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Journal

ChemPlusChem, 88(5)

ISSN

0010-0765

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Publication Date

2023-05-01

DOI

10.1002/cplu.202300184

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Peer reviewed

Degradation of Polyvinyl Chloride by Sequential Dehydrochlorination and Olefin Metathesis

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Abstract

Polyvinyl chloride (PVC) is a problematic waste plastic with limited options for recycling or upcycling. Herein, we demonstrate preliminary results in breaking down the long carbon chains of PVC into oligomers and small organic molecules. First, treatment with a substoichiometric amount of alkali base effects elimination of HCl to form a salt and creates regions of conjugated carbon-carbon double bonds, as determined by ^{1}H NMR and UV-Vis spectroscopy. Olefin cross metathesis with an added partner alkene then cleaves carbon-carbon double bonds of the polymer backbone. Addition of allyl alcohol to the dehydrochlorination step introduces allyloxy groups by substitution of allylic chlorides. Subsequent metathesis of the pendant allyloxy groups provides a reactive terminal alkene to promote insertion of the metathesis catalyst onto the olefins in the all-carbon backbone. The products obtained are a mixture of PVC oligomers with greatly reduced molecular weights and a small-molecule diene corresponding to the substituents of the added alkene, as evidenced by ^{1}H and DOSY NMR and GPC . This mild procedure provides a proof of concept towards harvesting carbon resources from PVC waste.

Introduction

An estimated 1 billion tons of PVC has been produced since 1960, over half of which is still in use.[1] In the coming years, PVC waste generation will see a large increase as long-lived products such as window frames and pipes come to the end of their usable lifetimes and enter the waste stream.[2]

Making productive use of PVC waste is a challenge. Mechanical recycling is difficult because different PVC products each contain different blends of plasticizers, stabilizers, and other additives; combining these additives leads to diminished mechanical properties.[2,3,4] Meanwhile, incineration of PVC is an issue because it produces corrosive HCl and toxic chlorinated dioxins, a class of persistent organic pollutants.[3] Changing regulations also present an issue: harmful plasticizers such as diethylhexylphthalate (DEHP) still present in legacy PVC products are now banned in newly made (or newly recycled) PVC in the EU.[5] In the US, DEHP is restricted in childcare articles and food packaging.[6] Vinyloop®, a plant designed to recycle PVC from mixed waste by selective dissolution/precipitation, was shut down in 2018 due to its inability to remove phthalates.[7,8] Lead stabilizers found in legacy PVC products are similarly banned in new products, complicating attempts at PVC recycling.[4,9]

Chemical recycling and upcycling of polymers is a growing field of interest with the goal of creating a circular economy. Breaking down a polymer into monomer or other useful small molecules allows purification of the products and avoids the downcycling phenomenon seen in mechanical recycling. Polymers with labile ester or amide bonds in their backbone are more amenable to this treatment than polymers with an all-carbon backbone. For instance, polyethylene terephthalate and polyurethane can both be depolymerized by hydrolysis, alcoholysis, or aminolysis; the monomers or short oligomers obtained can be repolymerized to form the original polymer or other high-performance polymers.[10,11] Polymers with all-carbon backbones are more

challenging to controllably cleave, but many methods have been developed to break down polyethylene, polypropylene, and polystyrene into light hydrocarbon fuels, benzene derivatives, or H_2 gas. [10,11] However, even small amounts of PVC can contaminate these reactions and deactivate the catalyst, requiring PVC to be carefully removed first.[10,11]

Chemical upcycling of PVC is underdeveloped compared to that of other polymers, despite the fact that it is the third-most produced plastic in the world.[1] Most PVC degradation procedures explored have been carried out at high temperatures (200-900 °C) and focus on pyrolysis to small hydrocarbons or oxidation to carboxylic acids.[2,12,13] Pyrolysis of PVC is complicated by the release of HCl, which corrodes equipment and deactivates catalysts. Solutions to this include pre-treatment with base, or pyrolysis in the presence of base or bio-waste. In some cases, products are a mixture of acetone, benzene, and other aromatics. In other cases, alkanes or syngas (CO and H_2) are produced.[12,13]

Oxidation of PVC has been performed using oxygen in water,[14] using hydrogen peroxide and a palladium catalyst,[15] or using electrooxidation.[16] Extensive oxidation leads to formation of carbon dioxide; small carboxylic acids such as oxalic acid are formed along the way. The Yoshioka group has focused on maximizing the ratio of oxalic acid to CO_2 produced. Oxidation of PVC in oxygen and aqueous NaOH at 250 °C yields up to 30% oxalic acid from rigid PVC waste,[17] as well as from flexible PVC waste.[18] The Yanagisawa group used a two-step process wherein PVC was first dehydrochlorinated in KOH/PEG/THF, then treated by aqueous O_2 oxidation. They found that by decreasing the temperature to 100 °C, little to no CO_2 was produced and the majority of the carbon in PVC was converted into formic, maleic, fumaric, and other carboxylic acids.[19]

In 2003, Partenheimer developed an aqueous O_2 oxidation of PVC in the presence of a vanadium and bromide catalyst to produce a 38% yield of succinic acid.[20] In a study by the Xiu

group, oxidation at 300 °C with a limited amount of oxygen was used to selectively form benzaldehyde and acetophenone as the major oil products, although the total yield was not reported.[21] Aside from harvesting the carbon, waste PVC can also be used as a chloride source to trap heavy metals,[22] or as a hydrogen donor to upconvert CO_2 into formic acid.[23]

