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# Building Tunable Degradation into High-Performance Poly(acrylate) Pressure-Sensitive Adhesives

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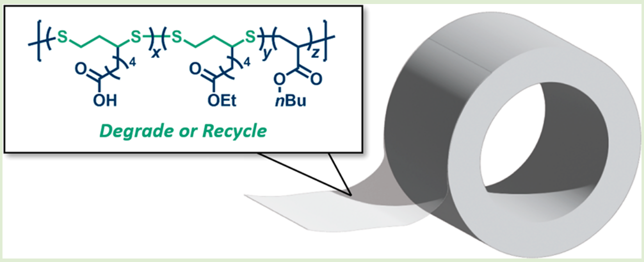

**ABSTRACT:** Pressure-sensitive adhesives (PSAs) based on poly(acrylate) chemistry are common in a wide variety of applications, but the absence of backbone degradability causes issues with recycling and sustainability. Here, we report a strategy to create degradable poly(acrylate) PSAs using simple, scalable, and functional 1,2-dithiolanes as drop-in replacements for traditional acrylate comonomers. Our key building block is $\alpha$-lipoic acid, a natural, biocompatible, and commercially available antioxidant found in various consumer supplements. $\alpha$-Lipoic acid and its derivative ethyl lipoate efficiently copolymerize with *n*-butyl acrylate under conventional free-radical conditions leading to high-molecular-weight copolymers ($M_n$ > 100 kg mol$^{-1}$) containing a tunable concentration of degradable disulfide bonds along the backbone. The thermal and viscoelastic properties of these materials are practically indistinguishable from nondegradable poly(acrylate) analogues, but a significant reduction in molecular weight is realized upon exposure to reducing agents such as tris (2-carboxyethyl) phosphine (e.g., $M_n$ = 198 kg mol$^{-1}$ → 2.6 kg mol$^{-1}$). By virtue of the thiol chain ends produced after disulfide cleavage, degraded oligomers can be further cycled between high and low molecular weights through oxidative repolymerization and reductive degradation. Transforming otherwise persistent poly(acrylates) into recyclable materials using simple and versatile chemistry could play a pivotal role in improving the sustainability of contemporary adhesives.

Adhesives are an important class of polymers used in a wide variety of applications, from commodity materials for construction and packaging to cutting-edge technology such as cell phones, cars, aircraft, and medical devices.[1,2] One popular example familiar to consumers and businesses alike is pressure-sensitive adhesives (PSAs). PSAs are conveniently manufactured on soft, flexible substrates to form products including labels, tapes (e.g., painter's, masking, duct, and Scotch), and the omnipresent Post-it Note.[2] A key feature distinguishing PSAs from other types of adhesives is their easy application and removal without leaving residue on the surface of interest, a striking feat of modern materials science and polymer design.[2−4] The global market demand for PSAs is around \$13 billion and growing (estimated to reach over \$17 billion by 2027), representing a sizable fraction of the overall adhesive industry (ca. \$65 billion per year).[5,6]

A contemporary challenge facing most applications of polymers, including, but not limited to, PSAs, relates to sustainability. Although advances have been made in recycling common plastics [e.g., poly(ethylene), poly(propylene), and substitutes thereof],[7−9] less progress is evident in the context of adhesives. Most PSAs are cumbersome or impractical to remove from a substrate (due to the insolubility of cross-linked networks), which causes adhesive residue to contaminate recycling equipment and prevents even recyclable plastics, paper, and cardboard from being reused (the so-called "stickies" problem[10−12]); methods to circumvent this challenge involve time-consuming and expensive swelling with harsh chemical agents (e.g., NaOH, amine solvents) followed by rigorous scrubbing.[13,14] In addition, like polyolefins, adhesives released into the environment or buried in landfills primarily contain C−C bonds along the backbone of each polymer chain, creating long-lived waste ("microplastic") that accumulates over hundreds of years.[15] These issues are particularly acute for poly(acrylates), which dominate the PSA industry (roughly 60% by volume)[5] and are key ingredients in other structural adhesives, sealants, rubbers, and plastics as well.[2]

