

Electrocatalytic Grafting of Polyvinyl Chloride Plastics

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ABSTRACT: Polyvinyl chloride (PVC) plastics require high loadings of plasticizers and stabilizers to achieve commercially useful bulk properties. However, these non-covalent additives leach from PVC over time, resulting in the loss of their tailored functionality. This work details the electrocatalytic functionalization of PVC to covalently graft plasticizing additives directly onto the polymer backbone. Here, mechanistic insights guided the design of electrocatalysts capable of modifying C–Cl bonds of PVC under mild conditions with high selectivity while suppressing side reactions such as elimination and chain scission. Functional groups that mimic PVC plasticizers are covalently installed into the backbone of PVC to create new materials with distinct bulk properties from the original polymer. The degree of polymer grafting is easily controlled by simply changing the redox capacity that is passed during electrolysis. This strategy is employed to create chemically- and leach-resistant PVC materials by directly electrolyzing mixtures of consumer PVC products.

INTRODUCTION

Polyvinyl chloride (PVC) ranks third among the most consumed plastics worldwide, following only polyethylene (PE) and polypropylene (PP).^{1,2} PVC plastics are used in myriad applications including siding, flooring, plumbing, wiring, and medical packaging. Despite the breadth of properties exhibited by these commercial PVCs, pure PVC has a surprisingly narrow range of bulk properties. Many of these properties, such as brittleness and thermal instability, are undesirable in plastics. Additionally, modifying these properties through the synthesis of the polymer itself, like with catalyst-controlled PE or PP synthesis,^{3–7} is difficult because PVC is prepared by free-radical polymerization.⁸

Altering the undesirable bulk properties of pure PVC relies on high loadings (up to 50%) of plasticizers, stabilizers, and impact modifiers.⁹ Such formulations are only possible because PVC is polarized by its C–Cl bonds, and the polymer can interact with additives to form homogeneously-dispersed materials.¹⁰ However, these non-covalent additives migrate to leach or “bloom” from PVC plastics over time. The continuous loss of plasticizing additives as the plastic ages compromises the integrity of the plastic, causing the material to exhibit the undesirable properties of pure PVC (Figure 1a, top).¹¹ The aged materials deteriorate and shed microplastic particulates.^{12–14} As a result, the aged materials must be replaced more frequently, and the wastes

contain more defects that limit the recyclability of the plastic. End-of-life disposal of aged PVCs is equally problematic. Unlike conventional polyolefins, PVCs do not cleanly burn because of their high chloride content. Recycling with other plastics in high-temperature melts releases corrosive (HCl) byproducts that damage recycling facilities.^{15,16} Finally, the leached plasticizers themselves can be harmful, and many are banned from use in food or medical supplies by the FDA.^{11,13}

The impact of these and other accumulated plastics on the environment, food, and drinking water has spurred efforts to develop new chemistries for upcycling, recycling, and modifying polymers.^{17,18} One synthetic strategy that could address many of the highlighted limitations of PVC materials would be to covalently graft plasticizing additives directly to the PVC backbone (Figure 1a, bottom). Such synthetic methods could reduce or eliminate the reliance on non-covalent formulations for altering the bulk properties of PVC. This strategy would also create chemically-resistant PVCs that retain the flexibility of highly-plasticized formulations.