There remains a need for new approaches to chemically break down PVC. Expanding the toolbox of reactions that can controllably degrade PVC will allow a wider range of products to be made, and bring the world closer to the goal of harvesting plastic waste as a resource. Olefin metathesis is a promising method for polymer breakdown because it cleaves carbon-carbon double bonds, which can readily be introduced into the PVC backbone. Olefin metathesis has been used to degrade polybutadiene,[24,25] natural rubber, [26,27,28] and styrene-butadiene-styrene (SBS) rubber.[29] In particular, the Wagener group was able to depolymerize polybutadiene to almost exclusively monomer rather than oligomers using Grubbs 2 and copper iodide.[30] Abu Omar et al. broke down polyethylene into oligomers in a three-step process. First polyethylene was brominated, then elimination of HBr produced carbon-carbon double bonds, which were then cleaved by olefin cross metathesis with ethylene.[31] In 2016, Huang et al. paired iridium pincer catalysts with a Re_2O_7/γ-Al_2O_3 metathesis catalyst to perform a one-pot dehydrogenation/olefin metathesis/rehydrogenation, breaking down polyethylene into low-molecular-weight alkanes.[32] In 2021, Beckham et al. performed a similar one-pot reaction using $SnPt/\gamma$-Al_2O_3 as the (de)hydrogenation catalyst and Re_2O_7/γ-Al_2O_3 as the metathesis catalyst.[33]

We envisaged a method of chemically degrading PVC in two steps. First, elimination of HCl by addition of base will create carbon-carbon double bonds, while sequestering the chloride as a salt. Subsequent olefin metathesis with an added alkene will cleave the double bonds, resulting in scission of the all-carbon polymer backbone.
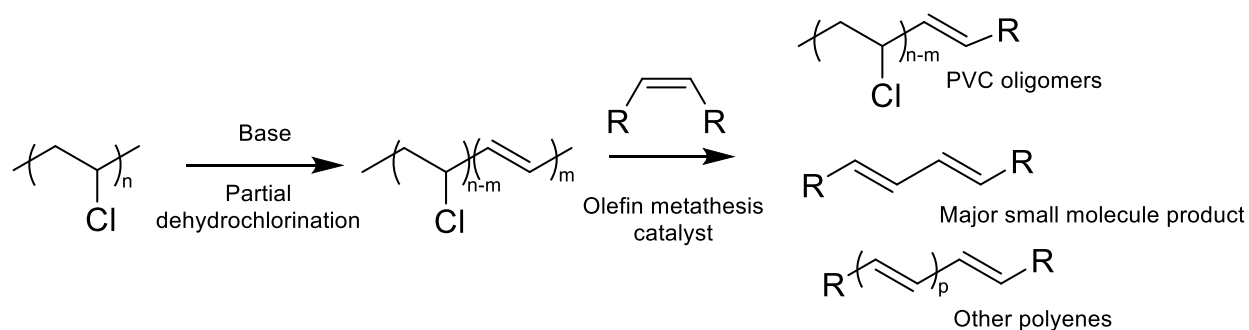
Scheme 1: General strategy for PVC degradation by olefin cross metathesis

Elimination of HCl from PVC has been extensively explored, ranging from partial elimination[34] to full elimination forming polyacetylene.[35,36] Elimination likely begins at defect sites such as allylic chlorides. Once the first elimination reaction occurs, the neighboring chloride becomes allylic, making it the most likely to react next. This "zipper" reaction leads to long stretches of conjugated alkenes between regions of unreacted PVC.[37] Polyacetylene is insoluble; use of substoichiometric amounts of base allows the resultant polymer to retain some solubility.[38] The use of hydroxide for the initial dehydrochlorination step has the added benefit of hydrolyzing harmful phthalate esters present in flexible PVC waste into the safer phthalic acid,[18] making this an appealing strategy.

Conjugated double bonds are less reactive towards olefin metathesis catalysts than isolated double bonds,[39] however there is precedent for olefin metathesis on conjugated polymers,[40] including polyacetylene,[41,42,43] which closely resembles the conjugated stretches of alkenes in dehydrochlorinated PVC.

**Results and Discussion**

Elimination

The course of the elimination reaction is influenced by the solvent, the amount of base used, and the presence or absence of competing nucleophiles (**Scheme 2**). Treatment of PVC with an excess of KOH in a THF/PEG-1000 solvent mixture produced fully eliminated PVC (polyacetylene) as a black precipitate, as reported in the literature.[36] Polyacetylene is insoluble in all solvents;[38] our attempts to perform olefin metathesis on this insoluble polyacetylene with added olefin gave no reaction.

