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Understanding the competition between hydrodechlorination and Friedel–Crafts alkylation in PVC dechlorination with silylium ions†

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The combination of hydrodechlorination and Friedel–Crafts alkylation using silylium ions is a rapid route to fully dechlorinate poly(vinyl chloride) (PVC), while producing organic and chlorine-based products that have value for a second life. This silylium reaction has been optimized for full dechlorination under ambient conditions for a range of temperatures. Additionally, tetramethyldisiloxane is introduced as a cheaper and more moisture-stable silane, which shows similar activity as triethylsilane. While high selectivity for Friedel–Crafts alkylation has been achieved for molecular silylium chemistry, analogous attempts with PVC as a substrate have revealed a maximum arene incorporation below 30%. However, reaction conditions and choice of aromatic solvent show dramatic changes in thermal properties of the poly(ethylene-co-poly(vinyl arene)) polymer product. These differences in thermal properties align with a variable side reaction of secondary Friedel–Crafts alkylation, either intramolecularly to form polyindene repeating units or intermolecularly to form crosslinks.

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Introduction

Poly(vinyl chloride) (PVC) is a versatile polymer for countless applications, making it the third-most produced plastic worldwide.¹ However, this material has one of the most harmful ends-of-life, leading to low recycling rates and initiatives to ban the use of PVC. The consequential end-of-life of PVC often lies in the leaching of toxic additives, including heavy metals and plasticizers, and the generation of hydrochloric acid and dioxins upon thermal or UV treatment.² The diverse additives prevent practical mechanical recycling of PVC items. Although PVC is not accepted at most recycling facilities, its presence, even as small impurities, can harm the polyolefin streams (polyethylene and polypropylene), where the hydrochloric acid (HCl) can disrupt both pyrolysis and mechanical recycling of these polymers.³ With the large quantities already produced

and the difficulty to replace PVC for many applications, environmentally friendly management of PVC waste is a critical need.

There have been several emerging strategies to repurpose PVC waste.^{4,5} Most strategies have aimed to improve efforts for pyrolysis or mechanical recycling of polyolefin waste by minimizing the impact of HCl produced and/or converting the polymer chain to better represent the general polyolefin waste stream. One route has been to perform a pre-dechlorination step *via* dehydrochlorination, at a lower temperature in the presence of a base prior to pyrolysis.^{6–15} This lowers the amount of HCl in a pyrolysis reactor and prolongs the lifetime of a pyrolysis catalyst. However, when pyrolyzed, the polyacetylene-like product still disrupts product distributions through the formation of polyaromatics. One way to improve upon this strategy is to introduce a sequential hydrogenation reaction to convert the polyacetylene-like product to polyethylene.^{16–18} Hydrogenation reactions to high conversion without disrupting the polymer backbone are still challenging with this strategy, as the conjugation in polyacetylene resists functionalization. Direct hydrodechlorination of PVC can eliminate HCl production entirely, while producing polyethylene-like materials for pyrolysis or mechanical recycling.^{19–21} Although metal-catalyzed routes and silylium-catalyzed routes have been realized, cross-linking and branching formation have altered materials from linear polyethylene. While these strategies

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decrease the toxicity of the waste PVC and could serve an important role in the processing of mixed plastics waste, they do not add value to the organic product and may not produce valuable chlorinated products.

There are even fewer examples focused on the conversion of PVC to value-added organic and chlorinated products, without the production of harmful byproducts (Fig. 1). These strategies would be much better suited to create value through the repurposing of direct PVC waste streams. Groups have been interested in the dehydrochlorination of PVC, followed by olefin metathesis to generate small molecule olefins (Fig. 1a).^{22,23} While the PVC materials have been broken down into smaller molecules, full dechlorination and selectivity for a molecular product have not yet been achieved. McNeil and coworkers have taken a unique strategy to electrochemically repurpose the chlorine through the chlorination of arenes (Fig. 1b).²⁴ Excitingly, plasticizer additives that are often considered challenges for catalyst survival are crucial for this route, making this method well-suited for commercial PVC items. However, the partially chlorinated polymer product is not prioritized, which maintains a degree of waste. Stache and coworkers have reported an alternative photothermal route to generate and

use the HCl from PVC to hydrochlorinate styrene and other alkenes (Fig. 1c).²⁵ In most of these cases, either the chlorine or the organic material is prioritized, leaving the remaining material as waste.

