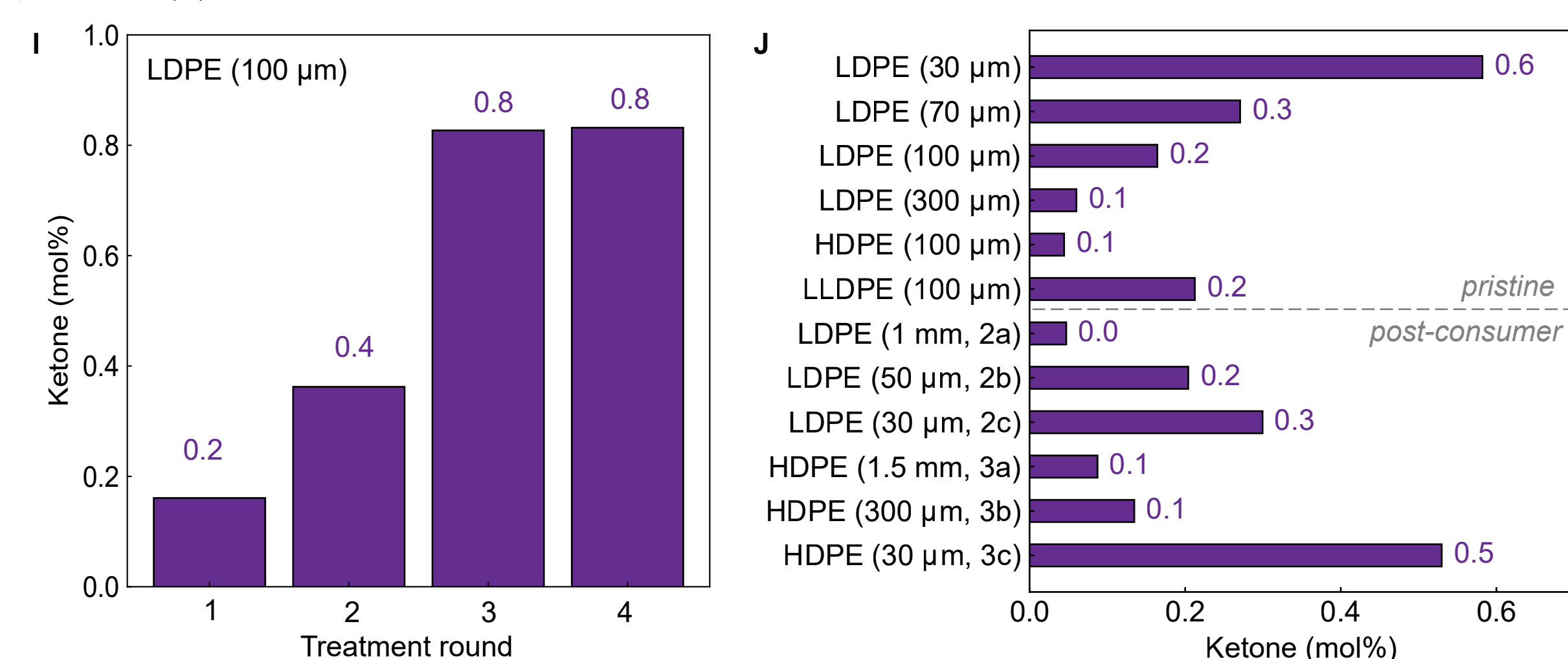
Oxidation of PE catalyzed by 0.001 mol% of **1** produces exclusively ketones as measured by ¹H nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS) (E,F). The ketone feature in the XPS was removed within several cycles of depth profiling XPS with monoatomic Ar⁺ etching, suggesting that the carbonyl group resides predominantly at the surface.



Fourier transformed infrared (FTIR) spectra of the surface contained one prominent ketone carbonyl stretch which was absent when the reaction was performed without either catalyst, oxidant, or without both catalyst and oxidant (G). A time course of PE oxidation monitored by both FTIR and NMR reveal the extent of surface ketones is fit well by first order kinetics and reaches a maximum after approximately 24 hours of 0.3 mol% ketone for a 70-μm thick film (H).