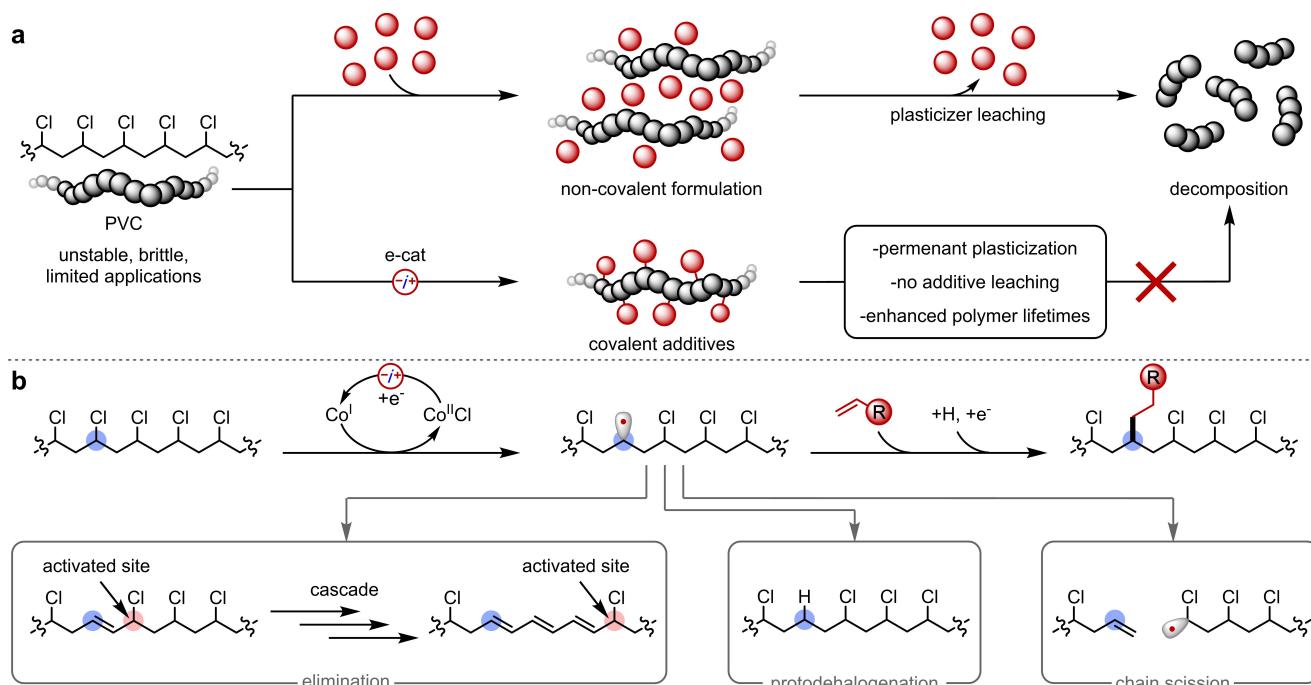


Figure 1. PVC plastic life cycle (a) Traditional PVC formulations and proposed solution. (b) Possible mechanistic pathways for radical PVC functionalization.

However, synthetic methodologies that could be applied to polymer modification often fail because the reaction conditions were originally developed for small-molecule analogs. As an example, mild and selective C-H functionalization reactions are known for a breadth of small molecule substrates,¹⁹ but metal-catalyzed C-H bond modification of PE and PP without polymer scission has only recently been realized.^{20–23} Minor side reactions that might cause a negligible erosion of product yield for small-molecule substrates can have outsize influences on macromolecular substrates. The effects of these undesired reactions are amplified when modifying polymers because the modification reaction occurs repeatedly on the same polymer chain. Eventually, the undesired reaction will occur to create defects in the polymer or cause chain scission, which ultimately compromises the material.

Chemical modification of PVC similarly suffers from deleterious side reactions because error-free functionalization of the secondary chloroalkyl sites found in PVC is a challenging reaction on even small molecule substrates. The most common side reactions encountered during modification of PVC include protodehalogenation, chain scission, and elimination (Figure 1b).^{24,25,34–36,26–33} Elimination reactions within PVC are particularly problematic because the resulting alkene destabilizes the adjacent chloride towards further elimination, and a cascading elimination reaction propagates down the polymer chain. PVC modification reactions by nucleophilic substitution are particularly susceptible to elimination reactions and typically rely on azides and multi-step processes,^{37–41} or require designer nucleophiles based on thiols²⁸ that are synthetically tedious to prepare, limiting the flexibility of reagents that can be grafted onto the PVC backbone.

Herein, we report the electrocatalytic grafting of plasticizers onto PVC polymers. Plasticizer mimics are covalently bound to the polymer backbone via C-C bond formation by electroreductive C-Cl bond alkylation under mild conditions. Tuning of the $E_{1/2}$ and the steric properties of the catalyst was shown to suppress side reactions such as protodehalogenation, elimination, and chain scission. The degree of polymer grafting is easily controlled by simply changing the redox capacity that is passed during electrolysis. These grafted polymers exhibit different material properties than those of raw PVC and can be altered based on their grafting density. This methodology establishes a new approach to plasticization of both PVC plastics and poly-chlorinated wastes.

RESULTS AND DISCUSSION

Recent efforts from our group have targeted electrocatalytic methodologies to activate and functionalize C-Cl bonds of simple chloroalkanes.⁴² If mild enough, such reactions could potentially be translated to on-bond reactions of PVC, and electrochemistry could serve as a controllable and scalable means to deliver reducing equivalents. While catalytic reactions of activated chloroalkanes are known,^{43–50} reactions of unactivated secondary C-Cl bonds like those found in PVC remain rare.^{51–54} To this end, we recently reported that salen complexes of Co serve as excellent electrocatalysts for reductive alkylation of unactivated chloroalkanes with acrylates and other conjugated olefins (Figure 2a).⁴² Acrylates were strategically selected as coupling partners for small-molecule chloroalkanes because the resulting alkyl esters mimic the poly(methyl methacrylate) (PMMA) and di-(2-ethylhexyl)phthalate (DEHP) esters used as plasticizing additives in commercial formulations of PVC.⁵⁵

