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Catalytic Borylation of Poly(vinyl chloride) Produces Adhesive Materials

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Abstract

Post-polymerization functionalization of polymers can create new applications for existing materials, while retaining their most favorable, intrinsic properties. Polyvinyl chloride (PVC) is a widely used, commodity polymer that is particularly challenging to modify. We report a copper-catalyzed protocol that replaces a small fraction of the C—Cl bonds in PVC with C—B bonds to boronic esters. The reaction occurs with an inexpensive catalyst comprising copper(II) chloride and an NHC ligand derived from a common ionic liquid that is distinct from the N-heterocyclic carbene used for the borylation of small alkyl halides. The resulting materials adhere strongly to common surfaces, such as glass and metals, even more strongly than do commercial glues.

Graphical Abstract

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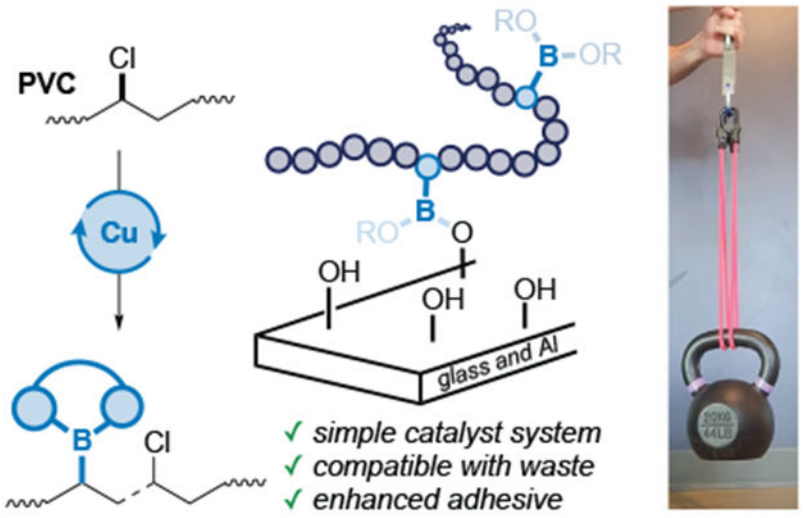


Poly(vinyl chloride) (PVC) is a high-volume commodity polymer, with 40–50 million tons made annually.[1] Pure PVC is a brittle solid, but additives, including plasticizers, yield flexible resins, and stabilizers minimize decomposition,[2] thereby rendering this polymer valuable for building materials, clothing, packaging, and medical devices. Additives in PVC, however, complicate recycling, and their leaching can compromise material properties.[3, 4]

We and others have demonstrated that post-polymerization functionalization of polymers produces materials with altered physical properties engendered by functional groups that are appended to the polymer chains.[5-10] The covalent attachment of such groups prevents their migration from the material, while conferring desirable properties, including enhanced toughness, adhesion to other materials, and wettability, all with sufficiently low degrees of functionalization that the strengths of the original polymer are retained.

Polymers containing boronic esters are known to adhere to glass and metal surfaces,[11] and we reasoned that a similar property could be achieved with PVC without additives if a small fraction of the chlorine atoms could be replaced with boryl groups. Covalent modification of PVC often relies on substitution with strong nucleophiles, such as thiolates or azide anion (Scheme 1A). [12-15] These transformations, or downstream click reactions, trigger changes to materials properties, such as self-plasticization.[13, 16] Nucleophilic substitution, however, can lead to chain scission and elimination[17] and is unsuitable as a strategy for the borylation of C(sp^3)—Cl bonds. Besides nucleophilic substitution, functionalization by grafting with radicals generated from either the tertiary alkyl chlorides present at defect sites within PVC[18] or from the secondary alkyl chlorides *via* Co-electrocatalysis[19] have also been demonstrated.

Our group has used homogeneous catalysts for the post-polymerization functionalization of commodity polymers, including borylation, by adapting catalyst systems for C—H functionalization of small molecules to polyolefins (Scheme 1B).[5-7, 20, 21] In our experience, significant modifications to the reaction conditions used for small molecules are necessary to accommodate the solubility profiles of polymers and to minimize side reactions, especially

cross-linking and chain scission. Functionalizing PVC is especially challenging because it undergoes elimination reactions at elevated temperatures or in the presence of base,[22, 23] and small degrees of dehydrochlorination accelerate subsequent elimination of the resulting allylic chloride, leading to insoluble poly(acetylene-*co*-vinyl chloride) materials.[24]

Here, we describe the borylation of the secondary C—Cl bonds in PVC with a copper catalyst (Scheme 1C). Modification of the catalyst structure, as well as procedural tactics, proved critical to achieving consistent control of the borylation reaction across scales. The resulting materials adhere strongly to both glass and metal.

