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Peer Review File

Upcycling of Polyvinyl Chloride into Polyalphaolefin Lubricants

Corresponding Author: Professor Guoliang Liu

Any redactions in this file are there to maintain patient confidentiality, the confidentiality of unpublished data, or to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)
General Comments:
This manuscript presents a truly innovative and compelling approach to addressing the formidable challenge of PVC waste. The work by the authors is exceptional, showcasing a novel catalytic process that not only valorizes a problematic plastic but also transforms it into high-performance lubricants with clear economic potential.
They provide a method of recycling PVC to high-volume, high-value material, which is promising in industrial applications, and avoiding expensive catalysts and the use of ionic liquids.
The concept of using PVC as a template for alkylation to create vinyl-derived polyalphaolefins (vPAO) is ingenious and represents a significant advance beyond conventional recycling or upcycling methods. The study is comprehensive, integrating sophisticated catalysis, detailed product characterization, techno-economic analysis, and validation using real-world waste streams. The results are robust and strongly support the conclusions. The potential impact of this work on the fields of polymer recycling and sustainable lubricant production is undoubtedly high, making it a strong candidate for publication in Nature.

This reviewer recommends the acceptance of this manuscript after minor revisions. The following points are not criticisms of the work's validity but are suggestions to further strengthen the narrative, clarify certain aspects, and solidify the claims, thereby enhancing the manuscript's impact for a broad readership.

Specific Points for Revision:
Quantifying the suppression of undesirable pathways: The authors correctly identify that immediate alkylation suppresses the formation of polyenes and carbonaceous materials. To make this key advantage more quantitative, it would be valuable to include a comparative analysis. For instance, a thermogravimetric analysis (TGA) comparison of the solid residues from the control reaction without α-olefins (which presumably contains polyenes/carbon) versus the final hydrogenated vPAO could visually demonstrate the improved stability and purity of the target product. Data on the yield of gaseous products in the presence vs. absence of α-olefins would further solidify this claim. In addition, the Cl content in PAO lubricants can be detected by Titration or elemental analysis, complete dichlorination needs a strict test. Cl might be unfavorable for the application of lubricants

Contextualizing the tribological performance: The wear performance of v10PAO surpassing commercial PAO40 is remarkable. To make this claim even more powerful, please consider: Adding the wear volume or scar width data for PAO40 to Figure 4c for a direct visual comparison; discussing the potential scientific reason behind this superior performance despite the lower viscosity. Is it related to the unique "comb-like" structure and minimal short-chain branching, which might facilitate the formation of a more resilient lubricating film? A sentence or two of speculation would intrigue the readers and point to future fundamental studies.

Robustness of the process with real-world waste: The application to mixed PVC waste is a major strength. To address

potential scalability concerns, the authors should briefly comment on the fate of common additives (e.g., pigments, fillers like CaCO3) during the dissolution/precipitation pre-treatment step. Were any significant challenges encountered? A sentence acknowledging this and stating that the insoluble residues were effectively removed by filtration would reassure readers about the process's robustness for heterogeneous feedstocks.

Techno-economic analysis assumptions: TEA is a welcome addition. Please briefly state the key assumptions for the 1-decene price in the base case scenario, given its identified sensitivity. Furthermore, the authors mentioned securing affordable α-olefins as a future goal. It would be beneficial to suggest one or two potential avenues e.g., sourcing bio-derived or waste olefins, to demonstrate a forward-looking strategy for mitigating this cost factor.

Minor Polishes:
The abbreviation "vxPAO" is introduced but could be confusing. Consider using a more descriptive notation in the caption of Fig. 1d (e.g., "vPAO-6, vPAO-8, vPAO-10"); Please ensure all references to figures and tables in the text are correct (e.g., the reference to Fig. S17 for viscosity index and friction coefficient).
In conclusion, recycling PVC is a huge challenge, the authors provide a competitive, practical way to use PVC waste as the resource. This is an outstanding piece of work that presents a transformative solution to chloride-containing plastic PVC pollution. This reviewer is confident that addressing these minor points will elevate the manuscript to its fullest potential, ensuring it receives the high impact it deserves upon publication.