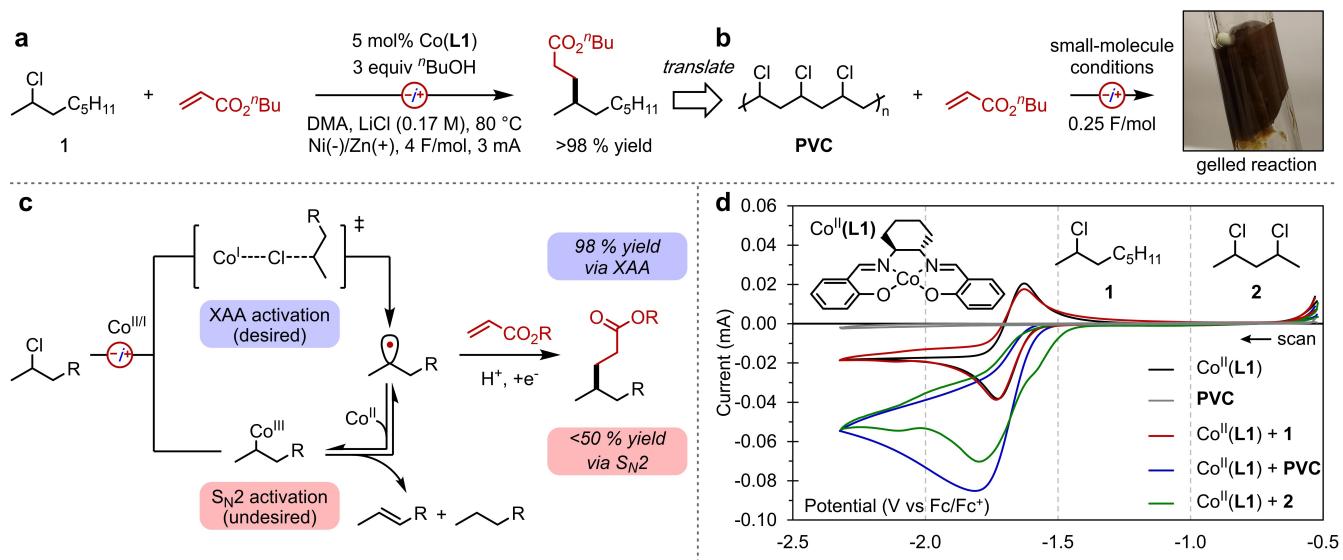


Figure 2. Mechanistic studies comparing small molecule and macromolecular polychlorinated alkanes. (a) Previous strategy for alkyl chloride functionalization. (b) Translation of small molecule reaction conditions to macromolecular setup. (c) Mechanistic analysis of small molecule reaction pathways. (d) CV analysis of chloride sources with Co(L1). Conditions: 176 mM LiCl/DMF, 10 mM Co(L1), 500 mM alkyl chloride, room temperature.

Secondary alkyl chlorides such as 2-chlorooctane (**1**) undergo reductive alkylation with acrylates in near quantitative yields. However, our first attempts to translate this methodology from small molecule substrates to PVC failed (Figure 2b). Reactions with 31 mg/mL PVC (0.5 M pseudo concentration of the repeating ethylene chloride fragment) gelled upon application of a current. The stark difference in reaction outcomes between the two substrates led us to compare the reactivity of the reduced catalyst with PVC against chloroalkane **1** using cyclic voltammetry (CV). Previous studies on small molecule substrates using CV revealed that yields of alkylated products are closely tied to the mechanism of C-Cl bond activation. Specifically, reactions that occur predominantly by nucleophilic displacement of chloride by a reduced Co^I intermediate generally form products in low yields (Figure 2c, S_N2 pathway). The Co^{III}(alkyl) intermediates formed through this substitution mechanism can fragment to form the desired alkyl radical but can also form alkenes and alkanes from respective elimination or proto-demetallation. Nucleophilic activation of C-Cl bonds can be suppressed in favor of halogen atom abstraction (XAA) through ligand design and the use of supporting electrolytes of coordinating halides, such as LiCl (Figure 2c, XAA pathway). Reactions proceeding by XAA efficiently form alkyl radicals with none of the byproducts and generate products with near-quantitative yields.

Distinguishing these two mechanisms proved trivial by CV. Chloroalkane C-Cl bond activation by S_N2 forms a Co^{III}(alkyl) intermediate that is detectable by a distinct cathodic wave at -2.1 V vs. Fc/Fc⁺ (see the SI Figure S6). In contrast, reactions that proceed by XAA regenerate Co^{II} following halogen abstraction, and CVs exhibit only a single, irreversible reduction at the Co^{III/II} couple ($E_{1/2} = -1.7$ V Fc/Fc⁺) with a catalytic current increase. While elevated tem-

peratures (80 °C) are required for any significant catalytic current in CVs of Co(L1) and 2-chlorooctane **1**, those with added PVC revealed catalytic currents at just room temperature (Figure 2d, blue trace). CVs of a small-molecule substrate (**2**) that mimics PVC with a gamma-dichloride substituents revealed similar catalytic current responses (green trace), while those with the monochloride **1** were unchanged at room temperature (red trace). These results suggest that the increased reactivity of PVC towards the reduced catalyst is the result of the dichloride substitution pattern, rather than an artifact of a unique polymer-electrode interaction. The room temperature activation of C-Cl bonds in the 2,4-dichlorinated substrates likely stems from a greater destabilization of the starting material than from the stability of the alkyl radical.^{56,57}

These insights guided our evaluation of milder conditions and less reactive complexes for reactions of PVC than for those of simple 2° alkyl chlorides. We first reduced the temperature of PVC grafting reactions from 80 °C to room temperature. We next restricted electrolysis to 0.25 electron equivalents per alkyl chloride unit as a baseline standard of comparison. Reactions at this reducing capacity provide a theoretical grafting of **1** in 8 chlorides of the PVC backbone (12.5% graft density). Reactions under the modified conditions were completed within 3.5 h at constant current, and the solutions never gelled. An off-white solid was recovered by precipitation with methanol (Figure 3a, right photo), and residual organics were rinsed away with toluene. Infrared spectroscopy of the modified PVC solid (**PVC-1**) revealed a strong absorbance at 1727 cm⁻¹, which is consistent with the carbonyl stretch of an ester fragment. The presence of esters in the isolated material was further supported by ¹H NMR spectroscopy. Resonances of methylene protons alpha to oxygen (4.1 ppm) of the butyl ester are observed in the ¹H NMR

spectrum of **PVC-1** (Figure 3b, red trace) but are absent in spectra of unmodified PVC (black trace).