We considered multiple protocols for the borylation of secondary alkyl chlorides catalyzed by iron,[25] manganese,[26] cobalt,[27] and nickel complexes,[28] but each requires organolithium or Grignard reagents as bases or high catalyst loadings (≥5 mol%), making them unsuitable for the functionalization of PVC. In contrast, a protocol reported by Marder and coworkers includes a copper/N-heterocyclic carbene system with relatively low catalyst loadings (1 mol%) without Grignard reagents.[29]

However, the conditions reported by Marder for the borylation of secondary alkyl chlorides in small molecules did not lead to consistent borylation of PVC granules. The polymer dissolved slowly in tetrahydrofuran (THF) at typical reaction concentrations (1 M C—Cl), leading to heterogenous mixtures and side reactions that included dehydrochlorination, as evidenced by the formation of black insoluble precipitates attributed to poly(acetylene). To address this issue, we added a solution of PVC in THF to a pre-mixed suspension of diboron reagent, potassium alkoxide base, and copper catalyst in THF. Heating the resulting mixture at 65 °C with the optimal catalyst systems reported by Marder comprising $CuCl_2$ and either IMes (**L1**) or IPr (**L2**) as ligand led to detectable borylation of the polymer, but with low efficiency, as determined by solution ^{1}H NMR analysis (Table S1, entries 1–2). No appreciable alkene content was detected by ^{1}H NMR spectroscopy (<0.1 mol%), consistent with the ability of the diboron reagent to buffer the basicity of the alkoxide and suppress hydrodechlorination.[28]

We reasoned that long *n*-alkyl chains on the ligand, which we previously reported led to higher activity of copper catalysts for the amination of polyethylene C—H bonds,[7] could lead to more active catalysts for the borylation of PVC. We therefore evaluated a series of NHC precursors with alkyl chains of varying lengths (Figure 1, Table S1) and found that catalysts formed by combining commercially available imidazolium salts **L3–L5**, which are often used as ionic liquids, with potassium bis(trimethylsilyl)amide (KHMDS) in the presence of $CuCl_2$ are more active than those from IMes (**L1**) and IPr (**L2**).[30] Moreover, an increase in the efficiency of the reaction with PVC was observed as the length of the carbon chain increased from methyl to *n*-butyl and to *n*-decyl. Further evaluation led to the reaction conditions reported at the top of Figure 2 (see the SI).

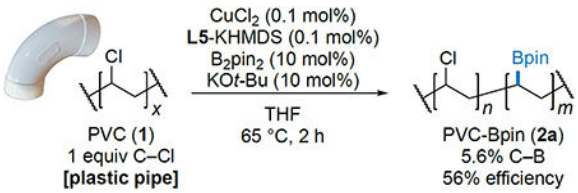
To determine if the catalyst from imidazolium **L5** is more active across molecular sizes than those from **L1** and **L2**, or more active specifically for the polymer, we compared the yields of the borylation of a small molecule model (chlorocyclohexane **3**) with the same panel of catalysts. Consistent with Marder's findings,[29] the yields of reactions of chlorocyclohexane

with IPr **L2** were the highest, as determined by GC analysis, and were higher than those with the preferred ligand for borylation of PVC, **L5** (Figure 1, Table S2). Mechanistic studies of the borylation of alkyl halides with copper and alkoxide base are lacking, but alkyl radicals are likely intermediates.[28, 29] We previously hypothesized that catalysts with longer alkyl chains would diffuse more readily in the viscous, nonpolar media containing dissolved polyolefins to capture polymeric radicals more efficiently before they engage in side reactions,[7] and studies in our laboratory are evaluating this hypothesis in reactions of polymers versus small molecules with transition-metal catalysts.