Referee #2

(Remarks to the Author)
This manuscript reports a Lewis-acid-mediated strategy that combines PVC dichlorination with α-olefin oligomerization to produce chlorine-free, PAO-like lubricants with tunable viscosity and promising tribological performance. While each elementary transformation involved is individually well precedented, their integration into a single process explicitly aimed at generating lubricant-grade PAO analogues from PVC-containing feeds appears to be unprecedented. To my knowledge, no prior work has demonstrated the direct synthesis of PAO base-stock-like fluids via a one-pot Lewis-acid route starting from PVC. The work is conceptually appealing and potentially impactful.

However, in its current form, there are several major gaps that significantly weaken the claims.

In particular:

1) The manuscript and SI rely primarily on the disappearance of the C–Cl FTIR band (~617 cm^{-1}) and of the ~4.4 ppm ^{1}H NMR signal as evidence for complete dichlorination. While supportive, these techniques are not quantitative and may fail to detect residual organochlorides at ppm–0.1 wt% levels, which are highly relevant for lubricant applications. The lack of quantitative halogen analysis on the final vPAO (and ideally also on volatile fractions and aqueous work-up streams), for example by ICP-based methods, therefore significantly weakens the claim of complete dichlorination.

2) A key question is what fraction of the final lubricant carbon skeleton originates from PVC versus from α-olefin oligomerization. The process employs ~1.2 equivalents of α-olefin per PVC Cl. Under such conditions, it is plausible that a substantial fraction of the product is effectively a conventional PAO-like oligomer formed under unusually high $AlCl_3$ loading. At present, convincing evidence (for example, experiments using ^{13}C-enriched PVC followed by thorough microstructural characterization of the sample) that PVC-derived carbon is substantially incorporated into the oil phase is lacking.

3) The branching structures proposed in Scheme 1 appear speculative and are not directly supported by spectroscopic evidence. Moreover, the branching ratio (BR) is estimated from ^{13}C NMR by integrating “methyl” versus “methylene” regions without reporting detailed peak assignments. This raises several concerns, among which: (i) methine carbons also resonate within the 18–44 ppm region; (ii) methyl groups resonances in long alkanes can appear in the 20–25 ppm range; (iii) chain-end methyl groups resonate in the 11–14 ppm region. Without explicit assignments, the BR values are difficult to assess.

4) The optimal conditions require ~50 mol% $AlCl_3$ relative to PVC Cl to achieve “complete dichlorination,” which is a very large amount in practical terms and closer to stoichiometric reagent use than to catalysis, particularly if $AlCl_3$ is converted to $AlCl_4^-$ or hydrated aluminum salts upon quenching. As presented, this substantially weakens the manuscript’s catalytic claims.

5) The mechanism proposed by the authors assumes relatively selective C–Cl activation in PVC followed by controlled alkylation with α-olefins, with PVC acting as a structural “template”. However, the authors did not provide enough experimental and computational evidence to support their claim. In particular, a key issue concerns the quantum mechanical molecular dynamics (QMMD) simulations: the calculated C–Cl bond cleavage energy (≈96 kcal/mol) assisted by AlCl3 is too high and completely inconsistent with the experimentally observed reactivity at 70°C, thus questioning the soundness of the computational methodology. Additionally, the reported free-energy differences of the order of ~0.5 eV per site between the “comb-like” and “branch-like” structures are likely within the intrinsic uncertainty of such calculations and cannot not be used to draw strong structural conclusions.

In view of these concerns, I feel that the manuscript, in its present form, does not reach the level of robustness required for publication in Nature.

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)
I am very pleased to see that the author has effectively addressed the questions raised by myself and the other reviewers, and has revised the manuscript accordingly. The revised paper is logically perfect, and I believe this work offers a practical pathway for the recycling and high-value utilization of PVC.

Referee #2

(Remarks to the Author)
I thank the authors for their detailed response and for the substantial additional work included in the revised manuscript. I have also considered the comments of Reviewer 1 and the authors' responses to them. I agree that the revised manuscript is significantly improved. The additional analyses of oxidative stability, gas-phase products, residual chlorine, waste-PVC purification, additive/metal content, tribological performance, and techno-economic assumptions strengthen the practical and application-oriented aspects of the work.