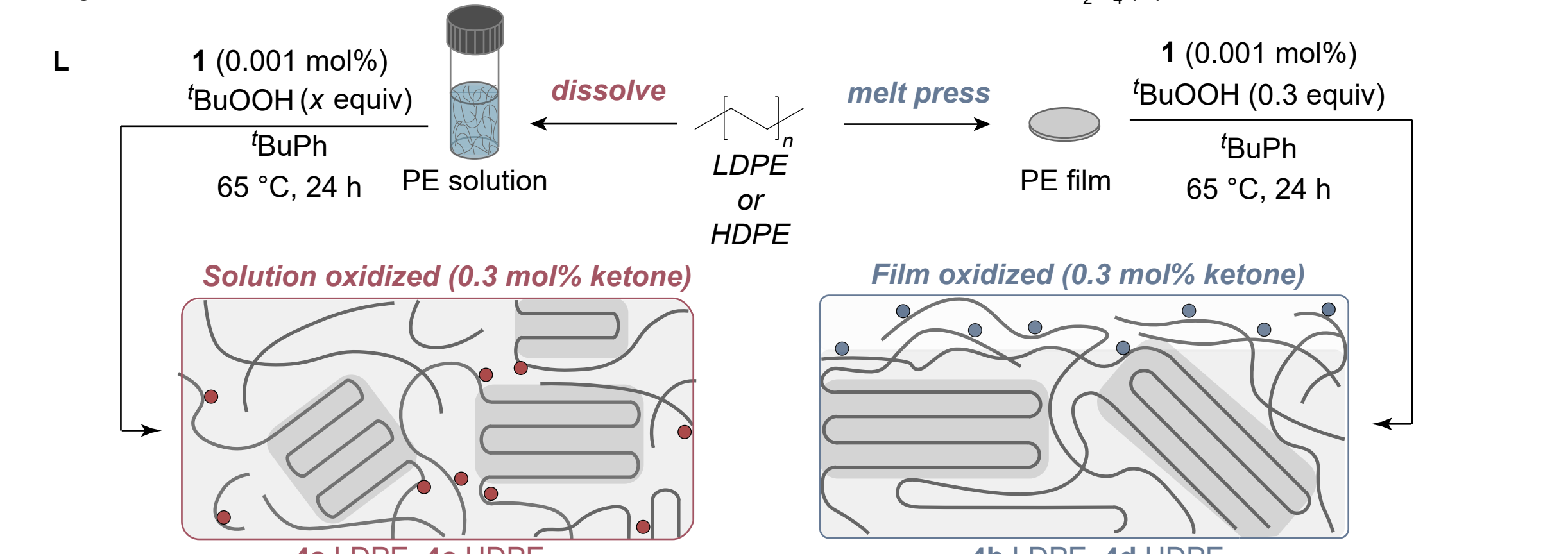


Resubjecting a film to additional oxidation cycles enhanced the amount of total oxidation at the surface after each cycle for two cycles (I). Oxidation of different PE films revealed both crystallinity and film thickness were inversely correlated to extent of oxidation (J). We observed no significant difference between the efficiency for the oxidation of post-consumer PE and pristine PE (K).