To tune the properties of the resulting polymers by varying the degree of functionalization, we evaluated the extent to which the borylation reaction occurred on the starting polymer at various loadings of diboron reagent and base (Figure 2). As the equivalents of these reagents were increased from 0.025 to 0.30, relative to vinyl chloride monomer, a monotonic increase in functionalization was observed, with reaction efficiencies ranging from 47 to 53%. Increasing the reagent loading beyond 0.30 equivalents did not increase the degree of functionalization above 15%.

A suite of materials was prepared with various degrees of functionalization with a series of boryl groups (Tables 1, S6). The reactions with diboron reagents derived from hindered diols, including 2,3-pinanediol (B_2pnd_2) and 3,4-diethylhexane-3,4-diol (B_2Epin_2), led to the borylation of PVC, but reagents derived from less hindered diols, such as neopentane glycol, 2-methyl-2,4-pentanediol, and catechol, led to low degrees of functionalization (<10% efficiency). In general, the molecular weights of the resulting polymers, as evaluated by size exclusion chromatography with multiangle light scattering, were higher than those of the starting PVC. This increase was more pronounced for polymers with a greater degree of functionalization (c.f. PVC-Bpin **2a-1** and **2a-3**, Table S6), and may be a consequence of reversible cross-linking that can occur between pinacol boronic esters,[31] although the apparent increase did not affect our ability to solvent process the polymers.

We also evaluated the borylation of waste-derived PVC. Shavings obtained by filing a used PVC pipe were first reprecipitated from THF and then subjected to the borylation conditions with 0.10 equiv of diboron reagent and alkoxide base (eq 1). A sample of PVC Bpin **2a** was obtained with a degree of functionalization of 5.6%, which corresponds to a reaction efficiency (56%) that is comparable to that observed with virgin PVC (Table S5, entry 4). Finally, the resulting boronic ester products were transformed to other PVC-boryl copolymers, including an alkyl trifluoroborate ionomer (**5**, eq 2)[32] and a boronic acid (**6**, eq 3).[33]



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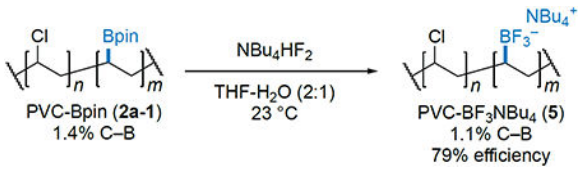

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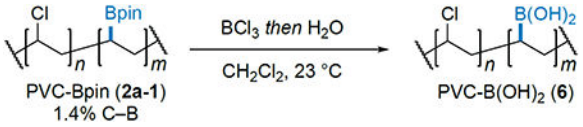

(3)

Characterization of the thermal properties of PVC materials obtained from the catalytic borylation was conducted by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are summarized in Tables 1 and S6. Generally the glass transition temperatures (T_g) of the boronic esters were slightly higher than the starting polymer (Table 1). Notable exceptions are BEpin derivatives **2b**, which show diminished T_g values at higher functionalization, a likely consequence of the larger size of BEpin, compared to Bpin, disrupting packing of the polymer chains.[12, 34] Moreover the PVC-boronic esters generally exhibited greater thermal stability than did unfunctionalized PVC, with an increase in the thermal decomposition temperature (T_d) up to 15 °C for PVC-BEpin **2b-2.**

The influence of functionalization on the mechanical properties of PVC was studied by conducting tensile tests with films prepared by solvent casting from a THF solution of the polymer. To obtain consistent data, it was essential to exhaustively remove the residual THF, which acts as a plasticizer,[35] from the films by extraction with chloroform and methanol, followed by drying in a vacuum oven.[36] Our data from tensile tests of the functionalized PVCs are summarized in Table S9. The Young's moduli of boronic esters **2a-c** are generally 76–95% of the value of unfunctionalized PVC **1**. This decrease varied with the size of the boryl group (largest for the PVC-BEpin **2b**, followed by PVC-Bpnd **2c**; and then PVC-Bpin **2a**) and was more pronounced with higher levels of functionalization. Consistent with the change in T_g, the larger boryl groups in PVC-BEpin **2b** appear to plasticize the resulting material, as evidenced by a 21% decrease in the tensile stress at maximum load for **2b-2** (5.3% functionalized). At the same time, no increase in elongation at break or toughness were observed. These results suggest that functionalized PVC-Bpin **2a** and PVC-Bpnd **2c** retain most of the rigidity of unfunctionalized PVC.