In principle, on-demand degradability would resolve these sustainability challenges associated with adhesives. For example, soft polyesters can be fashioned into degradable PSAs.[16−19] However, unlike poly(acrylates), they remain a negligible percentage of the adhesives market (<1%) due to

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synthetic complexity, cost, and reduced performance. A viable alternative to conventional poly(acrylates) lies in the design of comonomers containing degradable functional groups.[17] Several studies have demonstrated the copolymerization of cyclic ketene acetals (CKAs) with acrylates as a method of introducing cleavable ester bonds along each polymer chain.[20−24] Despite their utility, CKAs have a number of drawbacks, including (i) competing side reactions of the CKA that lead to noncleavable C−C bonds, (ii) poor reactivity with acrylates, and (iii) difficulty achieving high molecular weights (i.e., >100 kg mol$^{-1}$) that are crucial for adhesive applications.[18,21,23] Other cyclic monomers that may overcome these challenges, such as thionolactones pioneered by Gutekunst[25] and Roth[26] or cyclic allyl sulfides,[27] involve an expensive, multistep synthesis. An ideal degradable comonomer would be available at scale, readily copolymerize with acrylates, and contain a functional handle for optimizing adhesive performance.

To address these challenges, here we introduce a versatile platform of comonomers for designing degradable poly(acrylate) PSAs based on $\alpha$-lipoic acid ($\alpha$LA), an edible natural product found in vegetables, biological redox processes, and a variety of consumer dietary supplements.[28] $\alpha$LA is commercially available (produced on the ~250 ton scale per year)[29] and inexpensive, featuring a 1,2-dithiolane ring that undergoes ring-opening polymerization at elevated temperatures or when exposed to ultraviolet light.[30−33] The thermal polymerization of pure $\alpha$LA was recently exploited in constructing dynamic self-healing materials with potential applications as structural adhesives.[34−36] $\alpha$LA and its derivatives are also known to copolymerize with various vinyl monomers,[37] including acrylates.[38−40] Pioneering work from the Tsarevsky group reported the radical copolymerization of ethyl lipoate and ethyl acrylate generates disulfide bonds within lipoate−lipoate diads that can be degraded under reductive conditions.[39] However, these past studies were limited to low molecular weights (for acrylates, $\lesssim$22000 g mol$^{-1}$) that are too small for PSA (or adhesive) applications where a sufficient number of entanglements are needed to appropriately tune viscoelasticity and adhesion.[2]

Here, we demonstrate that high-performance, high−molecular-weight PSAs can be synthesized using $\alpha$LA as a key degradable building block. Our copolymer design begins with the major component of traditional acrylate-based PSA formulations, $n$-butyl acrylate, along with two drop-in replacements that impart degradability: (i) $\alpha$LA, which acts as an adhesion promoter and site for cross-linking during PSA formulation, and (ii) ethyl lipoate (ELp) as a degradable analogue of $n$-butyl acrylate with similar viscoelastic properties (vide infra) that cannot be achieved with $\alpha$LA alone. Importantly, the degradability of these materials can be easily tuned during polymerization by changing the absolute monomer concentration and temperature, providing convenient control over the average lipoate−lipoate (diad) sequence and size of subsequently degraded fragments. Optimal compositions yield an almost eighty-fold decrease in molecular weight after chemical disulfide reduction (i.e., $M_n$ = 198 kg mol$^{-1}$ → 2.6 kg mol$^{-1}$) and adhesive performance on par with commercial poly(acrylate) products. In addition, by virtue of the thiols generated at both chain-ends after degradation, these oligomers can undergo repeated oxidative repolymerization and reductive redegradation, highlighting opportunities to use this design strategy for closed-loop adhesive recycling. In summary, these insights provide a simple, scalable, and tunable approach to form high-molecular-weight and degradable poly(acrylates), important ingredients in state-of-the-art PSAs and, more broadly, the field of materials science.