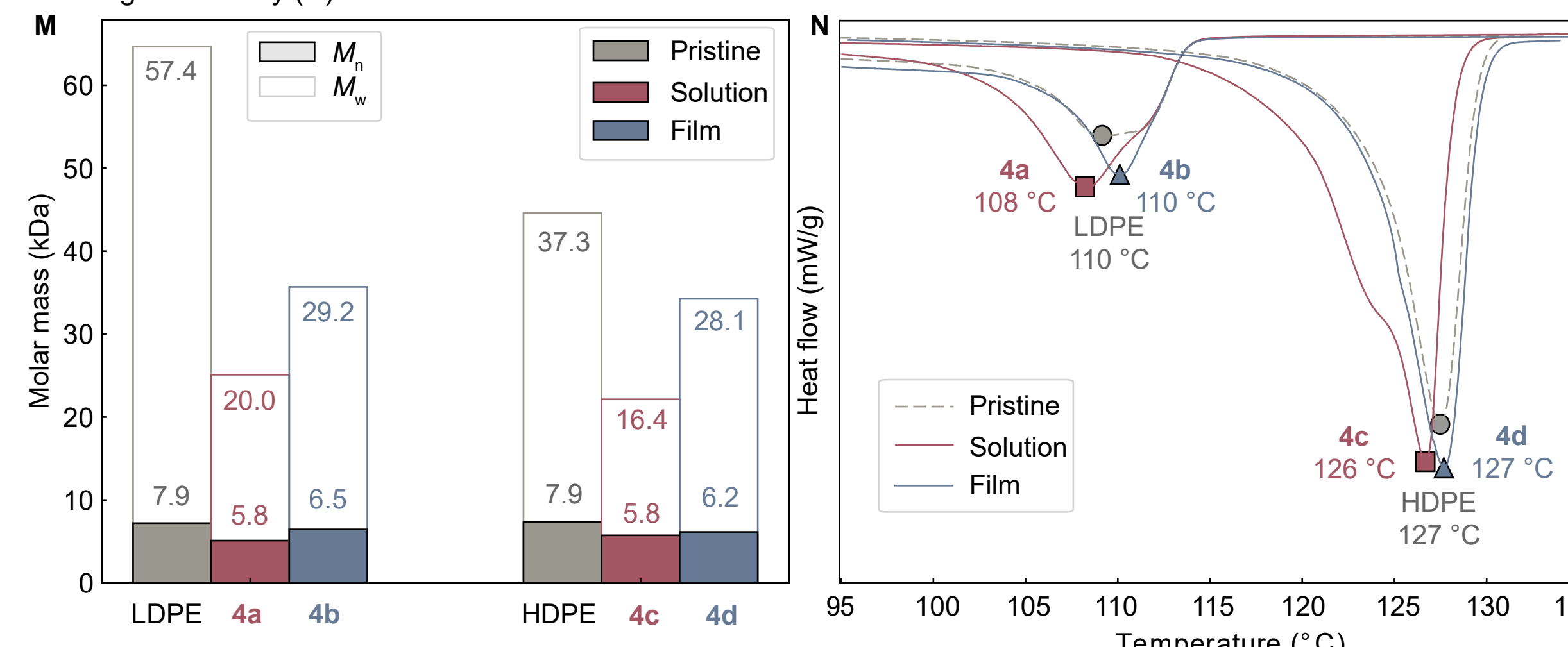


Bulk vs. surface oxidation

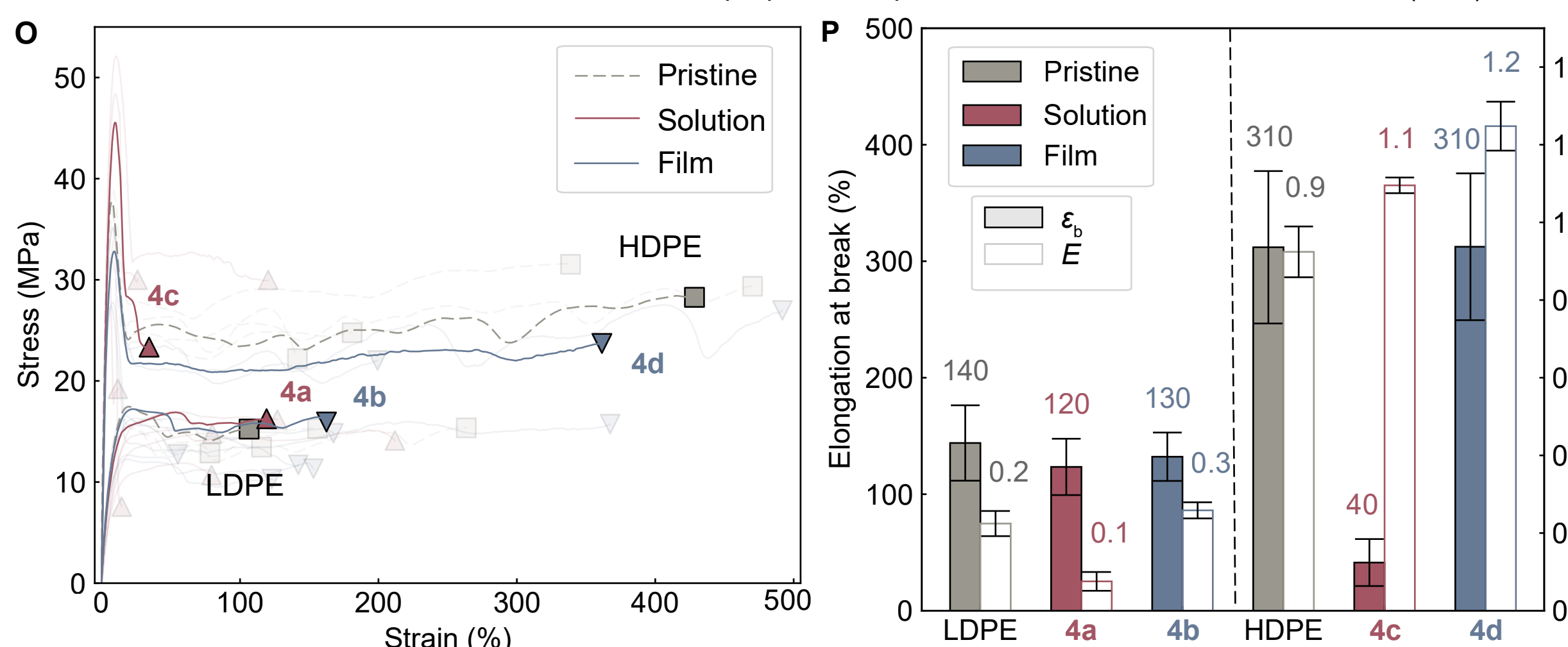
To study how catalytic oxidation at the surface differs from catalytic oxidation in a uniform medium, we oxidized both films and gel-like solutions of PE at 65 °C to a total extent of 0.3 mol% ketones versus C₂H₅ (L).