We envisioned that our PVC materials functionalized with boronic esters could exhibit enhanced adhesion to surfaces, such as glass and aluminum. Hydroxyl groups present on these surfaces have been proposed to bond covalently to polymer-bound boronic esters, thus forming adhesive joints.[11] Samples approximately 12 mm^2 in size of unfunctionalized

and functionalized PVC-Bpnd **2c** were layered between aluminum or glass and cured at elevated temperatures at various curing times (Figures S8-10). The results of lap-shear tests at the optimal curing times with these samples are shown Figure 3 and Tables S7 and S8. Joints formed from PVC-Bpnd **2c-1** were 2–3 times stronger than those formed from unfunctionalized PVC **1**. Most striking, the adhesion strength of PVC-Bpnd **2c-1** was also 2–3 fold higher than that of Original Gorilla Glue®, a commercial adhesive advertised to bond aluminum and glass.[37] A sample of PVC-Bpnd with a greater degree of functionalization (**2c-2**, 4.2%) did not form significantly stronger joints to glass and aluminum than PVC-Bpnd **2c-1** with lower levels of functionalization (2.3%), but the maximum adhesive strength was reached at shorter curing times (c.f. Figures S9 and S10). To illustrate the adhesive strength of PVC-Bpnd **2c**, we lifted a 20-kilogram (44-pound) kettlebell from a joint formed by just 0.1 cm^2 of the cured polymer between two aluminum billets (Figure 3, Movie S1).

In summary, we describe a catalytic approach to impart new properties to PVC by the borylation of C—Cl bonds. Differences between the reactivity of small chloroalkanes and PVC made the identification of a catalyst that is more reactive in the polymer-containing media crucial, and this study offers further insights into the translation of catalytic methods developed with small molecules to polymers. The resulting materials largely retain the mechanical properties of the initial polymer at the levels of boryl groups that enable adhesion to common surfaces without additives, and could be useful as compatibilizers for PVC and other materials, as many commercial adhesives do not bond PVC to other surfaces. Ongoing efforts to understand the differences in reactivities of small molecules and polymers with transition-metal catalysts will be reported in due course.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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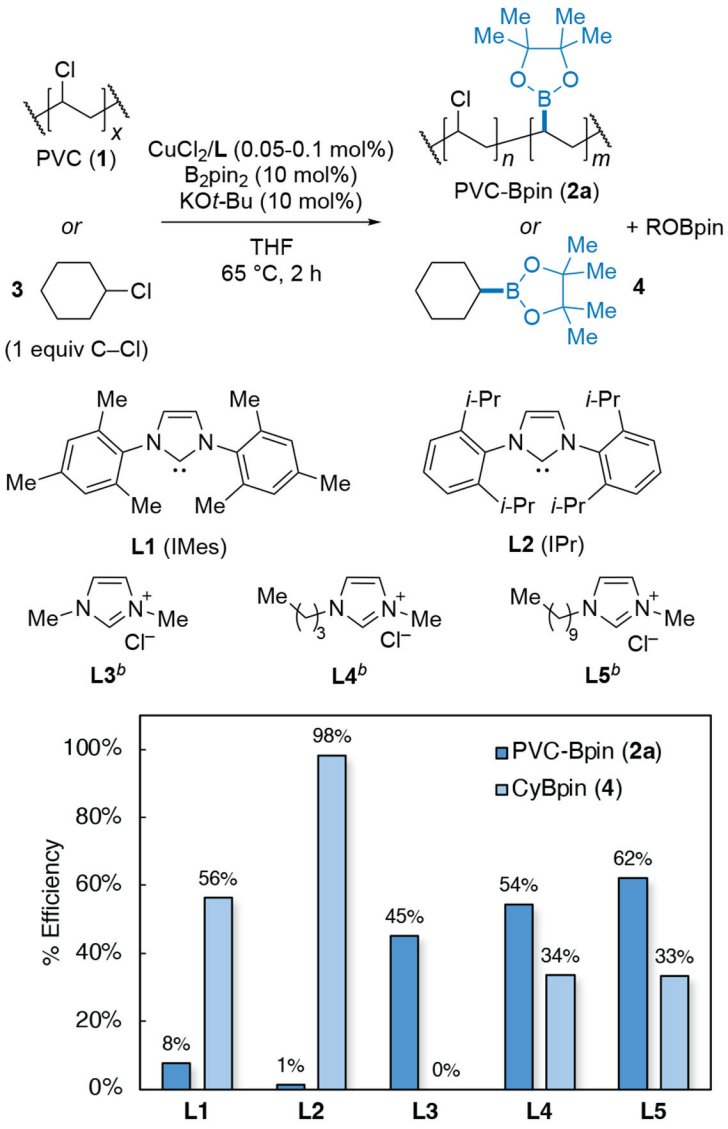


Figure 1.