Design and synthesis: Traditional poly(acrylate) PSAs contains two types of monomers: one with a low glass-transition temperature (e.g., $n$-butyl acrylate, $T_g$ = −49 °C) and a second, more polar component (e.g., acrylic acid, AA) in much smaller loadings (~5 mol %) to provide adhesion and improve cohesive strength after cross-linking (Figure 1A).[2]

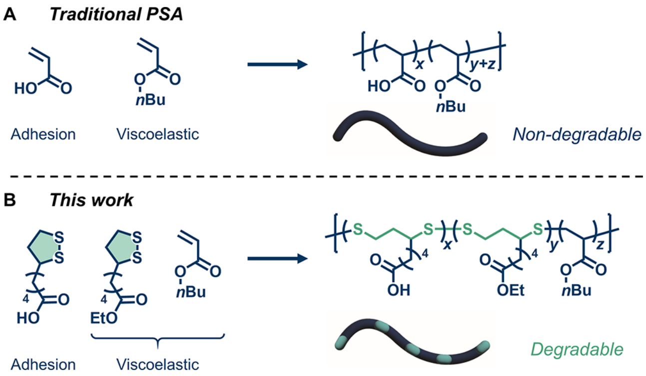

**Figure 1.** 1,2-Dithiolanes are drop-in, degradable monomers for poly(acrylate) pressure-sensitive adhesives. (A) A conventional statistical acrylic PSA comprises $n$-butyl acrylate (~97 mol %) and acrylic acid (~3 mol %). (B) An analogous statistical degradable PSA with $\alpha$-lipoic acid and ethyl lipoate as drop-in degradable monomers.

The design of our degradable analogues leverages $\alpha$LA as a drop-in replacement for these traditional monomers in two ways (Figure 1B). First, $\alpha$LA mimics acrylic acid in polarity and cross-linkability as both contain carboxylic acids. Second, $\alpha$LA can be functionalized with ethanol to form ethyl lipoate (ELp, see Supporting Information, Figure S1) in a single, high-yielding step at large scales (>50 g). Importantly, our experiments indicate key viscoelastic and thermal properties of poly(ethyl lipoate) (PELp) mimic those of poly($n$-butyl acrylate) (P$n$BA), including entanglement molecular weights determined rheometrically, $M_{e,\mathrm{PELp}}$ = 31 kg mol$^{-1}$ vs $M_{e,\mathrm{P}n\mathrm{BA}}$ = 28 kg mol$^{-1}$ (Figures S2 and S3),[41] and $T_{g,\mathrm{PELp}} = T_{g,\mathrm{P}n\mathrm{BA}}$ = −49 °C (Figure S4). Partially replacing $n$-butyl acrylate with ELp and acrylic acid with $\alpha$LA should therefore retain the salient performance of poly(acrylate) PSAs but confer degradability and increase sustainability.

To demonstrate the drop-in potential of 1,2-dithiolanes as building blocks for the synthesis of degradable poly(acrylate) PSAs, ethyl lipoate (ELp) and $n$-butyl acrylate ($n$BA) were selected as a model system and copolymerized at 2 M total monomer concentration using conventional free-radical polymerization at 40 °C with V-65 as a thermal azo-initiator.[42,43] Comprehensive characterization experiments (Figures S5−S9) indicate both monomers copolymerize efficiently with ELp incorporating more readily than $n$BA. Importantly, the resulting material has a significantly higher number-average molecular weight ($M_n$ = 143 g mol$^{-1}$) than previous reports, a range that is suitable for PSAs where a sufficient number of entanglements are needed to tune the viscoelasticity ($M \gg M_e$). Initial degradation experiments (Figure S10) indicate a substantial reduction in molecular weight ($M_n$ = 143 kg mol$^{-1}$ → 3.9 kg mol$^{-1}$) upon exposure to tris (2-carboxyethyl) phosphine (Table S3), a chemical