Our group has recently identified a method to use silylium cation catalysis to perform a tandem Friedel–Crafts alkylation and hydrodechlorination (or reduction) to form polyethylene (PE)-*co*-polystyrene (PS) random copolymers (Fig. 1d).²⁶ In this method, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ serves as the initiator, triethylsilane (Et_3SiH) serves as a hydride and silylium cation source, and the arenes used were benzene, toluene and xylenes. When using methylated arenes, at 0.25 mol% catalyst loading and 1.1 equiv. Et_3SiH , full dechlorination of PVC could be realized in less than 5 minutes at 110 °C. In all cases, arene incorporation into the polymer chain was always close to 20%, with high selectivity for PE at approximately 80% incorporation. These copolymers are of interest for battery membrane applications and as compatibilizers,^{27–34} but they can be difficult to make from ethylene and styrene directly,^{35–38} which has often led to creative synthetic strategies with metathesis polymerization.^{34,39–42} The chlorine byproduct, Et_3SiCl , has a higher cost than the original Et_3SiH and has numerous commercial uses, leaving minimal waste and adding value to all products in the overall process.

Silylium catalysis has been used in molecular chemistry to prioritize reduction or Friedel–Crafts alkylation selectivity, but not prioritizing a combination of both methods in the same pot.^{43,44} The result of this type of catalysis in the case of repurposing PVC would vary the amount of PE and PS-like repeat units in the polymer product, presumably altering the properties.⁴⁵ As an extreme, our group has recently reported the direct selectivity to PE, where we achieved polymer products that match the properties of polyethylene with tunable degrees of branching under mild conditions and on the benchtop with the same silylium chemistry.²⁰

Herein, the efforts made to better understand the method for dual hydrodechlorination and Friedel–Crafts alkylation of PVC to form polyethylene-*co*-poly(vinyl arene) copolymers are reported. Efforts to increase arene incorporation into the polymer product have led to the discovery of intramolecular Friedel–Crafts alkylation to form polyindene-like repeating units in the product. Polyindene formation can be tuned based on the arene reactant and the reaction temperature, leading to a wide variety of polymer products with tunable thermal properties.

Results and discussion

Prior studies showed that dechlorination can be achieved with benzene, toluene and xylene, with toluene and all three xylenes showing more rapid dechlorination than benzene.²⁶ In addition to the influence of the electron-donating methyl substituents, this difference in reactivity is likely due to the formation of more cross-linked materials with benzene, through secondary Friedel–Crafts alkylation reactions on the same aro-