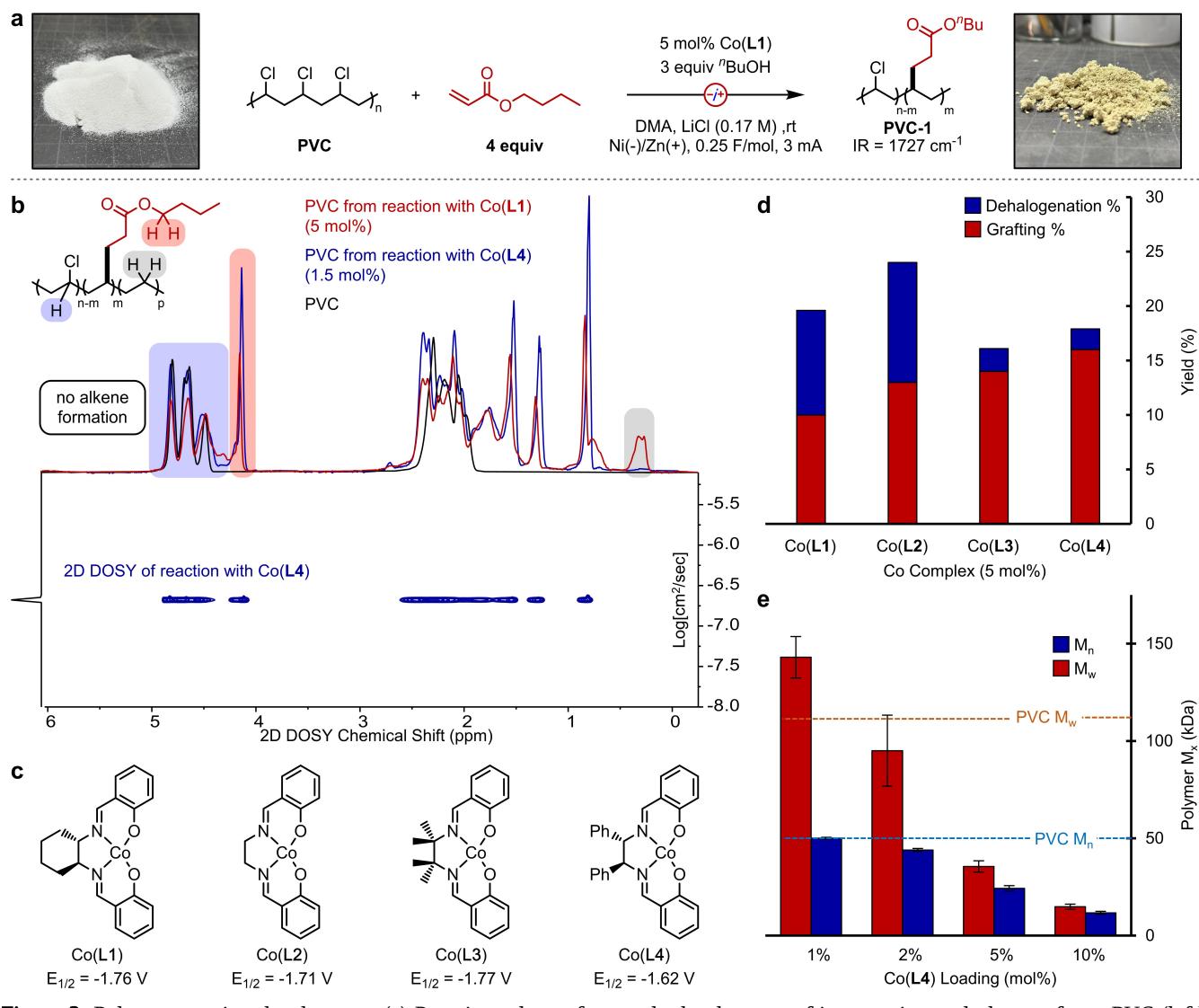


Figure 3. Polymer reaction development (a) Reaction scheme for standard polymer grafting reaction and photos of raw PVC (left) and grafted polymer (right). (b) 2D DOSY NMR of grafted PVC mixed with butyl acrylate. 1D ¹H NMR spectra depict products grafted with Co(L1) (red trace) and Co(L4) (blue trace) under the standard reaction conditions. (c) Catalyst screening for PVC functionalization. E_{1/2} values are referenced versus Fc/Fc⁺. (d) Comparison of grafting percentage and protodehalogenation for Co salen catalysts. (e) Comparison of average number molecular weights (M_n) and the weight average molecular weights (M_w) of grafted polymers at different catalyst loadings.