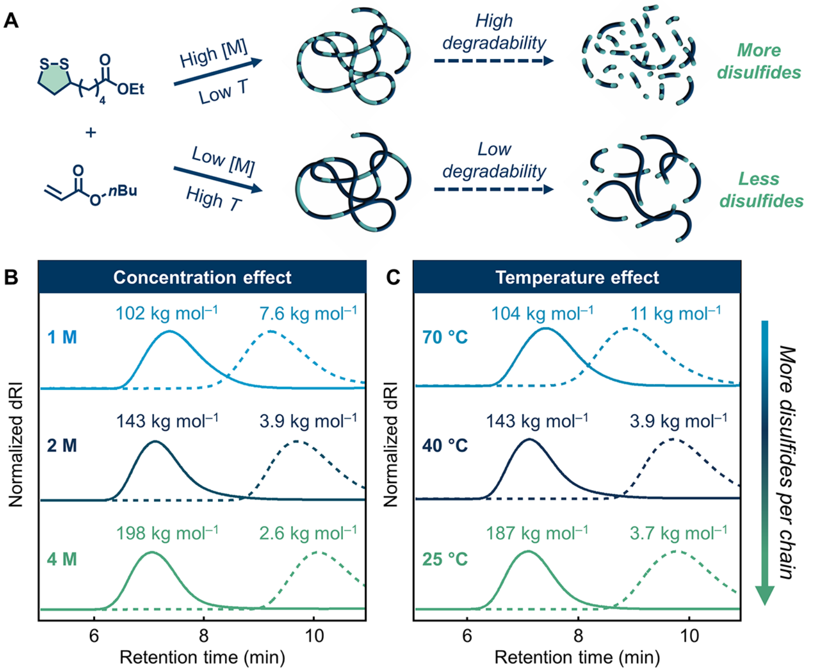

**Figure 2.** Tunable degradation of poly(acrylate) copolymers by controlling the concentration and temperature of polymerization. (A) The degradability of lipoic-acid−acrylate copolymers can be synthetically tuned through polymerization conditions that control the average number of disulfide bonds per polymer chain. (B, C) As evidenced by size-exclusion chromatography, (B) higher monomer concentrations ([M]), and (C) lower polymerization temperatures ($T$) improve degradability.

reductant that reduces the disulfide bond in ELp−ELp diads (see Figures S8a and S9).

A crucial observation made while synthesizing *n*BA−ELp copolymers is that diad sequence and degradability strongly depends on the reaction conditions used during polymerization (Figure 2A). Larger absolute monomer concentrations (total [M], Figure 2B) and lower reaction temperatures ($T$, Figure 2C) result in higher as-synthesized molecular weights yet smaller oligomers after degradation (see the Supporting Information for further details, Figures S10−S13). Although unexpected based on common acrylate copolymerization behavior,[44] these results can be understood through an analysis of reaction kinetics. In the "terminal model", wherein the rate of monomer addition depends only on the chemical identity of a propagating chain end, the "copolymer equation" is often used to relate the feed and polymer compositions at any instance in time (eq S2).[45] Within this framework, the absolute concentration (e.g., expressed in mol cm$^{-3}$) of monomers 1, $[M_1]$, and 2, $[M_2]$, has no influence on polymer composition since $[M_2]/[M_1]$ always appears as a ratio.[45] Any temperature-dependence is also minimal because the various propagation rate constants typically exhibit small differences in activation energy and are subsumed into so-called reactivity ratios $r_1$ and $r_2$.[45] However, the copolymer equation is predicated on each propagation step being irreversible.[44] Literature suggests this may not be true for *n*BA−ELp copolymerization as ELp homopolymerization exhibits a ceiling temperature ($T_c$ = 139 °C) that is characteristic of an equilibrium arising from reversible monomer addition.[46−49] In 1971, Wittmer[44] derived an analogue of the copolymer equation that addresses reversible monomer addition for one (shown below) or both components:

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + r_1\frac{[M_1]}{[M_2]} - r_1\frac{K_1}{[M_2]}(1 - x_1)}{1 + r_2\frac{[M_2]}{[M_1]}} \qquad (1)$$