Decreasing the amount of base used from three equivalents to less than one equivalent led to partially dehydrochlorinated PVC (DPVC) that was fully soluble in THF. Using tetrabutylammonium bromide (TBAB) and KOH in THF, DPVC with up to 8% loss of HCl was formed (**DPVC1**). ^{1}H NMR spectra are in agreement with the literature for similar levels of dehydrochlorination.[34]
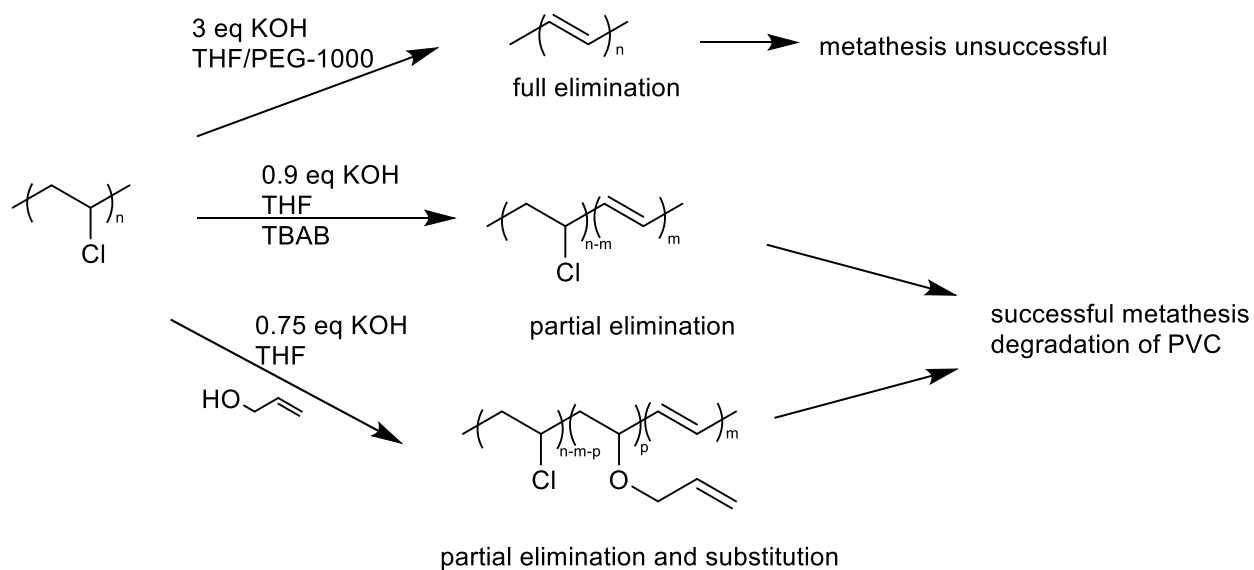
Scheme 2: Formation of polyacetylene (top) DPVC1 (middle) and DPVC2 through DPVC5 (bottom)

We envisaged that allyl ethers grafted to the PVC would undergo an intramolecular ring-closing metathesis reaction similar to that seen in polybutadiene at the 1,2 residues,[25,44] cleaving the chain and providing the catalyst access to the internal double bonds of the polymer (**Scheme 3**). To this end, elimination was performed with KOH in 2:1 THF/allyl alcohol as a solvent. The allyl oxide generated in situ can act as both a base and a nucleophile (**Scheme 2**, bottom pathway) To vary the ratio of substitution to elimination, reactions were done at three temperatures: room temperature (~20 °C) (**DPVC2**), 50 °C (**DPVC3**), and 80 °C (using anisole instead of THF) (**DPVC4**), see Table 1.
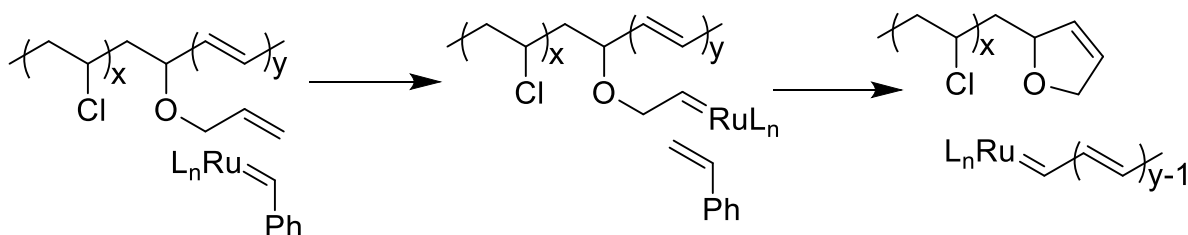
Scheme 3: proposed ring closing metathesis strategy to introduce the metathesis catalyst onto the internal double bonds of allyl-grafted DPVC

It is possible that competing S_N2 by hydroxide could introduce OH groups on the polymer backbone, interrupting the double bonds without providing a reactive site. To avoid this possibility, a separate elimination was performed using potassium *tert*-butoxide as the base in anhydrous THF/allyl alcohol (**DPVC5**). The DPVC samples were analyzed by NMR (**Figure 1**), and the percent elimination and substitution calculated using equations 1 and 2 respectively.