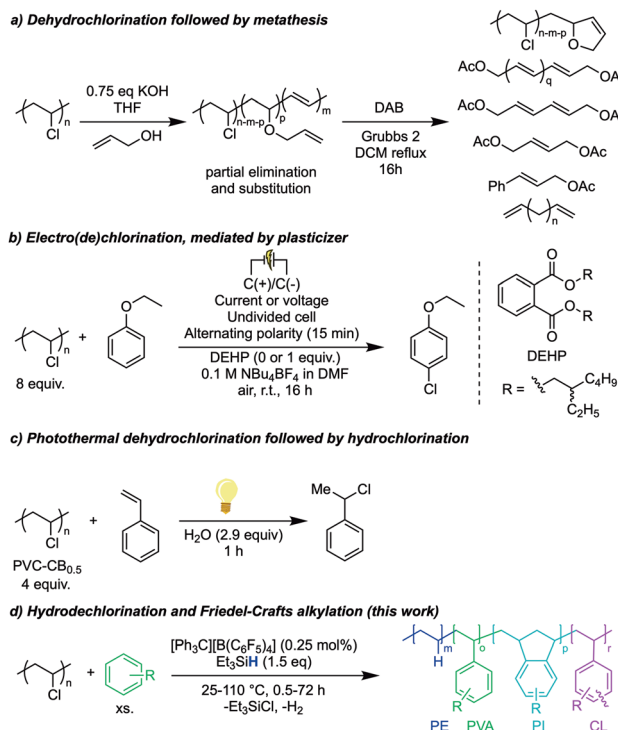


Fig. 1 Past work to generate value from waste PVC using strategies including: (a) dechlorination followed by metathesis to form diene macromonomers, (b) electro(de)chlorination to chlorinate arenes, (c) photothermal dehydrochlorination followed by hydrochlorination of styrene (PVC-CB_{0.5} includes 0.5 wt% carbon black ground into a homogeneous mixture with PVC), with plausible products that can be obtained from the hydrochlorinated styrene product and (d) hydrodechlorination and Friedel–Crafts alkylation, which generates polyethylene (PE), poly(vinyl arene) (PVA) and polyindene (PI) repeating units, as well as presence of cross-linking (CL).

matic ring, generating less soluble products. Evidence of this cross-linking was previously seen in Friedel–Crafts alkylation of PVC with benzene and other catalyst systems.^{46–49} Toluene was selected as the primary aromatic solvent for these studies, as the polymer products are more soluble and toluene is a common, inexpensive solvent. Chlorine loss from the product is confirmed by attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy and ¹H nuclear magnetic resonance (¹H NMR) spectroscopy.

Air stability of the method

Repetitions of the prior reported air-free toluene studies for 5 minutes did not lead to full dechlorination of PVC, leaving 12 mol% PVC remaining in the polymer. This inconsistency could be due to several factors, including the humidity, water content in the aromatic solvent, and the purity of the batch of Et₃SiH and [Ph₃C][B(C₆F₅)₄] purchased. In our prior report, this tandem process could be achieved under ambient conditions, with benzene, Et₃SiH and PVC all stored outside the glovebox and [Ph₃C][B(C₆F₅)₄] taken out of the glovebox right before the reaction.²⁶ Using the prior optimized air-free conditions for dechlorination with toluene as the solvent did not support full dechlorination of PVC under ambient conditions either.

Further optimization of this method with toluene, as described in the ESI,[†] was able to achieve reproducible, full dechlorination of PVC under ambient conditions (Table 1, entry 1). In this case, the low 0.25 mol% initiator loading could be maintained, while the Et₃SiH loading needed to be slightly higher (1.5 equiv.), toluene was dried in a solvent system, and 30 minutes of reaction time was needed. This presents a trade-off between reactions conducted air-free, which require more preparation, and ambient conditions, which require more reagent and longer time. Additionally, control reactions showed that the [Ph₃C][B(C₆F₅)₄] initiator can be stored outside of the glovebox as long as 71 days without losing the ability to fully dechlorinate PVC. Nevertheless, reproducible full dechlorination of PVC under ambient conditions in less than 2 hours is still quite rapid and eliminating

the need to dry and store all reagents air-free allows for faster reaction set-up.

Selectivity for organic product

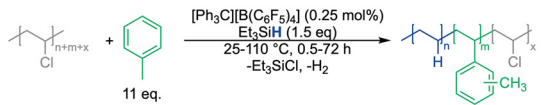
Previously, the toluene incorporation into the product was consistently near 20 mol%, with approximately 80 mol% ethylene units formed on the backbone, based on ¹H NMR spectroscopy. It is important to note that the ¹H NMR spectra of these samples are extremely broad, making it difficult to observe subtle changes in the arene incorporation. The broad ¹H NMR spectra also speak to a key difference in these materials from polyethylene with precise phenyl groups added, which have sharp and easily resolved peaks.^{34,40,41} The ability to tune the arene incorporation to a wider array of products would improve the practicality of this method for commercial PVC repurposing.