where $d[M_1]/d[M_2]$ is the instantaneous composition of polymer formed, $K_1$ is an equilibrium constant characterizing the rate of depropagation vs propagation, and $x_1$ ($r_1$, $K_1$ $[M_1]$, $[M_2]$) is a function of the same variables and abbreviated in eq 1 for clarity (see the Supporting Information for a full definition, eqs S3 and S4). Here, we define component 1 as ELp and 2 as *n*BA. As is evident in eq 1, the instantaneous composition of polymer includes a term that scales as $K_1/[M_2]$, which depends on both the absolute concentration $[M_2]$ and temperature through the equilibrium constant $K_1$. Apparently, the copolymerization of ELp or αLA with *n*BA exhibits reversibility in the propagation of 1,2-dithiolane monomer, which explains the pronounced dependence of degradability on both the concentration and temperature ($T$) used during polymerization. $[M_2]$ and $T$ control the average sequence of monomers along a polymer chain, with higher $[M_2]$ and lower $T$ favoring the formation of ELp−ELp units containing degradable disulfide bonds (see Figures S10 and S12). Additionally, application of eq 1 at low monomer conversions provided an estimate of the reactivity ratios for *n*BA−ELp copolymerizations (Figure S8): $r_{\mathrm{ELp}}$ = 18.5 and $r_{n\mathrm{BA}}$ = 0.36. These values accentuate two features of acrylate−1,2-dithiolane polymerizations that are necessary for efficiently forming degradable poly(acrylates): (i) lipoate is readily incorporated into growing polymer chains ($r_{\mathrm{ELp}} \gg 1$, $r_{n\mathrm{BA}} < 1$), and (ii) lipoate radicals preferentially add to lipoate monomer ($r_{\mathrm{ELp}} \gg 1$), both of which generate degradable disulfide bonds along the polymer backbone.

Adhesive performance: With optimized synthesis and degradation conditions identified, we turned to studying

**Figure 3.** $\alpha$LA/ELp/*n*BA copolymers are general purpose PSAs, i.e., easy to apply, remove, and reuse without leaving residue on common surfaces.

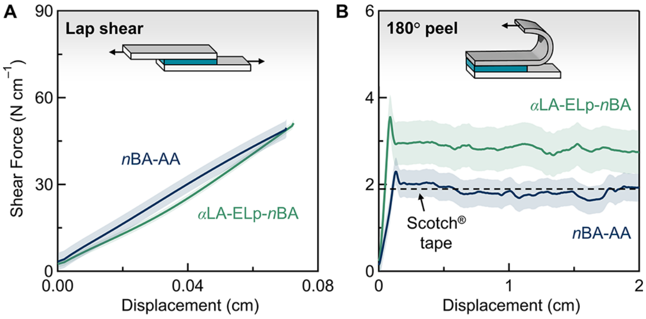

**Figure 4.** Conventional and degradable poly(acrylate) PSAs have similar adhesive performance. Degradable $\alpha$LA-ELp-*n*BA PSAs have similar cohesive and adhesive properties as conventional *n*BA-AA copolymers. (A) Lap shear with a uniaxial extension rate of 0.5 mm min$^{-1}$. (B) 180° peel test with a uniaxial extension rate of 100 mm min$^{-1}$. Error envelopes represent two standard deviations from replicate runs. Commercial values for Scotch tape were obtained from literature.[52]

these materials as pressure-sensitive adhesives (Figure 3). A small library of statistical terpolymers was synthesized from three components in various ratios: $\alpha$LA, ELp, and *n*BA (recall Figure 1B, see Table S5). All of these copolymers were bench-stable for at least one year (Figure S20). The following analysis will focus on a poly(lipoic acid-*co*-ethyl lipoate-*co*-*n*-butyl acrylate) ($\alpha$LA-ELp-*n*BA) copolymer comprising 3:58:39 mol % $\alpha$LA/ELp/*n*BA, although a variety of compositions achieve a suitable balance of adhesive performance and degradability, which allows for further tunability. As is common in commercial poly(acrylate) PSAs,[50] $\alpha$LA/ELp/*n*BA was formulated with $Al(acac)_3$ at low loadings to improve cohesive strength through light cross-linking (Figure S24). Above 0.3 wt % $Al(acac)_3$, formulations failed adhesively as desired, with 0.4 wt % (approximately 3 cross-links per chain) selected for a detailed comparison of physical properties. A control adhesive, poly(*n*-butyl acrylate-*co*-acrylic acid) (*n*BA-AA) with a composition of 97:3 mol %, was also designed and synthesized to mimic traditional commercial adhesives without additional plasticizer or tackifier.