$$\%\text{elimination} = \frac{A - B/2}{A - B/2 + E} \quad (1)$$

$$\%\text{substitution} = \frac{B}{A - B/2 + E} \quad (2)$$
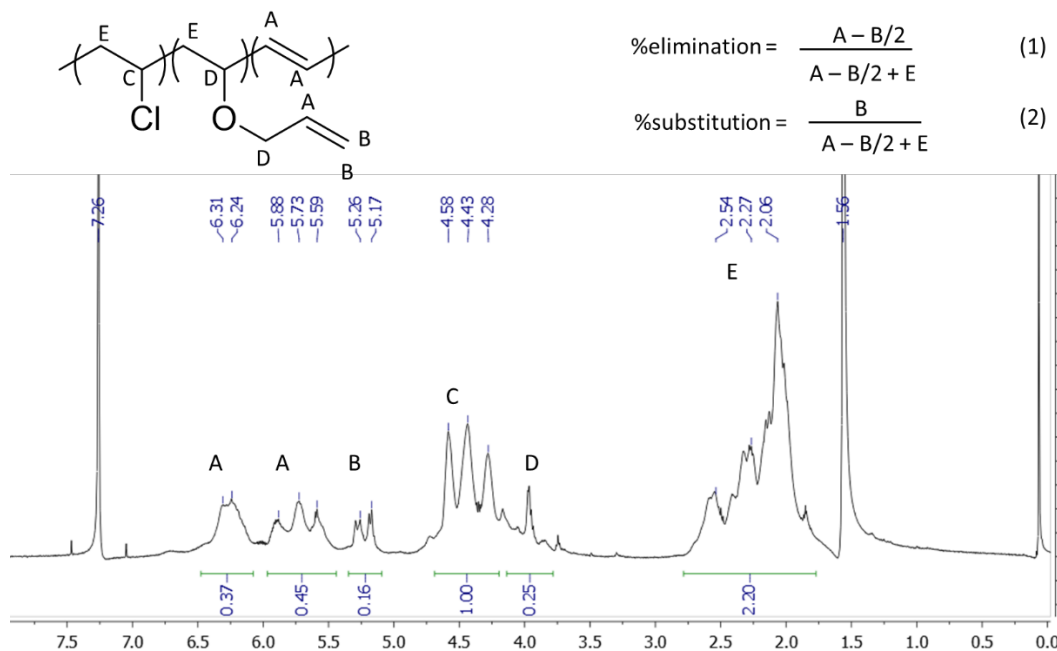
Figure 1: ^{1}H NMR spectrum of DPVC5 in CDCl$_3$ with formulas for determining % elimination and % substitution

Table 1

	% elimination[a]	% substitution[a]	Conjugation length[b]	MW[c] (kDa)
PVC	-	-	-	65 ± 3
DPVC1	8	-	4-13	44 ± 6
DPVC2[d]	16	4	4-13	29 ± 5
DPVC3[d]	21	5	4-13	12 ± 2
DPVC4[d]	23	8	4-13	14 ± 1
DPVC5[d]	23	5	4-13	10.9 ± 0.2

[a]Determined by ^{1}H NMR in CDCl$_3$. [b]Determined by UV-Vis in THF. [c]Determined by GPC vs linear polystyrene standards. ± Values are from duplicate GPC runs. [d]Not fully soluble in CDCl$_3$ or THF. For analysis only, insoluble portion was filtered before GPC and UV-Vis.

Note: the molecular weight of the PVC as purchased is 22kDa, compared to the 65kDa measured using GPC with polystyrene reference standards, indicating that these standards do not behave the same as PVC in solution. However, these standards are regularly used, and are helpful in comparing the differences in molecular weights between samples. The lower apparent molecular weights for DPVC2 through DPVC5 may be due in part to insolubility of high MW fractions after extensive elimination. For analytical purposes, insoluble portions were removed by filtration prior to GPC analysis.
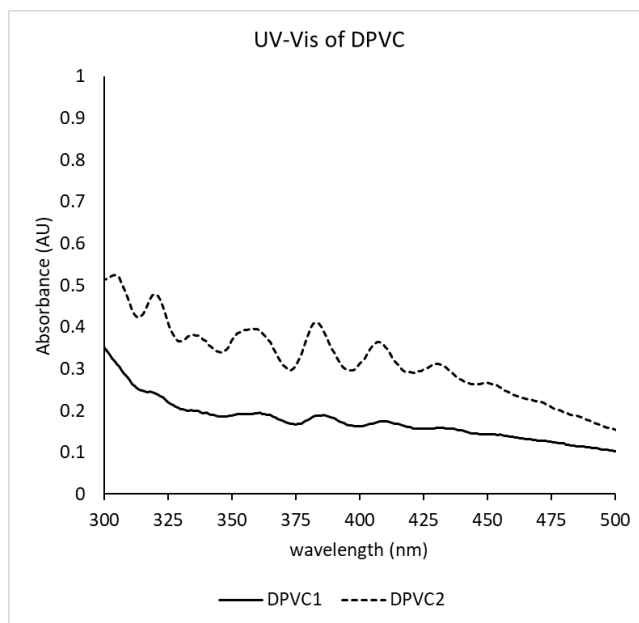

Figure 2: UV-Vis spectra of DPVC1 (solid line) and DPVC2 (dotted line) in THF

The UV-Vis spectra of all DPVC samples (**Figure 2**) are similar to those from previous reports of DPVC[45] and polyacetylene.[41] All exhibit long conjugated regions due to the zipper reaction. Peaks at 305, 321, and 336 nm correspond to conjugation lengths as low as 4 double bonds, while the highest distinguishable peak at 452 nm corresponds to a conjugation length of 11-13 double bonds.[45]