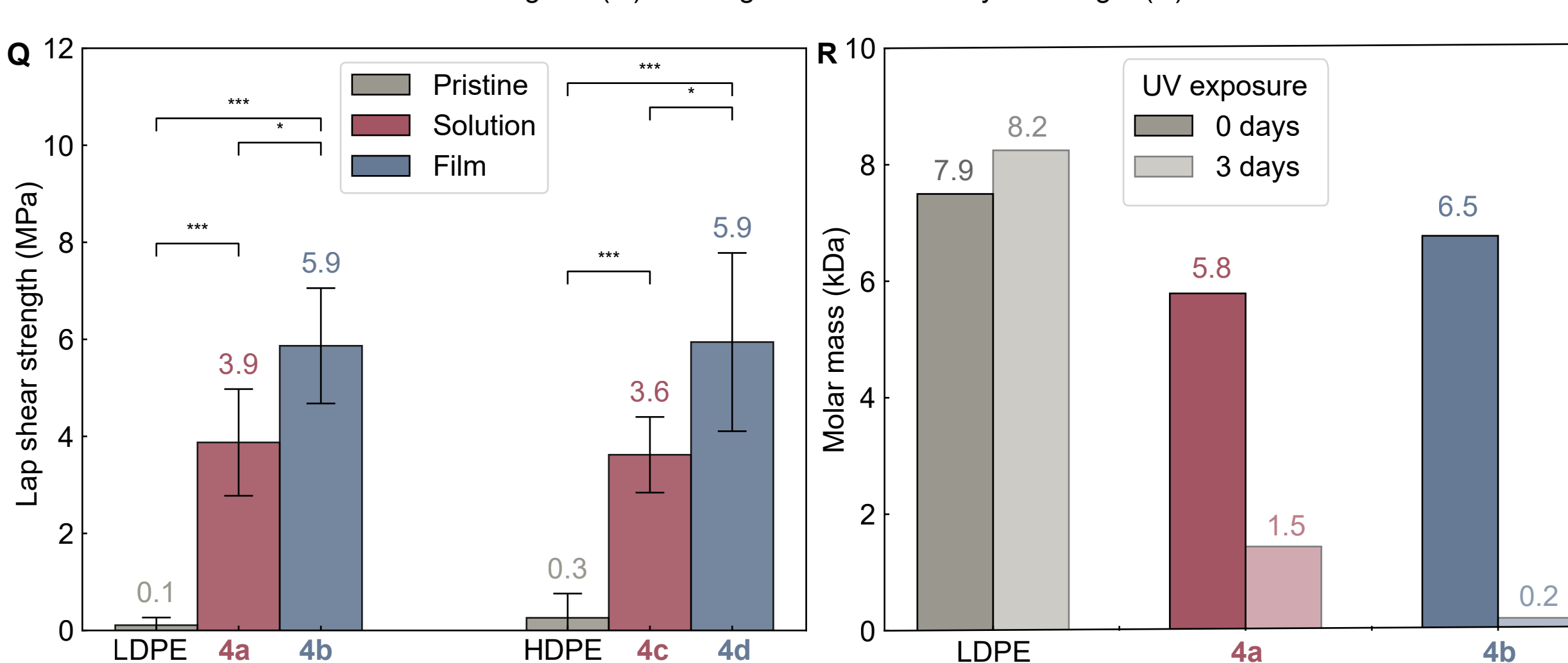
PE oxidized as a film underwent less free radical chain scission as measured by size exclusion chromatography (M) compared to PE oxidized in solution and retained nearly identical melting behavior to pristine PE as measured by differential scanning calorimetry (N).