For the optimized ambient reaction conditions with toluene, variations were made to alter the arene incorporation into the polymer product. As previously demonstrated, removal of the arene solvent can lead to full hydrodechlorination of PVC and formation of PE products.²⁰ In this case, the silane loading impacted how much carbocation rearrangement could occur, leading to tailored branching in the product. Therefore, adjustments to the reaction conditions were conducted to increase the arene incorporation, to get closer to a PS-like polymer. Molecular literature indicates the rate-determining step to likely be the dehalogenation with a silylium cation.⁵⁰ Therefore, product selectivity likely relies on the relative reactivity of the carbocation with the silane and the aromatic solvent.

Silane and arene stoichiometry. While both hydrodechlorination and Friedel–Crafts alkylation rely on the Et₃SiH to turn-over the cycle, we hypothesized that slow addition of Et₃SiH could lead to increased preference for Friedel–Crafts alkylation. However, lowered concentrations of Et₃SiH significantly slowed dechlorination, with just over 50% conversion of PVC after 2 hours (Table 1, entry 2). This indicates that the silane or silylium cation concentration is likely important for the rate law of both reactions. Even so, the arene incorporation is less than 20 mol% of the product repeating units, counter to the hypothesis. Although toluene is already in excess as the solvent, attempts to double the toluene loading did not increase arene incorporation (Table 1, entry 3).

Temperature. One hypothesis was that varied temperature reactions could show a lowered preference for one pathway. Reactions with the optimized conditions as in Table 1, entry 1 were run at three lower temperatures than the base conditions. At 80 and 60 °C, the reactions were still able to reach full dechlorination within an hour (Table 1, entries 4 and 5, respectively), with arene insertion maintaining near 20 mol%. Reactions at room temperature (approximately 25 °C) could show full dechlorination, albeit inconsistently and often requiring reaction times of 64 hours or longer (Table 1, entry 6). However, approximately 20 mol% arene incorporation was still maintained at room temperature. These results counter the hypotheses described above and indicate that temperature

Table 1 Dechlorination conditions to target changes in arene incorporation into the polymer product

					
Entry	Temp. (°C)	Time (h)	PE ^a (mol %)	Aryl ^a (mol %)	PVC ^a (mol %)
1	110	0.5	80	20	0
2 ^b	110	2	48	11	41
3 ^c	110	18	79	22	0
4	80	1	81	19	0
5	60	1	79	22	0
6	25	72	84	16	0

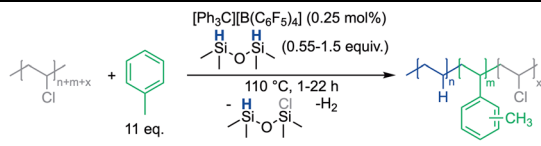
^a Determined by relative ratios in ¹H NMR spectra. ^b Et₃SiH was added slowly throughout the reaction. ^c 22 equiv. toluene was used.

is not an option to vary the preference difference for hydrodechlorination or Friedel–Crafts alkylation.

Silane structure

While Et_3SiH has been the most common silane source for silylium chemistry, it is a stoichiometric reagent, therefore cost is important. However, the Et_3SiCl byproduct is often sold at a higher price than its precursor and can be used in applications such as drying metal salts and in polymerizations.⁵¹ Nonetheless, having a less expensive silane source could provide additional options for this strategy. One such option that is more moisture-stable is 1,1,3,3-tetramethyldisiloxane (TMDS); however, there are no reports using it for dehalogenation of organic molecules. It was questioned whether both hydrides could be used, in which the method would only need 0.5 equivalents of a cheaper silane source. As shown in Table 2, TMDS is an active silane source for the dechlorination of PVC. Yet only one hydride is consumed, even when less than 1 equivalent of TMDS is provided and the reaction is run for 22 hours (Table 2, entry 1). Due to its higher moisture stability, consistent full dechlorination can be achieved with just 1.1 equivalents of TMDS, making it more efficient under ambient conditions than Et_3SiH (Table 2, entry 5). Even with this dramatically different silane structure, arene incorporation remains near 20 mol%. It was hypothesized that TMDS might degrade in the reaction conditions at 110 °C, which could explain why the second hydride cannot be used. Unfortunately, reactions performed at 60 °C were also not able to use the second hydride. It is therefore likely that once one hydride is replaced with a chloride, the second hydride is much harder to abstract. Calculations indicate that the use of the second hydride in TMDS should be thermodynamically favorable (as described in the ESI†), which could indicate a high kinetic barrier for this second hydride abstraction.