Metathesis

Olefin metathesis was performed using *Z*-1,4-diacetoxy-2-butene (**DAB**), DPVCx and Grubbs 2 catalyst in refluxing dichloromethane (DCM). Following olefin metathesis at many double bond sites, the expected products are PVC oligomers (from the non-eliminated segments) and a mixture of different-length polyenes (**Scheme 4**). If these polyenes continue to undergo metathesis and are equally reactive, an exponential distribution would form, with the largest fraction being starting alkene, followed by diene **1**, followed by triene, etc. However, the reactivities are likely not equal, leading to a complex mixture.
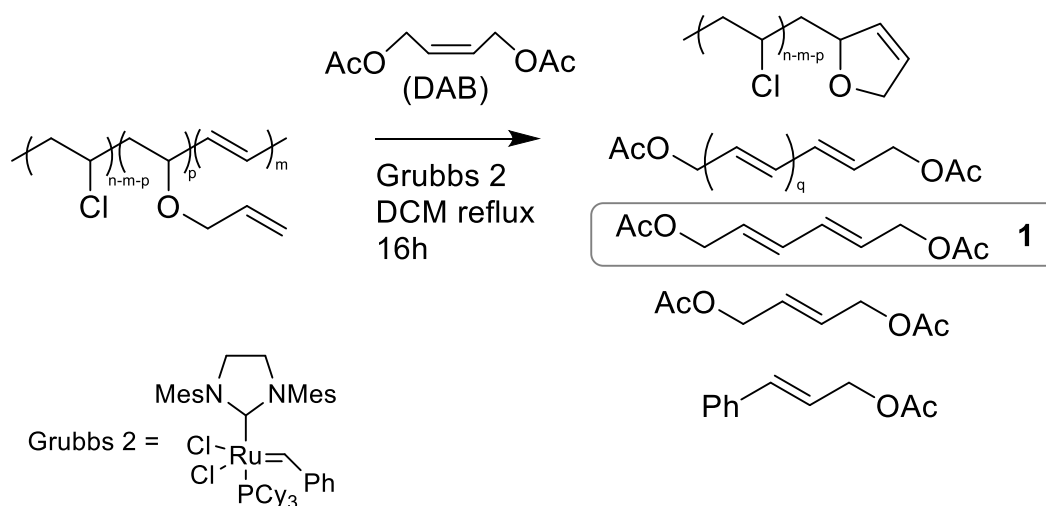
Scheme 4: Expected products from the metathesis reaction. Cinnamyl acetate is formed from the initial reaction of DAB with the Grubbs catalyst containing a Ph-CH= moiety. *Trans*-DAB is formed by self-metathesis of *cis*-DAB.

Diacetoxybutene was chosen as the partner olefin for cross metathesis instead of allyl acetate, to limit the formation of Ru=CH$_2$ species which are prone to decomposition.[46] The *Z*-isomer was used instead of the *E*-isomer due to the *Z*-diol being readily available. However, during the reaction the starting material is converted into mostly the *E*-isomer by self-metathesis. Diene

1 shown in Scheme 4 is expected to be the major product of repeated cross-metathesis, within a statistical mixture of other polyenes. Only the diene was positively identified by NMR and HRMS (Supporting Information page S5).

Table 2

| Entry	Polymer	Olefin partner	Temperature (^{o}C)	Solvent	MW[a] (kDa)	Corresponding diene formed?[b]
1	**DPVC1**	DAB	40	DCM	15.0	Yes
2	**DPVC2**	DAB	40	DCM	3.5 ± 0.8	Yes
3	**DPVC3**	DAB	40	DCM	3.0 ± 1.3	Yes
4	**DPVC4**	DAB	40	DCM	2.7 ± 0.5	Yes
5	**DPVC5**	DAB	40	DCM	3.8	Yes
6	DPVC4	**None**	40	DCM	1.9 ± 0.4	N/A
7	DPVC3	**Trans-stilbene**	40	DCM	2.8	No
8	DPVC3	**1-Hexene**	40	DCM	2.3	No
9	DPVC2	**Butyl acrylate**	40	DCM	5.4	No
10	DPVC5	DAB	**55**	**DCE**	1.9 ± 0.2	Yes
11	DPVC5	DAB	**55**	**CHCl₃**	1.8 ± 0.3	Yes
12 (**c**)	DPVC2	DAB	40	DCM	10.8	No
13 (**d**)	DPVC2	DAB	40	DCM	7.2	No
14 (**e**)	DPVC2	DAB	40	DCM	4.6	Yes
15 (**f**)	DPVC5	DAB	40	DCM	3.0	Yes

[a]Determined by GPC vs. linear polystyrene standards. ± Values are from duplicate reactions. Values without ± are from one reaction. [b]Determined by ^{1}H NMR, amount could not be quantified

due to peak overlap. [c] 1 mol% Grubbs 2 instead of 5 mol%. [d] 5 mol% Grubbs 3 instead of Grubbs 2. [e] 5 mol% Hoveyda-Grubbs 2 instead of Grubbs 2. [f] Freeze-pump-thaw deoxygenated, shielded from light.

Although none of the allylDPVC samples are fully soluble in the solvents used during metathesis, the reaction proceeds on the partially dissolved material to produce a homogeneous solution. The increase in solubility over the course of the reaction is likely due to a shortening of the polymer chains, as corroborated by GPC.