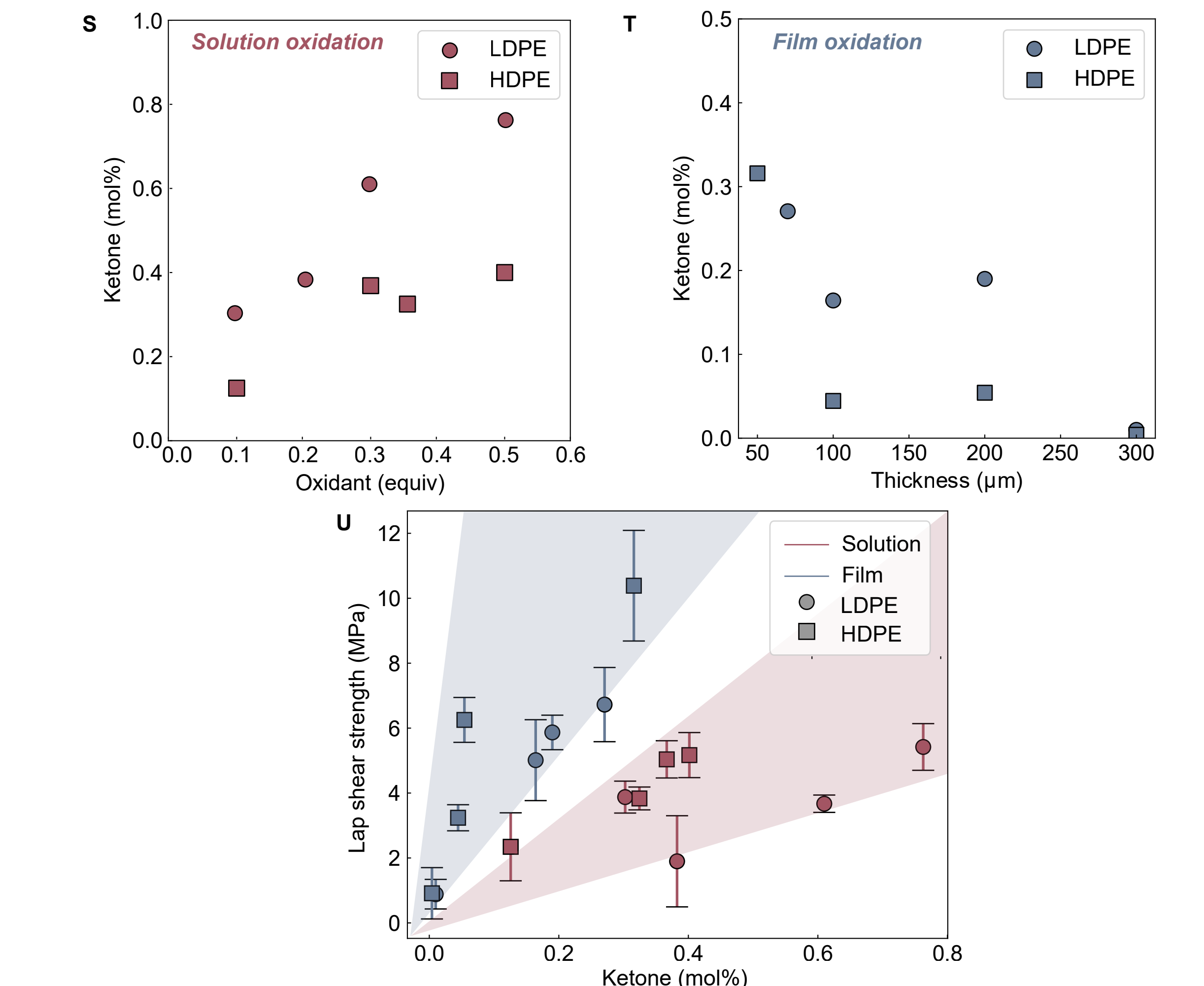
PE oxidized as a film exhibits more similar mechanical properties to pristine PE than PE oxidized in solution (O, P).



PE oxidized as a film adheres better to glass (Q) and degrades more readily in UV light (R) than PE oxidized in solution.