Table 2 Identifying activity of TMDS as a silane source for silylium-catalyzed hydrodechlorination and Friedel–Crafts alkylation of PVC



Entry	TMDS eq.	Time (h)	PE ^a (mol %)	Aryl ^a (mol %)	PVC ^a (mol %)
1	0.55	22	44	13	43
2	0.55	1	39	11	50
3	0.75	1	37	17	46
4	1	1	77	22	1
5	1.1	1	78	22	0
6	1.5	1	78	22	0
7 ^b	0.55	1	45	16	41
8 ^b	0.55	2	34	11	55
9 ^b	0.55	6	43	13	44
10 ^b	0.55	18	39	12	49

^a Determined by relative ratios in ^1H NMR spectra. ^b Reactions were run at 60 °C.

Arene substitutions

As shown in prior work, addition of methyl groups to the arene solvent enhanced the rate of dechlorination, but did not greatly impact the selectivity preference for hydrodechlorination over Friedel–Crafts alkylation. Reactions with benzene, and xylene (*ortho*, *meta* and *para*) at different temperatures show the same behavior as toluene, in which full dechlorination is achieved with approximately 20 mol% incorporation of the arene solvent (see Tables S5–S8†).

Thermal properties

In our prior report, the glass transition temperature (T_g) of the PE/PS copolymer products were much higher in temperature (>51 °C) than expected for a PE/PS copolymer.²⁶ Further, when comparing these products to past reported copolymers with approximately the same amount of arene content, the poly(ethylene-*co*-styrene) products from past literature had a lower T_g of around 17–23 °C.^{34,40,41} In these polymers, the arenes were evenly displaced across the polymer, and the ^1H NMR spectra contains reasonably sharp signals. However, ^1H NMR spectra of the polymer products in this study are extremely broad. One explanation for these observations could be due to a second, intramolecular Friedel–Crafts alkylation, leading to polyindene formation (Fig. 2). The proposed polyindene formed would be slightly different in structure than the product of indene polymerization, although the thermal properties are expected to be similar. Polyindene is shown to have broad ^1H NMR spectra and T_g s above 200 °C. Polyindene formation has been previously hypothesized as a side reaction in the Friedel–Crafts alkylation of PVC with AlCl_3 .^{46,47,52} Therefore, it was hypothesized that increased presence of polyindene would be a likely cause of the increase in the observed T_g for these materials.

DSC studies of the polymers produced with different arenes at different temperatures were measured (Fig. 3). While the ratios of hydrodechlorination to Friedel–Crafts alkylation did not seem to be changing, the difference between intramolecular and intermolecular Friedel–Crafts alkylation would be expected to be thermally dependent. In the case of toluene, the T_g of the material increases from 74 to 109 °C as the reaction temperature decreases from 110 to 25 °C, suggesting more polyindene formation at lower temperatures (Fig. 3a). This would be expected, as intramolecular reactions should be favored more at low temperature than the intermolecular hydrodechlorination or Friedel–Crafts alkylation. When shifting to benzene, the change in T_g is much more pronounced across the different reaction temperatures (74 to 124 °C) with

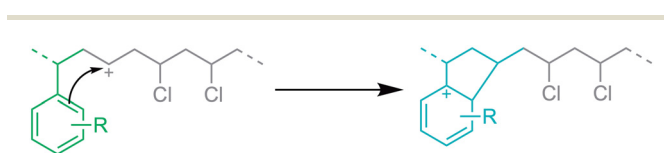


Fig. 2 Proposed intramolecular Friedel–Crafts alkylation leading to formation of polyindene segments.