DPVC1, the only DPVC sample lacking allyl pendants, shows a modest decrease in molecular weight upon metathesis (entry 1). DPVC2 through DPVC5 show a much greater MW decrease, indicating that the allyl ether pendants successfully facilitate cleavage of the polymer backbone. In addition to GPC, DOSY NMR measurements also show a distinct decrease in molecular weight (Supporting information page **S17**). Carrying out the metathesis reaction in the absence of an added olefin partner (entry 6) gives roughly the same molecular weights as in the presence of an added olefin, which implies that the ring closing metathesis reaction **(Scheme 3)** is the major driver of MW decrease. Use of trans-stilbene, 1-hexene, or butyl acrylate as the olefin partner did not produce the corresponding diene, but did decrease the MW of the polymer, indicating the ring-closing metathesis reaction occurred, but the conjugated double bonds of the DPVC did not undergo cross metathesis with these olefin partners. DPVC5, prepared using potassium t-butoxide, did not perform significantly differently in metathesis than DPVC3, prepared using potassium hydroxide.
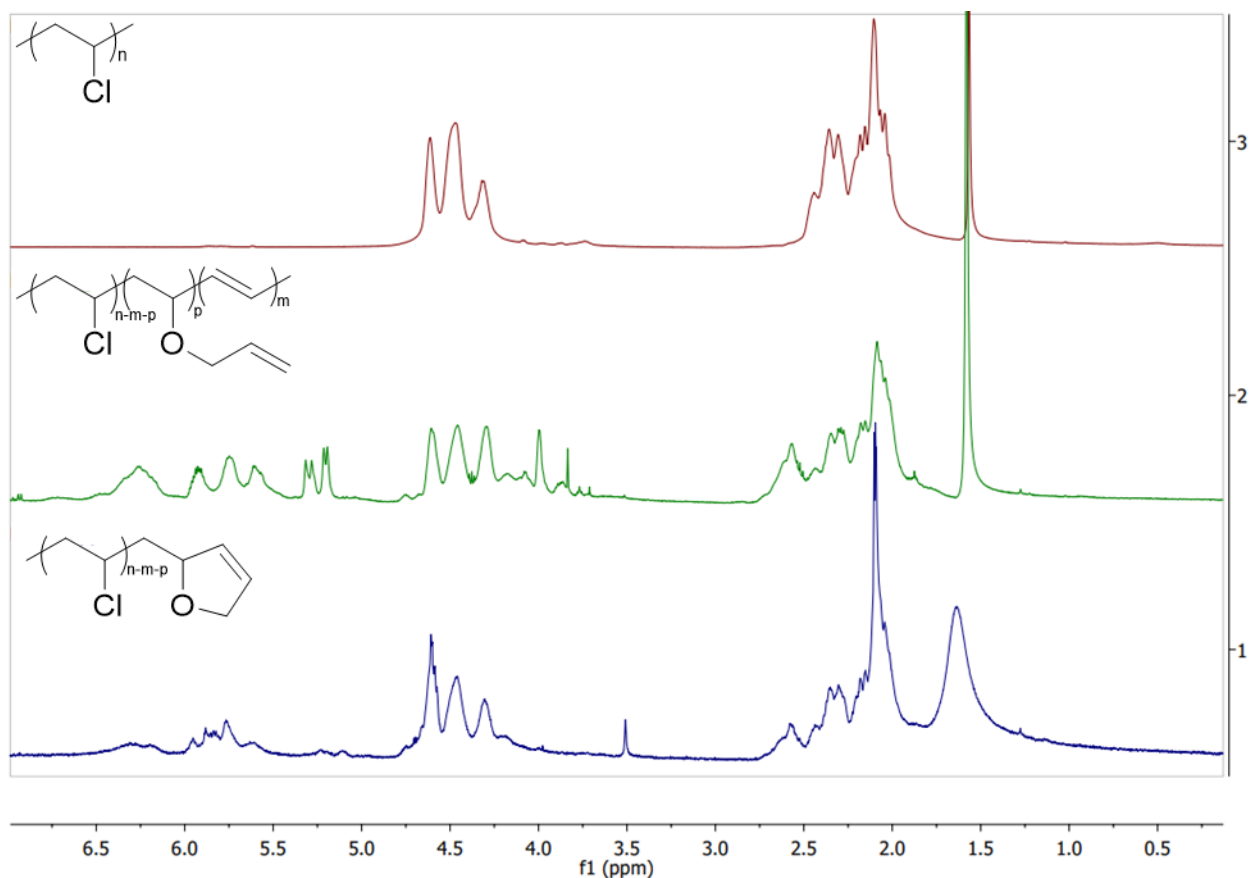
Figure 3: ^{1}H NMR Spectra of PVC (top), DPVC4 (middle), and PVC oligomers (entry 4, **table 2**) (bottom) in CDCl$_3$. After the metathesis reaction, the alkene peaks decrease but are not consumed entirely. The terminal alkene peaks at 5.20 and 5.30 corresponding to the allyl ethers are consumed.

The PVC oligomers obtained were separated from the small-molecule products by precipitation into methanol. By ^{1}H NMR, the oligomers appear quite similar to PVC, although some double bonds remain (**Figure 3**). The oligomers from the allyl DPVC (DPVC2 through DPVC5) show no distinguishable peaks on UV-Vis, indicating the long conjugated polyenes are no longer present. Following precipitation of the metathesis products, the methanol-soluble fraction shows only slight peaks at 320 and 353 nm, indicating no polyenes greater than five double bonds are present[45] (**Figure 4**, left). However, the oligomers made from DPVC1 (lacking allyl