We performed ¹H NMR diffusion ordered spectroscopy (DOSY) to confirm that the detected ester fragments were covalently bound to PVC, rather than separate impurities (e.g., polyacrylate) that may have co-precipitated with unmodified PVC. The ¹H NMR DOSY plot of **PVC-1** reproduced in Figure 3b reveals that resonances of protons alpha to chloride (4.7 ppm, blue highlight) as well as those of the ester (red highlight) have an identical diffusion coefficient ($10^{-6.7}$ cm²/s) and are therefore part of the same molecule. The diffusion coefficient of **PVC-1** is nearly identical to that of unmodified PVC ($10^{-6.4}$ cm²/s), and both macromolecules diffuse more slowly than the small-molecule solvents or acrylates (see the SI, Figure S4, $10^{-5.1}$ cm²/s).

The percentage of alkylated C-Cl bonds in PVC can be calculated by the relative ratios of fragments in the modified PVC as determined by ¹H NMR spectroscopy (see the SI, Eq. 1 and Figure S5). Reactions catalyzed by Co(L1) resulted in 10% grafting of the chloride sites on PVC. PVC products recovered from control experiments with the electrodes submerged in solution but without an applied current were largely unchanged and had only a trace of grafted acrylate (<3%) (see the SI, Table S2). Critically, alkenyl fragments that frequently form in conventional substitution reactions of PVC were not detected in the isolated materials, as revealed by the absence of alkanyl resonances in the 5-6 ppm region. However, a significant percentage of chloride sites had undergone

proto-dechlorination (9.6%) as indicated by the upfield, aliphatic resonances (Figure 3b, gray highlight). We hypothesized that the electron-rich properties of Co(**L1**) ($E_{1/2} = -1.76$ V), which made for an effective catalyst in reactions of small-molecule chloroalkanes, could enable competing and undesirable pathways for C–Cl bond activation in reactions of more reactive chloroalkanes like PVC. Indeed, CVs at low scan rates (10 mV/s) of Co(**L1**) and the PVC model 2 revealed a small cathodic wave at -2.1 V that corresponds to the reduction of a Co^{III}(alkyl) intermediate formed by S_N2 as a minor – but competing – pathway to XAA (Figure 2d, green trace).

To inhibit C–Cl bond activation by nucleophilic attack, we evaluated reactions of PVC catalyzed by complexes with more positive reduction potentials (**L2** and **L4**) or with more steric hindrance (**L3**) than the parent complex of **L1** (Figure 3d). Reactions catalyzed by complexes with Co(**L2**) at slightly less reducing potentials ($E_{1/2} = -1.71$ V) than Co(**L1**) resulted in polymers with similar levels of protodechlorination (11%) but higher grafting percentages (13%) (Figure 3e). Increasing the steric bulk around Co with the tetramethyl ligand **L3** dramatically improved the selectivity for grafting (14%) over dechlorination (2%) despite the similar redox potential to Co(**L1**). Finally, the combination of increased steric bulk and mild reduction potential is incorporated into Co(**L4**). Reactions catalyzed by this complex resulted in highest grafting percentages (16%). CVs of Co(**L4**) and the model substrate 2 are absent of a reductive wave for a Co^{III}(alkyl) intermediate, which indicates suppression of the undesired S_N2 pathway (see the SI, Figure S8).

Analysis of isolated products by ¹H NMR spectroscopy guided improvements to chemoselectivity of the reaction. However, size exclusion chromatography (SEC) revealed that the modified **PVC-1** had a significantly lower average molecular weight ($M_w = 32$ kDa) than that of the initial PVC (112 kDa). Butyl acrylates grafted in place of chlorides along the PVC backbone should increase, rather than decrease, the M_w of the polymer. These results suggest that polymers undergo chain scission during electrocatalysis. The decreased number average molecular weight ($M_n = 24$ kDa) of the product materials over PVC ($M_n = 50$ kDa) further supports the formation of polymer fragments.

Control reactions revealed that chain scission only occurs in the presence of catalyst during electrolysis (SI Table S2). SEC analysis of products from reactions catalyzed by complexes Co(**L1-L4**) indicated that the steric properties of the ligand had the greatest influence on the M_n of the modified polymer. Reactions catalyzed by complexes with bulky substituents on the diamine backbone, such as Co(**L3**), resulted in polymers with the highest M_n (40 kDa). In contrast, reactions performed with Co(**L2**), which lacks any substitution on the ethylene backbone, formed small polymer fragments ($M_n = 11$ kDa). Although the molecular weights of the modified polymers were lower than that of the initial PVC from reactions with even the bulkiest catalyst, these data provided valuable mechanistic insights towards improving the system further.