For general-purpose PSAs, frequency-dependent rheological properties are critical to properly control bonding (~0.01 Hz) and debonding (~100 Hz). To demonstrate the similarities between degradable ($\alpha$LA-ELp-*n*BA) and traditional (*n*BA-AA) PSAs, master curves were generated via rheometry with isothermal frequency sweeps ($0.1 \le \omega \le 100$ rad/s) at fixed strain amplitude over a temperature range from −35 to 85 °C. As shown in Figure S19 they are nearly indistinguishable, highlighting the potential of lipoate as a drop-in replacement for *n*BA-based adhesives. Indeed, measurements of cohesive (Figure 4A) strength confirm the similar performance of degradable (51 N cm$^{-1}$ ± 0.6) and nondegradable (48 N cm$^{-1}$ ± 1.5) analogues due to similarities in their chemistry and cross-link density.[10] The degradable material shows slightly superior adhesive performance (2.8 N cm$^{-1}$ ± 0.27 vs 2.0 N cm$^{-1}$ ± 0.15, Figure 4B), likely due to interactions between sulfur and the glass substrate.[35,51] See the Supporting Information for experimental details regarding these lap-shear and 180° peel tests.

Opportunities in recycling: The degradability of 1,2-dithiolane−acrylate copolymers derived from $\alpha$-lipoic acid creates multiple opportunities to recycle otherwise persistent adhesive materials. Figure 5A showcases the power of on-demand degradability in the context of labels attached to disposable plastic bottles made of poly(ethylene terephthalate). Unlike conventional acrylic PSAs, $\alpha$LA-ELp-*n*BA degrades cleanly from between the label and bottle when immersed in a solution of tris (2-carboxyethyl) phosphine (TCEP). TCEP is commonly used for biochemical applications[53] as a mild reducing agent in stark contrast to traditional degumming procedures that require caustic chemicals for label removal.[13,14] Other reducing agents promoted efficient degradation as well, including dithiothreitol (DTT; Figure S29) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with octanedithiol (Figure S30). Additional opportunities exist in recycling batteries, electronics, and packaging.[10] A second option exists related to closed-loop recycling that leverages the chemistry of these degradation products. In principle, reduction of the disulfide bonds along as-synthesized polymer chains yields telechelic fragments with thiols at each chain end (Figure 5B). (Note there is presumably a mixture of primary and secondary thiol chain ends based on the regiorandom incorporation of 1,2-dithiolanes during copolymerization, as well as possible thioether fragments within the oligomers that are not depicted for clarity.) Coupling experiments on degraded fragments with maleimide-Disperse Red 1 in the presence of DBU confirms the presence of reactive thiols at both chain-ends as monitored by SEC with a UV-absorbance detector (see Supporting Information, Figures S31). These thiols can be exploited to cycle between high molecular weight