13

pendants) still display several peaks in the UV-Vis, indicating unreacted conjugated double bonds (**Figure 4,** right).
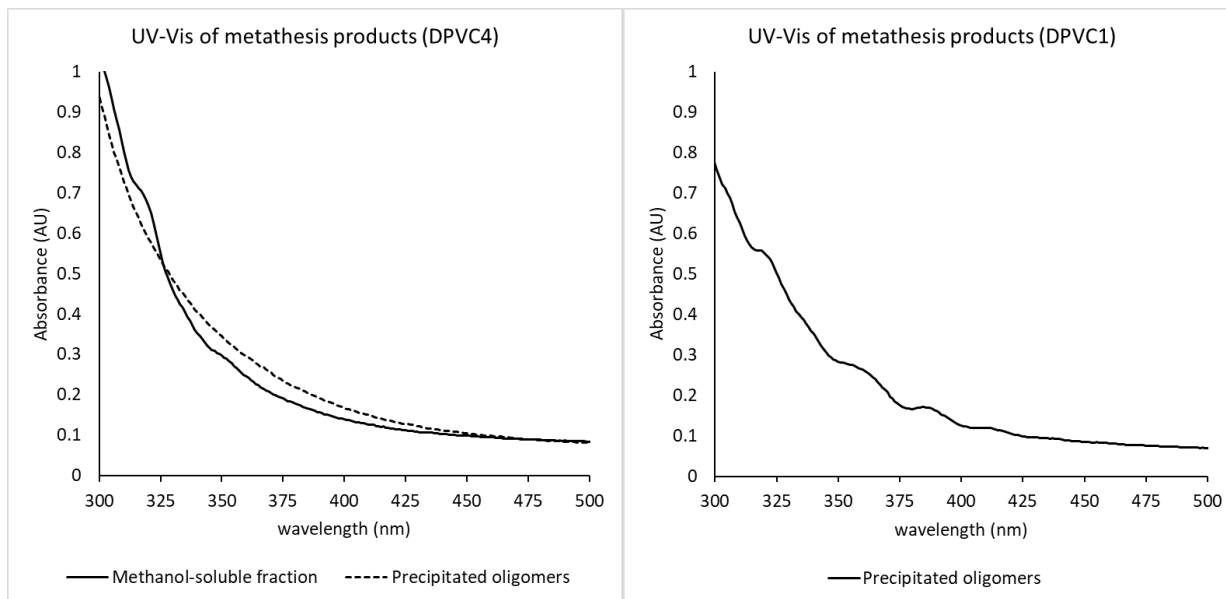
Figure 4: Left: UV-Vis of the metathesis products of DPVC4 (entry 4, **Table 2**). The fraction that precipitates in methanol is shown with a dotted line, and the remainder (recovered by evaporation of MeOH) with a solid line. **Right:** UV-Vis of the metathesis products of DPVC1 (entry 1, **Table 2**). The fraction that precipitates in methanol is shown. All UV-Vis spectra were taken in THF.

Although the significant decrease in molecular weight confirms successful breakdown of PVC, the production of small-molecule products is limited, with only a small amount of diene **1** formed. Due to peak overlap in the ^{1}H NMR, the yields could not be reliably quantified, but appeared to be no more than 12% (See Supporting Information page S6). **1** could be partially purified by column chromatography, and the structure confirmed by ^{1}H NMR, COSY and HRMS.

Polyacetylene is sensitive to oxygen, degrading into a mixture of products.[38] Oxidation of the polyacetylene segments may contribute to the low amount of diene **1** formed. To avoid possible

oxidative degradation, metathesis was performed on a fresh DPVC sample in the dark under argon atmosphere, immediately after the elimination reaction (**Table 2**, entry 15). Similar amounts of diene **1** and similar molecular weights for the PVC oligomers were observed.

Previous investigations by Tuba showed temperatures higher than 40 °C led to more effective metathesis on conjugated alkenes.[39] However, raising the temperature from 40 to 55 °C in either 1,2-dichloroethane (DCE) or CHCl$_3$ gave similar results to refluxing DCM (**Table 2**, entries 10 and 11). The Grubbs 3 and Hoveyda Grubbs 2 catalysts proved less effective than Grubbs 2 (**Table 2**, entries 13 and 14).

Multiple authors[41,42,43,47] have observed benzene formation from backbiting during metathesis of polyacetylene. However, ^{1}H NMR of the crude reaction mixture did not reveal the presence of benzene. This may be explained by the fact that *cis* double bonds are required for benzene formation, while dehydrochlorinated PVC likely contains mostly *trans* double bonds. Tandem isomerization/metathesis to produce benzene may be an interesting avenue to explore.

Because the oligomers obtained are predominately PVC, they should be able to undergo a second partial elimination, followed by a second metathesis step to break them down further. Initial attempts to perform elimination followed by metathesis on the oligomers using the same conditions used for PVC were unsuccessful. Further optimization of the conditions is being investigated.

Conclusion

We have successfully demonstrated that elimination of HCl followed by olefin metathesis with an added alkene effectively cleaves the all-carbon backbone of PVC to create much lower molecular weight oligomers. This effect was enhanced with the use of allyl pendants. Using 1,4-diacetoxy-2-butene as an added olefin, the expected diene product was identified, providing a

proof of concept for harvesting carbon from PVC. Given the paucity of upcycling options for PVC, the third-largest commodity plastic, this work provides an entry into the use of olefin metathesis to create new products from PVC waste.

Experimental

PVC (M_n= 22kDa, M_w= 43kDa, Aldrich) was purified by dissolving in THF and precipitation in methanol three times. Anhydrous THF was dried using a PureSolv-EN purification system. All other reagents were used as received.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III HD four channel 500 MHz Oxford Magnet NMR spectrometer with automation. High Resolution Mass Spectrometry (HRMS) was recorded with a Thermo Scientific LTQ-Orbitrap Velos Pro mass spectrometer. UV-Vis measurements were taken on a Shimadzu UV-2700 UV-Vis Spectrophotomter with samples dissolved in THF. Gel Permeation Chromatography (GPC) measurements were performed in THF using two Agilent PLgel 5μm Mixed-D columns, and a Waters 2410 refractive index detector, using linear polystyrene standards. IR was performed using a Perkin-Elmer Spectrum Two FT-IR with ATR.