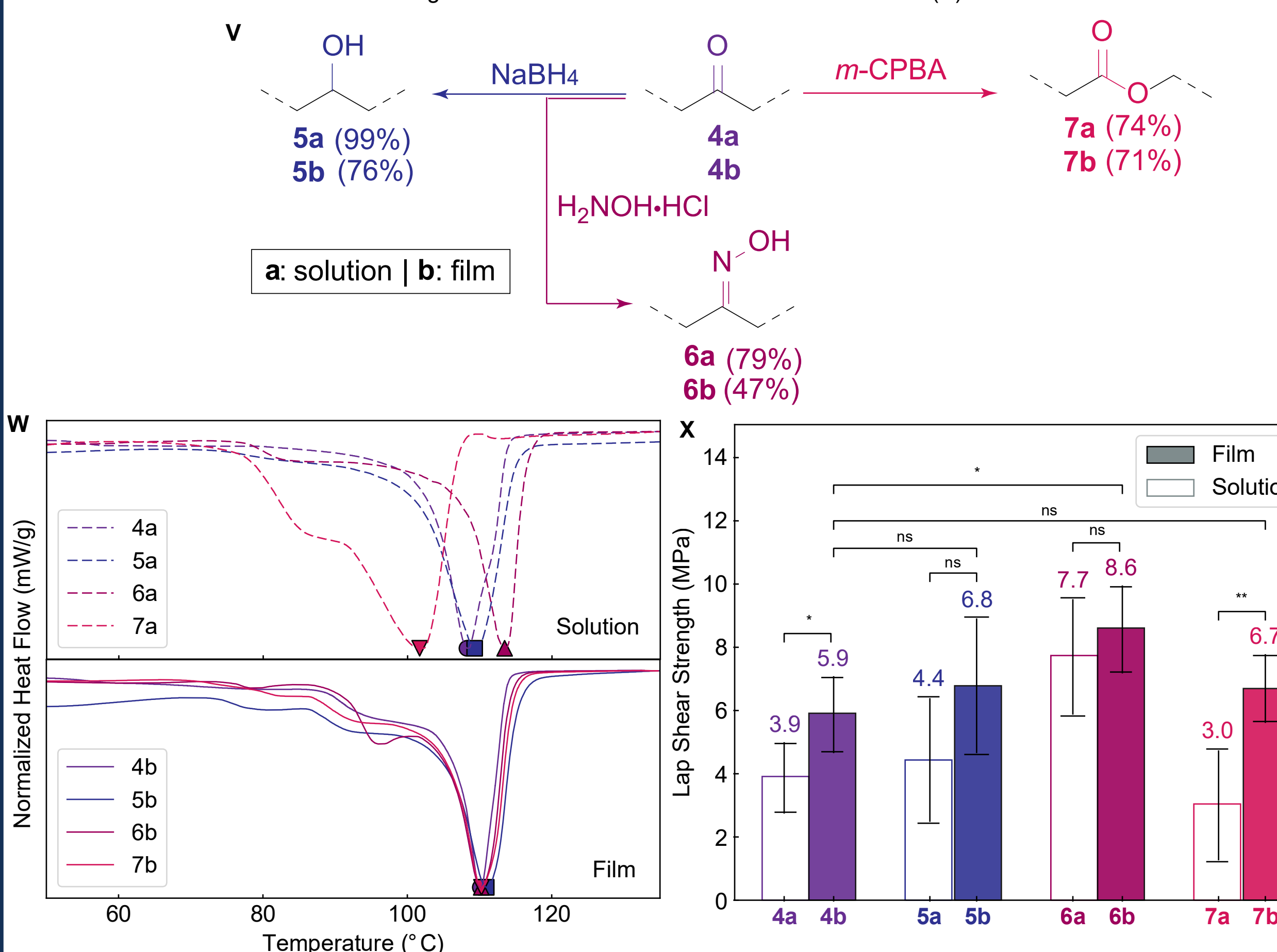


Oxidation levels correlated to oxidant concentration for oxidations in solution (S) and thickness for oxidations on films (T). Analysis of covariance (ANCOVA) of lap shear results demonstrated that the functionalization method significantly impacted adhesion strength ($p = 0.005$) (U).