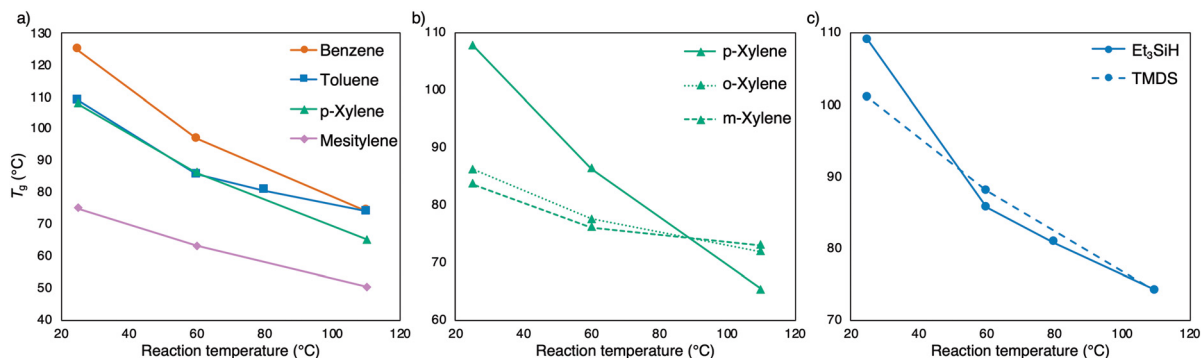


Fig. 3 T_g of polymer products from silylium catalyzed hydrodechlorination and Friedel–Crafts alkylation of PVC at 25, 60, 80 and 110 °C with: (a) aromatic solvents with 0–3 methyl substituents, (b) *ortho*, *meta* and *para* xylene, and (c) comparisons between Et_3SiH and TMDS as silane sources in toluene. All reactions were conducted with 0.25 mol% $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, 2.53 mL aromatic solvent, 1.5 equiv. Et_3SiH or 1.1 equiv. TMDS.

most T_g s being higher than the relative T_g s for toluene reactions. This is likely due to both polyindene formation and cross-link formation due to additional Friedel–Crafts alkylation to phenyl groups on a second polymer. Use of *para*-xylene shows a similar behavior to toluene, albeit with a lower T_g for the product of the reaction at 110 °C. Shifting to *ortho*- and *meta*-xylene show a significant drop in T_g of the products run at 25 and 60 °C, with a much lower change in T_g across the system (Fig. 3b). We hypothesize that the placement of the electron-donating methyl groups can negatively influence the intramolecular Friedel–Crafts alkylation. To further confirm that polyindene formation is responsible for the increased T_g , mesitylene was used as the aromatic solvent, in which methyl groups would block the intramolecular Friedel–Crafts alkylation (Fig. 3a). As expected, the resulting polymer for mesitylene reactions has a much sharper ^1H NMR spectrum. The T_g s are the lowest of all arenes studied, but still influenced by the reaction temperature, with a change from 51–75 °C. These results suggest that all arene solvents likely do allow some cross-link formation, though not enough to severely influence the solubility of the polymers. Importantly, all copolymers reported herein have higher T_g s than previously reported poly(ethylene-*co*-styrene) materials (17–23 °C), along with similar degradation temperatures ($T_{d,5\%} > 350$ °C). Due to their higher thermal rigidity, they may show improved applicability in battery membranes that require high operating temperatures. Finally, reactions done in toluene with the TMDS silane show very similar behavior to that of Et_3SiH , suggesting that the silane structure is not relevant for this selectivity difference (Fig. 3c). These results indicate that polymers with tunable, high thermal stability could be formed through silylium dechlorination of PVC.

Computational analysis

The starting point for the computations is the carbocation formed upon cleavage of one of the two secondary C–Cl bonds in the model PVC molecule by a silylium cation. The energy of this structure is added to that of two molecules of benzene and two molecules of triethylsilane to constitute the reference