Evaluation of NHCs and NHC precursors for the borylation of poly(vinyl chloride) and chlorocyclohexane.[a]

Efficiency refers to the percentage of C—Cl bonds transformed in the starting material relative to the amount of B_2pin_2 added. [a]The yield of boronic ester **4** was determined by GC analysis with adamantane as an internal standard. [b]An equal amount of KHMDS to the imidazolium chloride was added.

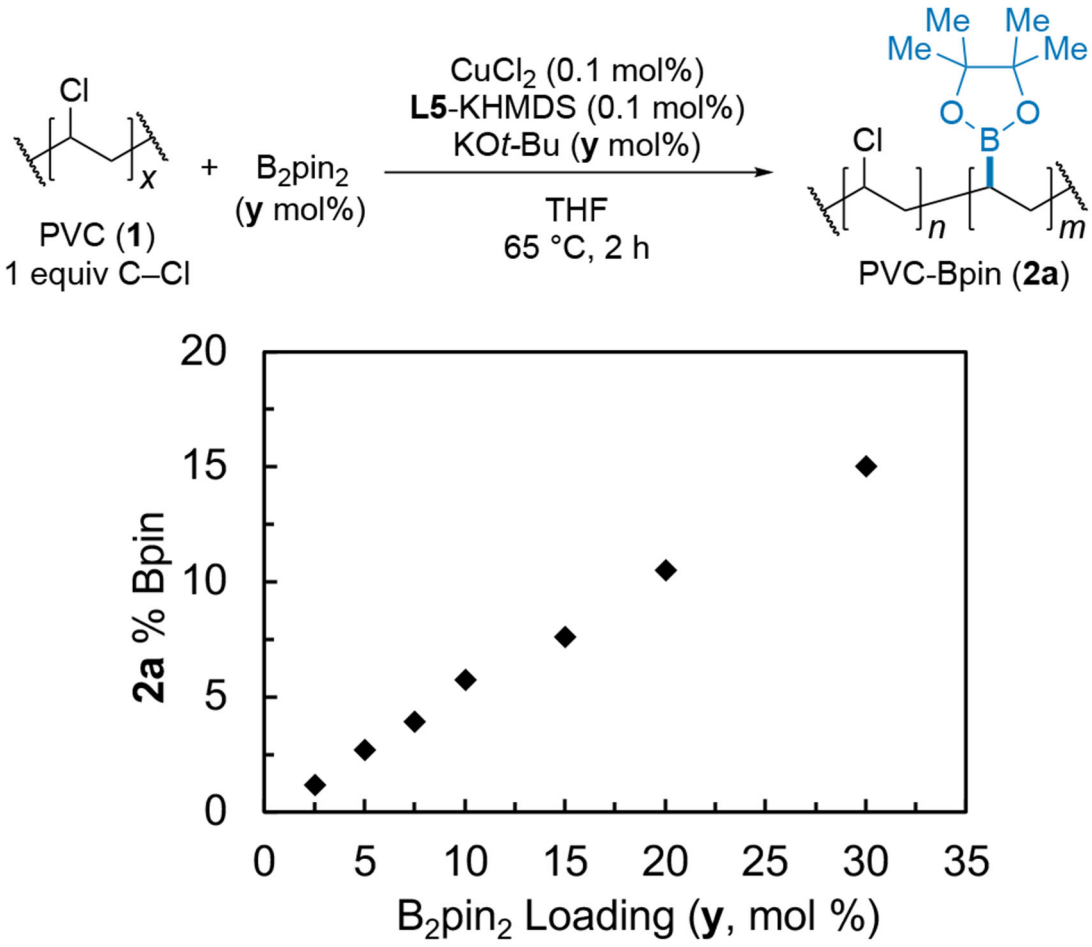


Figure 2.
Dependency of the degree of functionalization on the loading of diboron reagent and alkoxide base.