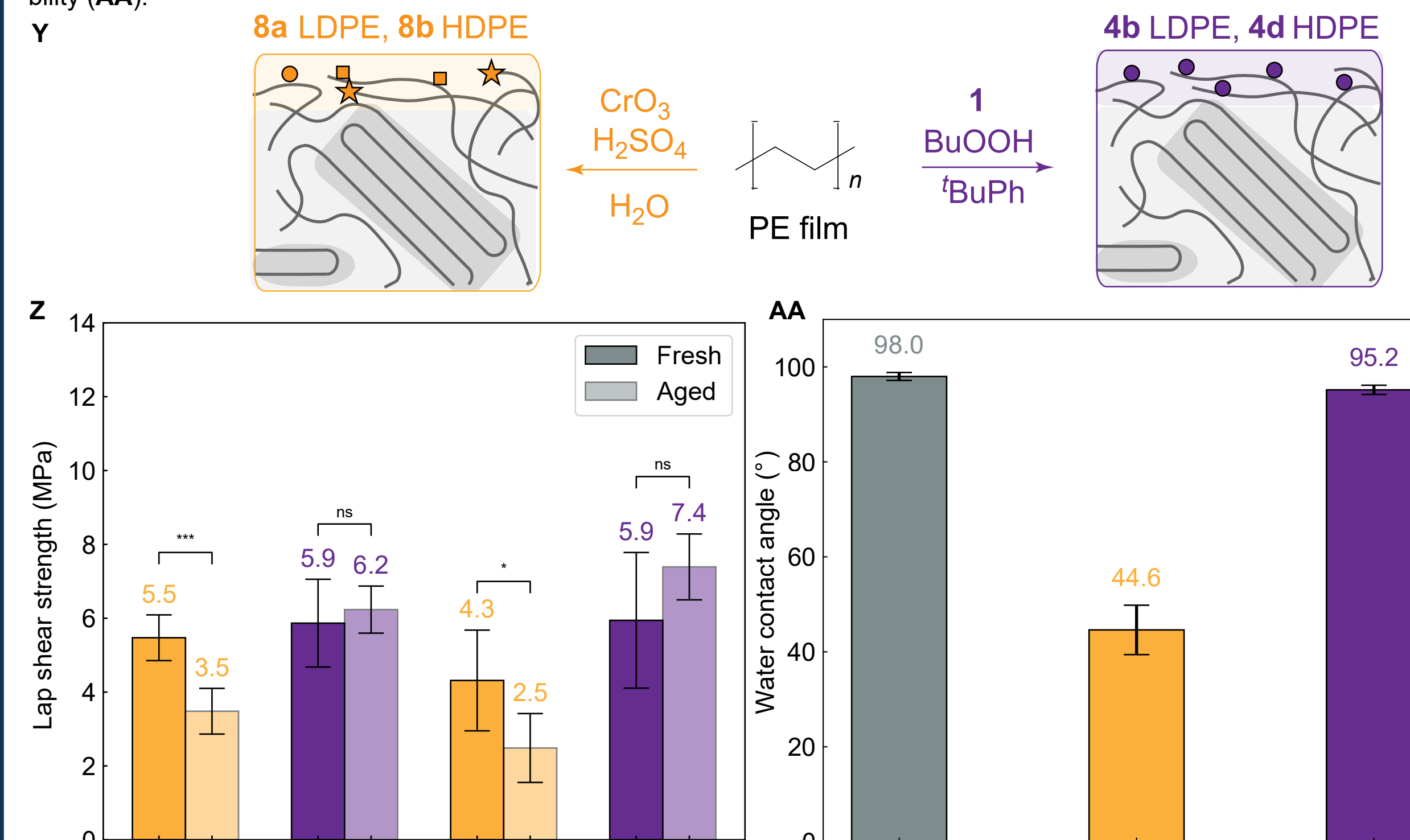
Derivatization of functionalized PE

LDPE functionalized with ketones was further derivatized into alcohols with NaBH₄, esters with *m*-CPBA, and oximes with H₂NOH·HCl both in solution and as films (V). PE functionalized in a solution exhibited significant deviations from the melting behavior of pristine LDPE whereas PE functionalized as a film did not (W). The average lap shear adhesion strength of LDPE functionalized as a film was higher than that of LDPE functionalized in solution (X).