We hypothesized that the high levels of chain scission were the result of competitive radical capture at Co^{II} rather

than acrylate (Figure 2c, reverse of Co-C homolysis step) and that bulky ligands inhibit radical capture at Co. This putative pathway for scission also implicates an inverse order dependence of catalyst concentration on the molecular weight of the polymer. We performed reactions with various concentrations of Co(**L4**) to slow or accelerate the competing Co-radical capture reaction. Results from these studies reveal a significant effect of catalyst concentration on both M_w and M_n of the grafted polymers. As shown in Figure 3e reactions with the highest catalyst loadings (10 mol%) resulted in polymers with the lowest molecular weights ($M_n = 12$ kDa). In contrast, reactions with 1 mol% of catalyst resulted in grafted polymers with molecular weights that are equal to or greater than those of PVC. Additionally, these drastic improvements to the macromolecular structure of the polymer were achieved with the readily available and inexpensive Co(**L4**) complex as catalyst, rather than the tetramethyl Co(**L3**) analog, which is prepared by multistep synthesis in low yields.⁵⁸ Finally, the decrease in catalyst loading almost completely inhibited proto-dehalogenation (<1%) and had no effect on the graft density of the reaction. The ¹H NMR spectrum of the grafted polymer (**PVC-1**) generated under these improved conditions is reproduced as the blue trace in Figure 3b. Collectively, these results support our mechanistic hypothesis and offer an attractive solution to mitigating scission pathways by simply reducing catalyst loading. Additionally, catalyst architectures that limit the formation of Co-alkyl intermediates by either S_N2 (mild $E_{1/2}$) or recombination processes (bulky ligands) further improve the chemoselectivity of the reaction.

The developed methodology enables grafting of PVC polymers with high selectivity and retention of chain integrity. ¹H NMR spectroscopy of **PVC-1** reveals that grafts are comprised of mono- rather than poly-acrylate fragments. Grafting a single equivalent of acrylate at an activated C–Cl site is favored when reactions are performed with protic additives (Figure 4a, Method A, butanol). Protic additives terminate polyacrylate growth by quenching enolate intermediates. In contrast, long-lived enolate intermediates in reactions without butanol (Figure 4a, Method B) propagate acrylate polymerization. The resulting PVCs are grafted with polyacrylate branches (**PVC-1_{PA}**) from the site of C–Cl bond activation. An overlay of ¹H NMR spectra of **PVC-1_{PA}** and pure polyacrylate reveals overlapping resonances compared to offset resonance from an overlay of polyacrylate and **PVC-1** (see the SI, Figure S9). ¹H NMR DOSY supports that the detected polyacrylate fragments in **PVC-1_{PA}** are indeed grafted to PVC. Additionally, trituration of **PVC-1_{PA}** with solvents that readily dissolve conventional polyacrylate, such as toluene, did not change the ratios of resonances from the polyacrylate and PVC fragments. The simple inclusion or omission of a protic additive in electrocatalytic reactions of various acrylates provides access to monoacrylate-grafted polymers **PVC-1** to **PVC-7** using Method A or polyacrylate-grafted analogs **PVC-1_{PA}** to **PVC-7_{PA}** using Method B.