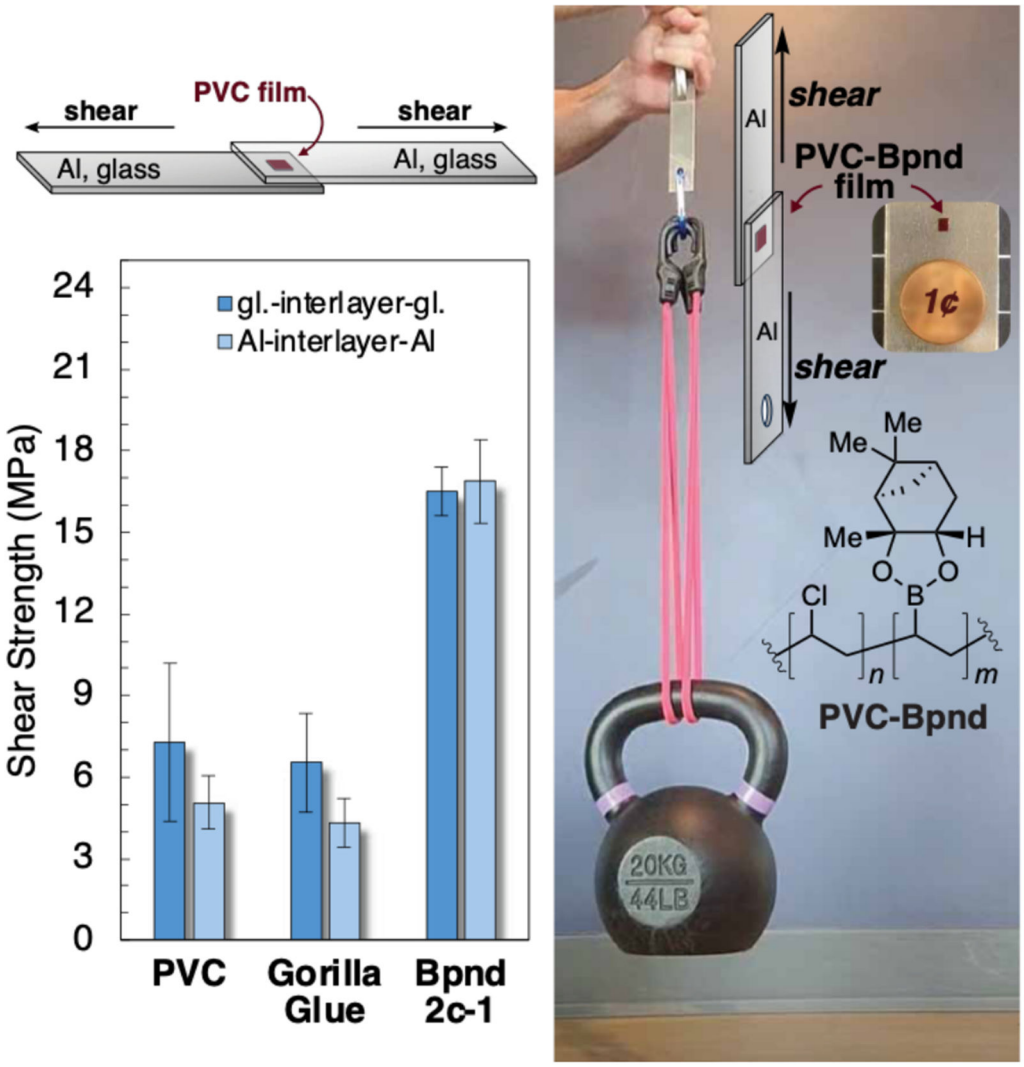
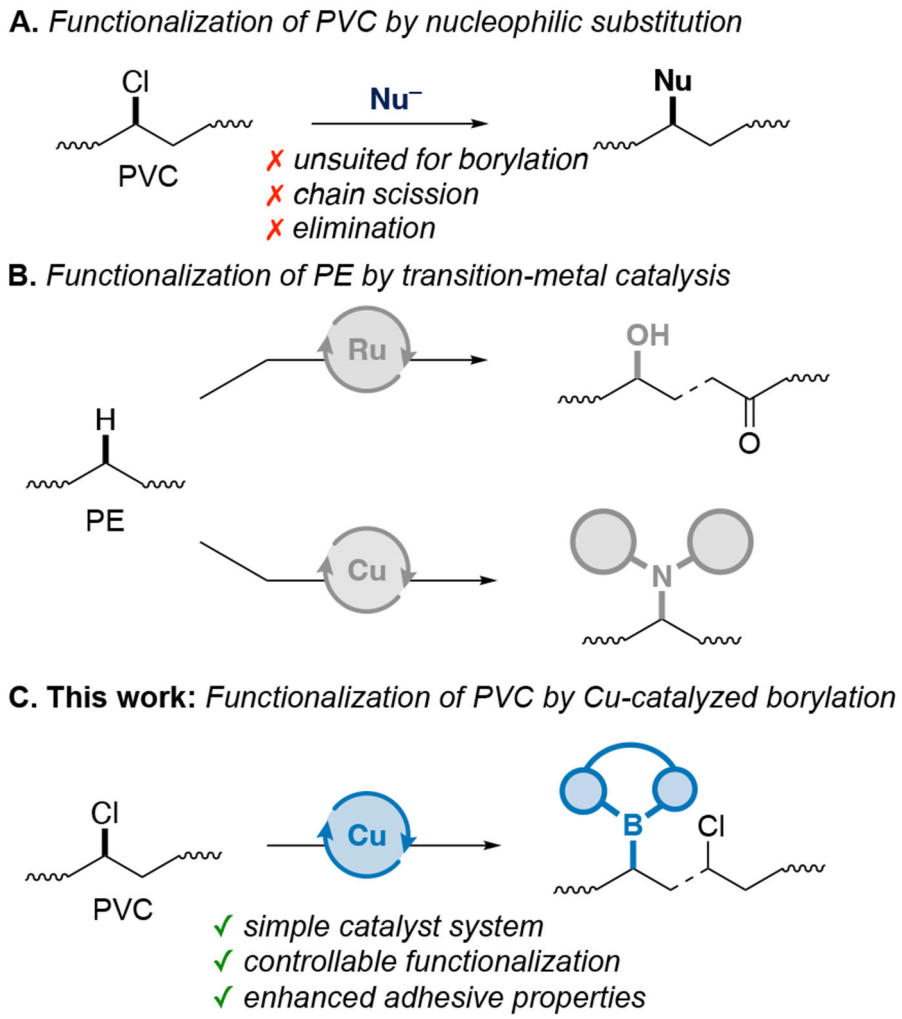