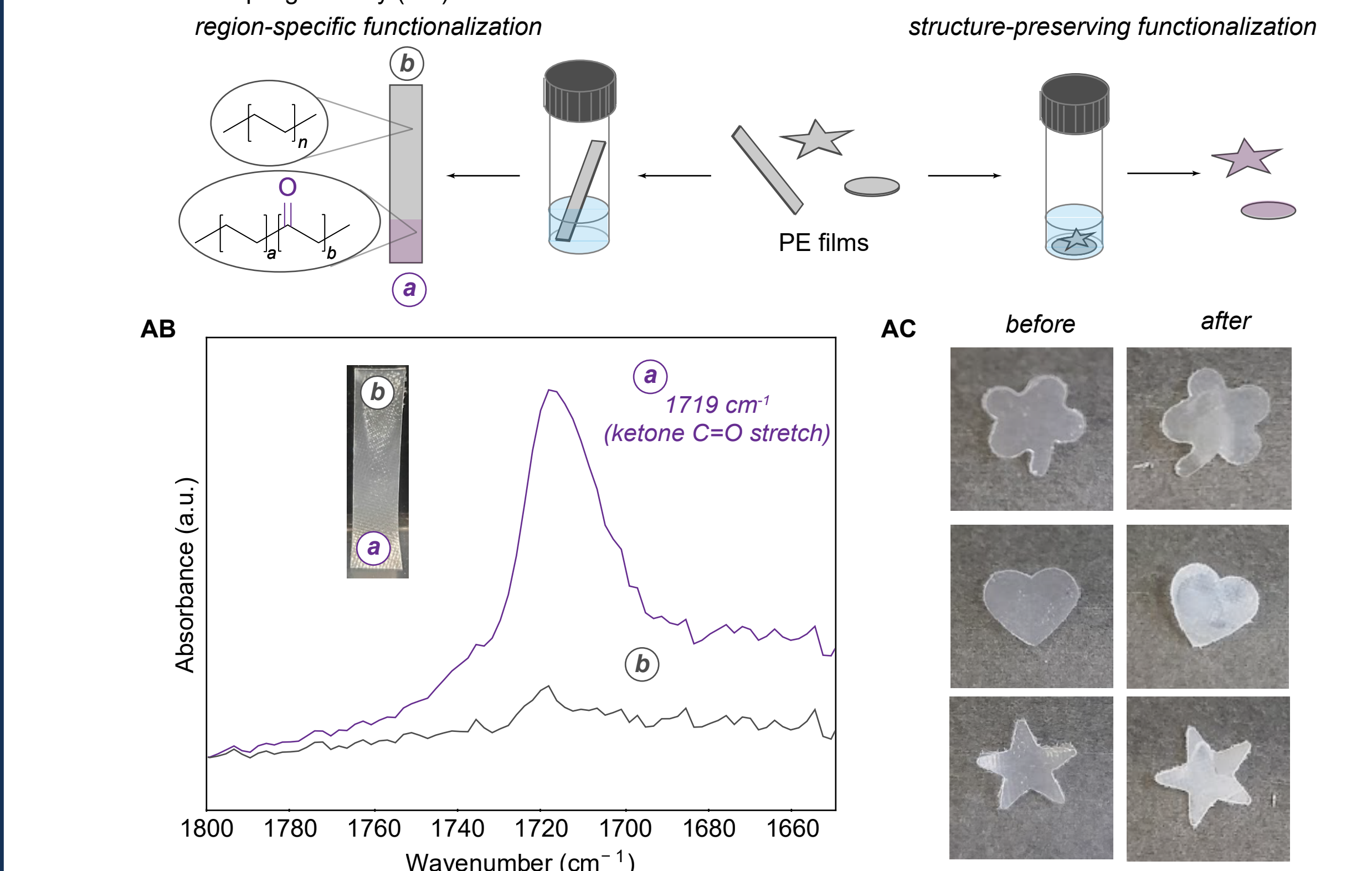
Chemical vs. catalytic surface oxidation

Catalytic surface oxidation produces exclusively ketone-functionalized PE, avoiding the complex mixture of functional groups typical of other chemical methods (e.g. Jones oxidation) (Y). Adhesion strength decays over two weeks for Jones oxidized PE whereas it is maintained for ketone-functionalized PE (Z). Water contact angle measurements indicate a more hydrophobic surface for ketone-functionalized PE, suggesting that reduced surface energy accounts for this improved stability (AA).



Spatial control of catalytic oxidation

Catalytic functionalization at the solid-liquid interface allows for alternative patterns of functionalization not accessible by solution-based methods, such as functionalization only on specific regions of a substrate (AB) and functionalization with retention of macroscopic geometry (AC).



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