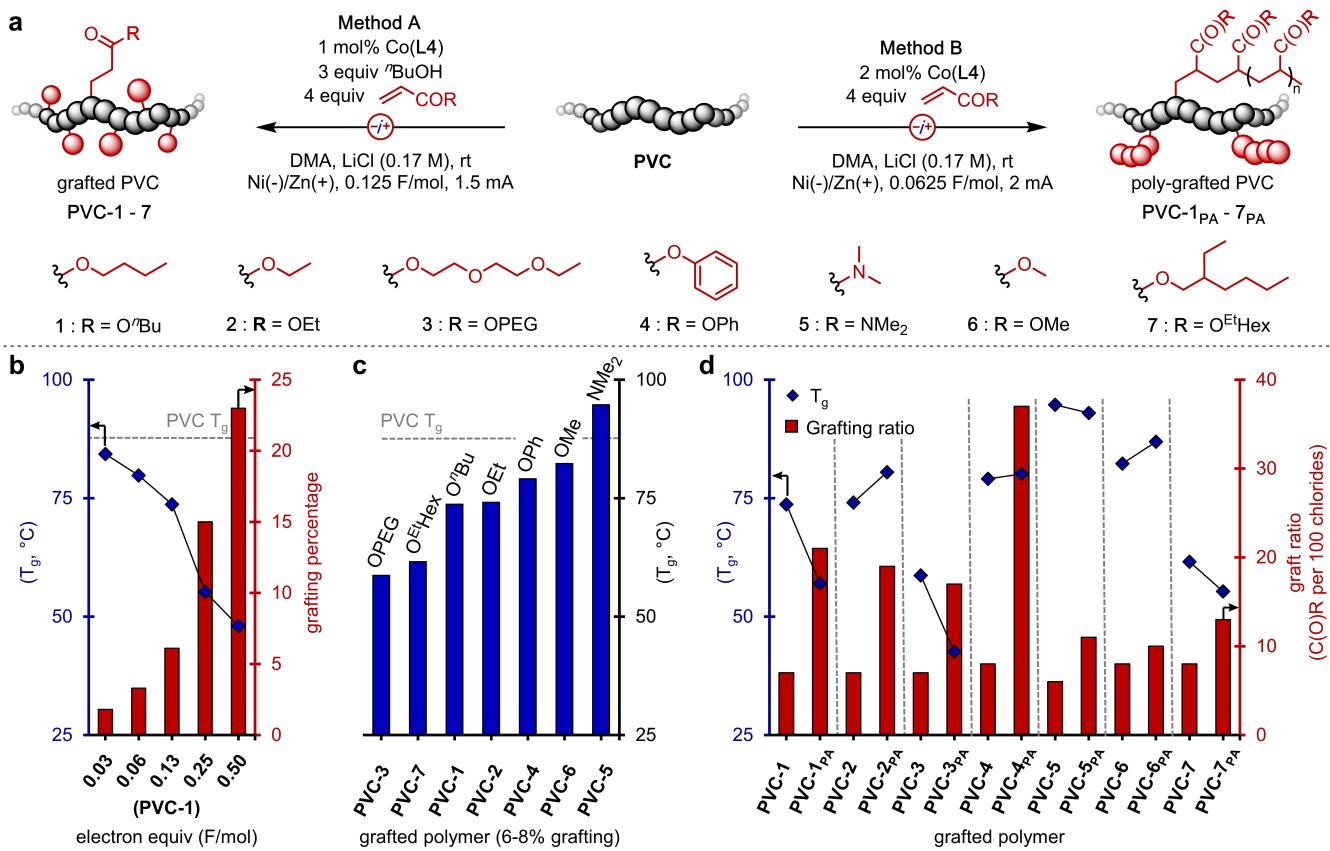


Figure 4. Reaction scope for PVC grafting (a) Visual representation of newly developed PVC grafting methods. (b) Analysis of the effect of increasing capacity on grafting percentage and glass transition temperature. (c) Comparison of functional group influence on T_g . (d) Influence of polymer grafting method on the grafted polymer's glass transition temperature.

Grafting reactions were conducted on 94 mg of unmodified PVC in 3 mL solutions at constant current using both conditions A and B. Modified PVCs were recovered from reactions under the standard conditions of 0.125 F/mol in similar masses to the initial loading of polymer (see the SI, Figure S11). The graft density of **PVC-1** generated from reactions with butyl acrylate was easily controlled from 1.5% to 23% by varying the electrolysis parameters from 0.03 to 0.5 F/mol (Figure 4b, red bars). Polymers with increased grafting undergo glass transition (T_g) at progressively lower temperatures as measured by differential scanning calorimetry (DSC) (Figure 4b, blue diamonds). We found that the structure of the grafted acrylate has an even greater effect on plasticization than the graft density alone (Figure 4c). Modified PVCs with similar grafting percentages (6-8%) of various acrylates or acrylamides have T_g values that can range above or below that of unmodified PVC. The most drastic reduction in T_g was observed from PVC grafted with polyether substituted acrylates (OPEG, **PVC-3**). Plasticizers containing these long-chain polyethers or branched alkanes (**PVC-7**) are known to have a greater influence on PVC plasticization than short-chain alkyl esters.³³⁻³⁵ In contrast, grafting reactions with acrylamide yields materials with increased T_g values over the parent PVC (**PVC-5**). Finally, we compared the grafted polymers generated by methods A and B (**PVC-1** to **PVC-7** versus **PVC-1_{PA}** to **PVC-7_{PA}**, Figure 4d). Polyacrylate-grafted

products generated by method B generally had higher acrylate incorporation than those generated by method A (Figure 4d, bar graph). The extent of acrylate loading in the polymer is reported as a ratio of incorporated acrylates per 100 chlorides. Although the structure of the acrylate had little impact on the grafting ratio from reactions with method A, a high variation in acrylate incorporation was observed from reactions with method B. The incorporation ratio reflects the relative rates of polyacrylate propagation, which is high for electron deficient acrylates like phenyl acrylate (**PVC-4_{PA}**) and low for electron rich acrylamide. Polyacrylate grafts containing long-chain fragments yield materials with lower T_g than the mono-grafted materials. However, polyacrylate grafting of PVC with short-chain acrylates, such as ethyl, phenyl, and methyl acrylates (**PVC-2_{PA}**, **PVC-4_{PA}**, and **PVC-6_{PA}**), generated materials with higher T_g values than the monoacrylate grafted analog (**PVC-2**, **PVC-4**, and **PVC-6**) despite the higher incorporation of acrylate.³⁵ As a result, the combination of selected redox capacity and acrylate structure provides access to materials with new and predictable properties. This methodology can also be scaled to multigram reactions under the standard conditions (see the SI, Figure S1). This synthetic accessibility allowed us to cast thin films of the polymers and evaluate the tensile properties of the new materials. For polymers containing esters with shorter carbon chains, such as **PVC-1_{PA}**, the tensile strength (25 ± 0.4 MPa) and elongation