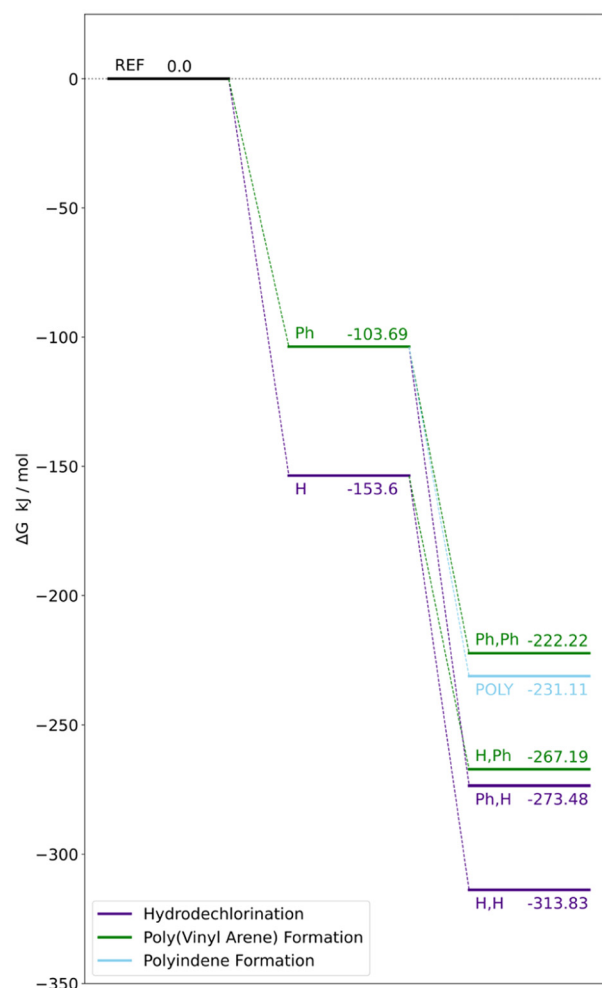


Fig. 4 Computationally predicted free energy changes (kJ mol^{-1} at 298 K) associated with hydrodechlorination, Friedel–Crafts alkylation, polyindene formation and combinations of these reactions for model PVC systems. The states are colored and labelled based on the reaction step: 'Ph' indicates benzene addition, 'H' to hydride addition, and 'POLY' to polyindene formation.

state, labelled 'REF'. The REF state is either attacked by a hydride from silane or undergoes Friedel–Crafts alkylation *via* benzene addition. Thermodynamic calculations comparing the free energies of formation of the hydrogenated (H) and alkylated (Ph) products are reported in Fig. 4. The data used to generate the figure and the structures constituting each state are reported in Table S12 and Fig. S123 of the ESI,[†] respectively.

The primary finding from the computational study is that hydrodechlorination is energetically more favorable than Friedel–Crafts alkylation, which agrees with experiments. If one C–Cl is replaced with C–H (or C–Ph), hydride addition is once again thermodynamically more favorable than Friedel–Crafts alkylation. Intramolecular Friedel–Crafts alkylation to form an indene product following the first Friedel–Crafts alkylation is energetically slightly more favorable than the addition of another phenyl group *via* Friedel–Crafts alkylation (POLY).

Conclusion

The combined hydrodechlorination and Friedel–Crafts alkylation of PVC with silylium ions and aromatic solvents to form polyethylene and poly(vinyl arene) copolymers have been optimized under ambient conditions, with full dechlorination being achieved with reaction temperatures between 25 and 110 °C. Extension to less expensive and less moisture-sensitive TMDS allows for full dechlorination of PVC, although only one of the two hydrides is delivered for every molecule of TMDS. Attempts to increase the poly(vinyl arene) repeating units in the polymer product could not go beyond 30 mol%, with most samples being near 20 mol% poly(vinyl arene) repeating units. With the same poly(vinyl arene) content, reactions run at different temperatures and/or different arene solvents revealed products with dramatically different T_g s, ranging from 51–124 °C, all of which are much higher than discrete polyethylene-*co*-polystyrene copolymers synthesized from ethylene and styrene monomers directly. These variations are attributed to secondary intramolecular Friedel–Crafts alkylations to form polyindene repeating units and intermolecular Friedel–Crafts alkylations to form cross-links. These results show that while the poly(vinyl arene) content cannot be varied widely, the thermal properties of the polymer products produced from PVC can be altered by impacting the presence and quantity of secondary Friedel–Crafts alkylations.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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