Figure 3.

Evaluation of the adhesive strengths of PVC-Bpnd **2c-1** to aluminum and glass surfaces by lap-shear testing.

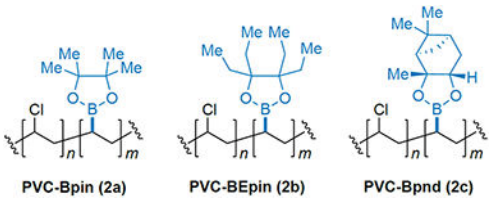


Scheme 1.

Prior reports of functionalization of PVC and polyethylene, and this work on the catalytic borylation of PVC.

Table 1.

Summary of polymers synthesized by catalytic borylation of PVC 1.[a]



Polymer	*m*/(*n*+*m*)	Efficiency[b]	T_g (°C)	T_d (°C)
PVC **1**	-	-	83.3	268.2
PVC-Bpin **2a-1**	0.013	53%	86.6	269.9
PVC-Bpin **2a-2**	0.026	52%	86.1	275.0
PVC-Bpin **2a-3**	0.059	65%	85.7	280.8
PVC-BEpin **2b-1**	0.028	55%	78.5	281.5
PVC-BEpin **2b-2**	0.053	53%	71.5	283.1
PVC-Bpnd **2c-1**	0.023	45%	86.5	276.2
PVC-Bpnd **2c-2**	0.042	42%	86.4	269.4

[a]Conditions: PVC **1** (1 equiv C—Cl), $CuCl_2$ (0.1 mol%), **L5**-KHMDS (0.1 mol%), diboron reagent (2.5–10 mol%), KO*t*-Bu (2.5-10 mol%), THF, 65 °C.

[b]Efficiency has the meaning defined in Figure 1.