at break ($5 \pm 0.6\%$) were both slightly lower than virgin PVC

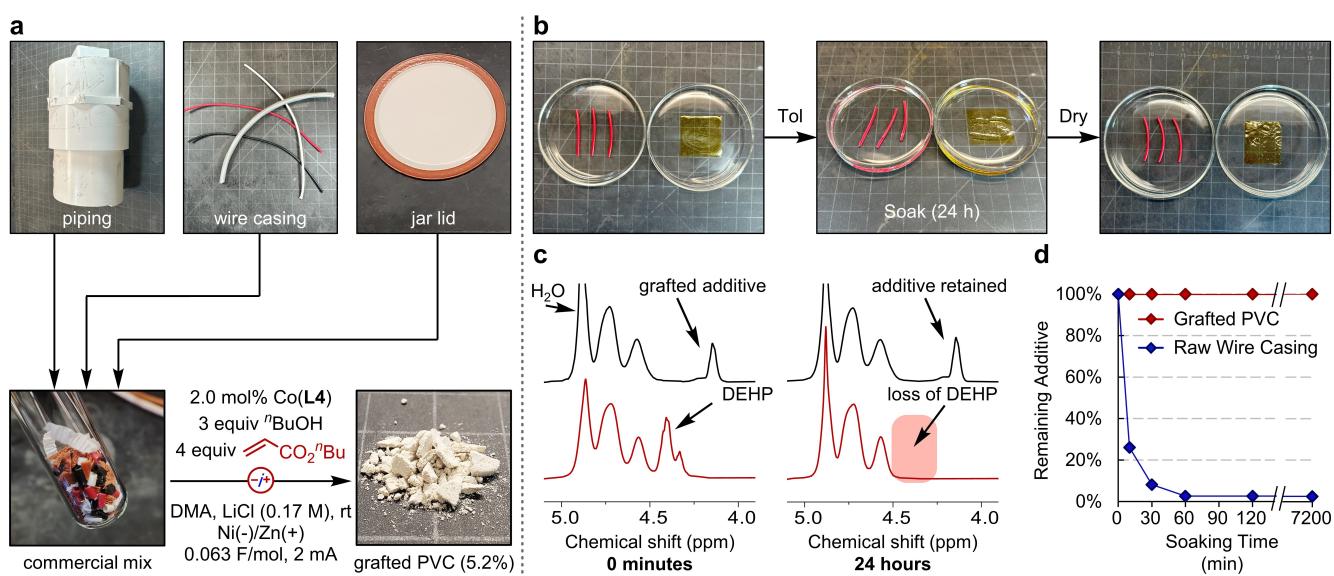


Figure 5. Consumer plastics application of covalently grafted materials. (a) Scheme for plasticizer migration study comparing consumer plastics to grafted plastics. (b) Migration study comparing the percent of plasticizer loss during organic solvent washing. (c) Electrocatalytic grafting of consumer PVC Products including piping, wire sheathing, and jar seals under standard reaction conditions.

(32 ± 0.7 MPa, $6 \pm 1\%$, see Figure S15 for details). However, longer chain substrates such as the PEG and ethylhexyl groups in **PVC-3_{PA}** and **PVC-7_{PA}** displayed significantly greater elongation at break ($114 \pm 5\%$ and $37 \pm 7\%$ respectively). Collectively, these comparative data underscore the breadth of materials that can be prepared and the control that electrocatalysis provides for tuning the macromolecular properties of PVC through covalent modification at the molecular level. We applied the grafting methodology to a combination of commercial consumer products made of common PVC formulations that exhibit high (drainpipe), medium (wire sheathing), and low (jar lid seal) rigidity (Figure 5a). These plastics model three potential waste streams of PVC. The materials were directly combined in a single reactor and simultaneously grafted under standard conditions without pre-treatment to remove plasticizers, coloring agents, or other additives. Analysis by ^1H NMR spectroscopy of the isolated material following electrolysis reveals a molecular structure that is nearly identical to that of PVC-1 (See SI Figure S13), which was originally prepared from pure PVC. These results underscore the compatibility of the electrocatalytic methodology with the myriad additives that might inhibit conventional approaches to C-Cl bond modification. Additionally, three distinct PVC plastics are controllably converged into a new material with predictable and controllable properties.

To showcase the utility of grafted PVCs, we evaluated the extent of plasticizer migration in a commercial PVC used for wire sheathing. Such PVCs are soft and contain significant loadings of ester additives. We selected **PVC-1** with a 6.4% grafting of butyl esters as a comparable mate-

rial because of its similar flexibility to the wire. Both materials were exposed to toluene, which is a common solvent found in household paint thinners (Figure 5b). Neither of the plastics dissolved, but samples of the solids were periodically collected and analyzed by ^1H NMR spectroscopy (Figure 5c) to quantify the percentage of remaining additive in the solid as a function of time. Nearly all of the plasticizing additives were extracted from the commercial PVC within just 30 minutes (Figure 5d, blue trace), and the resulting material lacked the flexibility of the original sheathing. The rapid loss of functionality to leave a brittle plastic upon exposure to common solvents is particularly problematic because PVC sheathing relies on its flexibility to insulate wires. In contrast, there is no change to the composition of the grafted plastic **PVC-1** even after days of soaking in toluene (red trace). **PVC-1** retains the bulk properties of the pre-soaked material to serve as a chemically resistant PVC plastic.

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact Prof. Christo S Sevov (sevov.1@osu.edu)

Materials availability

Unique and stable reagents generated in this study will be made available on request, but we might require payment and/or a completed material transfer agreement if there is potential for commercial application.

Data and code availability

All experimental data, analytical procedures, electrochemical cell designs, and copies of spectra and chromatograms are available in the supplementary information.

SUPPLEMENTAL INFORMATION

Supplemental information can be online.

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AUTHOR CONTRIBUTIONS

J.L.Z., B.L.T. and C.S.S. conceived the work. J.L.Z., V.S., B.L.T. and C.S.S. designed the experiments. J.L.Z., V.S., B.L.T., and E.J.V. performed all experiments and collected all data. J.L.Z. and C.S.S. wrote the manuscript, and all authors provided revisions.

DECLARATION OF INTERESTS

The authors have filed patent applications directed to the technology described here.

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