Z-1,4-Diacetoxy-2-butene was synthesized using the method of von Czapiewski.[48] Full elimination of PVC to polyacetylene was performed using the method of Guo.[36]

Partial elimination of PVC (DPVC1)

PVC (1.01 g, 16.2 mmol repeat unit) and tetrabutylammonium bromide (0.10 g, 0.31 mmol) were dissolved in 100 mL of THF. KOH pellets (0.8 g, 14 mmol) were crushed then added. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was precipitated

into methanol, filtered, dissolved in THF, and precipitated into methanol again to produce a brown solid (0.80 g, 83% yield).

Elimination of PVC with allyl alcohol (DPVC2)

PVC (0.97 g, 15.5 mmol of repeat unit) was dissolved in 20 mL of THF and 10 mL (150 mmol) of allyl alcohol. KOH pellets (0.64 g, 11.4 mmol) were crushed then added. The reaction mixture was stirred at RT (~20 °C) for 48 h. The mixture was concentrated by rotary evaporator then precipitated into methanol, producing a dark brown solid (915 mg, 102% yield).

DPVC3

PVC (3.00 g, 48.0 mmol of repeat unit) was dissolved in 60 mL of THF and 30 mL (440 mmol) of allyl alcohol. KOH pellets (1.97 g, 35.1 mmol) were crushed then added. The reaction mixture was stirred at 50 °C for 48 h. The mixture was concentrated by rotary evaporator then precipitated into methanol, producing a dark brown solid (2.74 g, 102% yield).

DPVC4

PVC (0.99 g, 15.8 mmol of repeat unit) was dissolved in 20 mL of THF and 10 mL (150 mmol) of allyl alcohol. KOH pellets (0.66 g, 11.8 mmol) were crushed then added. The reaction mixture was stirred at 80 °C for 19 h. The mixture was concentrated by rotary evaporator then precipitated into methanol, producing a dark brown solid (709 mg, 80.4% yield).

Elimination of PVC with allyl alcohol and t-butoxide (DPVC5)

A flame-dried flask was charged with potassium *t*-butoxide (833.4 mg, 7.426 mmol) and dried under vacuum. Allyl alcohol (10 mL, 150 mmol) was added. In a separate flask, PVC (1.01 g, 16.2 mmol of repeat unit) was dissolved in 20 mL of anhydrous THF. The PVC solution was

added to the *t*BuOK solution by syringe. The mixture was stirred at 50 °C for 4 h. The mixture was concentrated by rotary evaporator then precipitated into methanol, producing a dark brown solid (962.2 mg, 111% yield).

General procedure for olefin metathesis

DPVC3 (199.1 mg, 0.748 mmol of internal double bonds) was added to 20 mL DCE, which dissolved some of the polymer but left large amounts solid. *Z*-1,4-Diacetoxy-2-butene (127.1 mg, 0.738 mmol) and Grubbs 2 (33.4 mg, 0.0393 mmol) were added. The mixture was stirred at 55 °C for 16 h, resulting in a homogenous brown solution. The reaction mixture was concentrated by rotary evaporator, redissolved in a minimum amount of THF, and precipitated into methanol. The precipitate was filtered and rinsed with methanol. The filtrate was concentrated by rotary evaporator, then subjected to column chromatography (ethyl acetate 0 to 40% in hexanes). 1,6-Diacetoxy-2,4-hexadiene (**1**) coeluted with *Z*-1,4-diacetoxy-2-butene. ^{1}H NMR of **1** matches the literature.[49,50] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.28 (d, *J* = 14.6 Hz, 1H), 5.80 (ddd, *J* = 12.3, 9.7, 6.6 Hz, 2H), 4.60 (d, *J* = 6.0 Hz, 2H), 2.07 (s, 6H). HRMS: $[C_{10}H_{14}O_4Na]^+$ (M+Na)$^+$ calcd. 221.0785, obs. 221.0781.

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available: ^{1}H and DOSY NMR spectra, UV-Vis spectra and GPC retention times.

Keywords

Dehydrochlorination, Olefin Metathesis, Plastic waste, PVC, Upcycling

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TOC entry
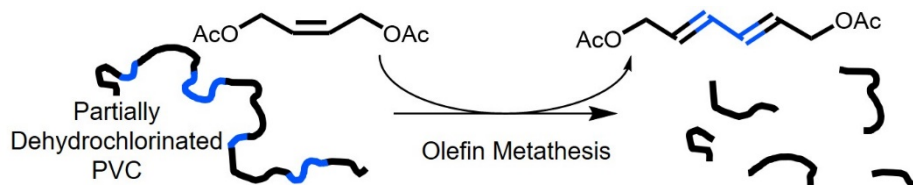
A two-step procedure for the degradation of Polyvinyl chloride (PVC) is demonstrated. Elimination of HCl using base affords double bonds on the polymer backbone, which are then cleaved by olefin metathesis with an added alkene. The molecular weight of the products is greatly reduced from the original PVC, and a diene corresponding to the added alkene is obtained. This provides an initial proof of concept towards upcycling PVC into new chemical products.