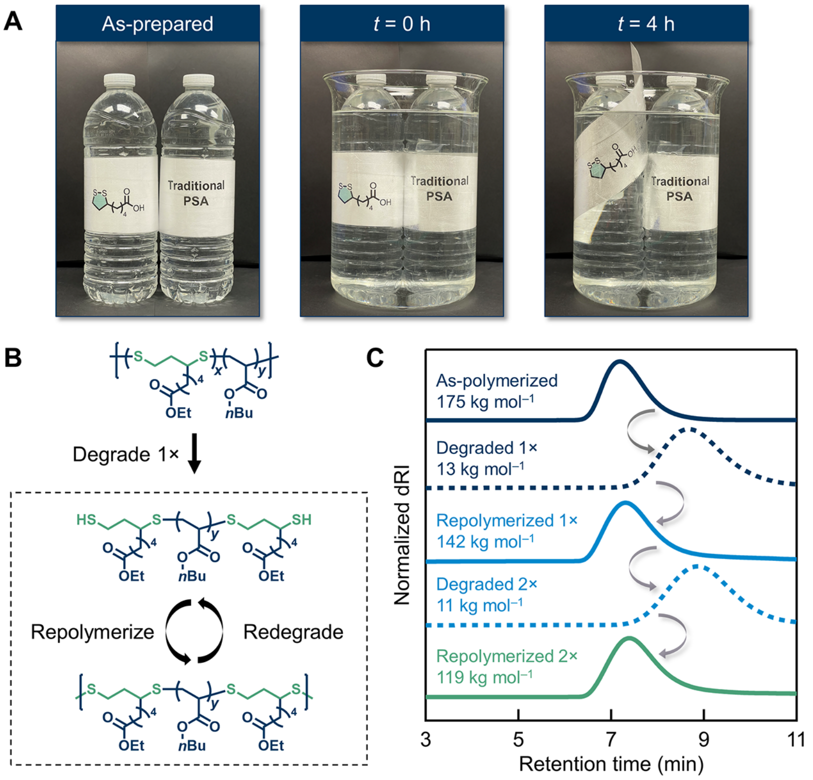

**Figure 5.** On-demand degradability and repolymerizability creates opportunities in recycling otherwise persistent adhesive materials. (A) Removal of label adhesive ($\alpha$LA-ELp-*n*BA and *n*BA-AA) attached to recyclable plastic bottles. (B) Model adhesive (ELp-*n*BA) with functional chain-ends produced after degradation can undergo repeated oxidative repolymerization and reductive degradation for closed-loop recycling, as evidenced by (C) size-exclusion chromatography analysis.

and low molecular weight copolymers. For example, an as-synthesized ELp-*n*BA copolymer ($M_{\text{n,original}}$ = 175 kg mol$^{-1}$) that was initially degraded into fragments with $M_n$ = 13 kg mol$^{-1}$ can be oxidatively repolymerized using $I_2$ and pyridine to reform disulfide bonds along the backbone and recover high molecular weight material ($M_{\text{n,1×}}$ = 142 kg mol$^{-1}$). Subjecting this sample to the same TCEP degradation conditions again reduces $M_n$ to 11 kg mol$^{-1}$ and another repetition of oxidative upcycling reforms the copolymer backbone with $M_{\text{n,2×}}$ = 119 kg mol$^{-1}$. Although there is a modest reduction in molecular weight after repeated cycling, these values remain sufficient for adhesive applications; we anticipate this behavior can be further refined based on the initial molecular weight, composition, and degradation/repolymerization conditions. Our results establish the utility of oligomeric dithiols produced after degradation, complementing past work on the full depolymerization of poly($\alpha$-lipoic acid) back to 1,2-dithiolane monomer.[31]

In conclusion, 1,2-dithiolanes are drop-in replacements for acrylates that transform poly(acrylates) into degradable pressure-sensitive adhesives without sacrificing performance. As exemplified by $\alpha$-lipoic acid and its derivative ethyl lipoate, these building blocks are simple, scalable, and versatile. The composition and associated degradability of poly(lipoic acid-*co*-ethyl lipoate-*co*-*n*-butyl acrylate) copolymers is readily tuned by varying the temperature and concentration of copolymerization reactions with this novel reactivity due to the reversible propagation of 1,2-dithiolane units. Lower temperatures and higher monomer concentrations generate more degradable lipoate−lipoate diads and associated disulfide bonds along the backbone, a powerful strategy to create recyclable pressure-sensitive adhesives via radical copolymerization that mimics commercial systems. We anticipate these results will further impact other areas of materials science where sustainability is crucial and poly(acrylates) are prevalent, for example, structural adhesives, sealants, and plastics.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

All curated data are available in the manuscript or the Supporting Information. Raw data are available from a permanent online repository at DOI: 10.25349/D9391Z.

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00204.

> Experimental methods, representative molecular characterization data (SEC, NMR, DSC), rheological analysis, and tensile data (PDF)

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### Author Contributions

K.R.A., Y.O., and C.M.B. wrote the paper. K.R.A., Y.O., C.C., and P.T.M. synthesized and characterized materials. K.R.A., Y.O., C.C. P.T.M., M.G., R.G., J.C.S., J.R.A., C.J.H., and C.M.B. designed experiments.

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### Notes

The authors declare the following competing financial interest(s): UC Santa Barbara has filed a patent application (PCT/US23/61259) on behalf of inventors K.R.A., C.C., M.G., J.R.A., and C.M.B. covering the technology described herein. The authors declare no other competing financial interest.

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