I also appreciate that the authors have moderated several claims in the revised manuscript. In particular, the discussion of residual chlorine is now more cautious, the structural interpretation of the "comb-like" motif is presented less definitively, and the computational results are described as supportive rather than conclusive. These changes improve the balance and credibility of the manuscript.

My remaining concern relates to the nature of the evidence supporting the central claim. I agree that the revised manuscript now provides a very large and internally consistent body of indirect evidence that PVC affects the reaction pathway and the properties of the final oil fraction. This evidence includes the comparison between cPAO and vPAO, differences in molar mass, viscosity, Tg, branching indices, tribological performance, and the additional NMR and control experiments. Taken together, these data make the authors' interpretation plausible.
However, these data remain indirect. They do not provide direct or quantitative proof of the extent to which PVC-derived carbon is incorporated into the final lubricant carbon skeleton. This distinction is important because the central framing of the manuscript is that PVC is upcycled into vinyl-derived PAO lubricants through a PVC-templated dichlorination/alkylation process.

The revised manuscript has addressed several of my original concerns, and I recognize that the remaining issue is primarily one of interpretation and framing. I therefore leave the final editorial judgement to the Editor, particularly in light of the strong conceptual and application-oriented aspects of the work and the positive assessment by Reviewer 1. If the manuscript is accepted, I recommend that the authors explicitly acknowledge that the evidence for PVC-derived carbon incorporation is extensive and coherent, but indirect rather than direct or quantitative.

Referee #3

(Remarks to the Author)
Liu and coworkers report a novel method for upcycling PVC to lubricants using a lewis acid mediated alkylation/scission of the PVC backbone. They demonstrate that using AlCl3 and an alpha olefin they can effectively dechlorinate and alkylate the backbone to give a branched structure. The authors showed that these materials were excellent lubricants.
Overall, this is a well-written manuscript and a high-impact study that would be of interest to the readership of Nature. I also went through the other reviewer comments and the authors responses. I believe they have adequately addressed the concerns raised by the reviewers.
My main concern with the current manuscript is the proposed mechanism in the supporting information. The mechanisms drawn in Scheme S3 and S4 show unreasonably high energy intermediates and should be revised or removed. Please take the following comments about these schemes into consideration:
Scheme S3
1) After alkylation, the authors show an oligomer with 3 adjacent carbocations. This structure would be unreasonably high in energy. While I understand the authors were trying to streamline their mechanism and show multiple alkylations, the formation of this intermediate is unreasonable. They should show single alkylations and termination of the carbocation at a time.
2) The authors show hydride transfer reactions to give the saturated product. Are they saying the hydride transfer occurs from solvent? Intramolecular hydride transfers would be more favorable. For example, a 1,6-hydride shift would give a tertiary carbocation. (or chain walking with 1,2-hdyride shifts)
3) The Beta-scission reaction shown is not the most reasonable pathway. The formation of a carbocation on a carbon attached to a chloride would be likely higher in energy than the secondary carbocation. From the authors results, it appears that more beta-scission occurs when the alpha-olefin is present, which suggests this reagent helps promote breaking of the PVC backbone. On this basis, please consider scission beta to a site that has already been alkylated. This would lead to a much more reasonable secondary carbocation. Additionally, if the first alkylation underwent elimination to the olefin the beta-scission reaction would lead to a much more stable allylic carbocation.

4) There also could be cyclization reactions occurring. This should also be considered.
Scheme S4
5) Scheme S4 has many of the same issues and should be revised. Additionally, in Scheme S4 the authors show a beta-scission to give a primary carbocation. This would be unreasonably high in energy (some scientists would argue that primary carbocations do not exist). These beta-scission events should be removed. Significantly more thought should be put into the mechanistic figures in the SI if they are kept.

As an additional sidenote, when the authors were responding to one of the reviewers, they discussed “thermodynamic energy barriers.” I do not understand what they mean by this, as energy barriers are related to the kinetics of the reaction. Do they mean the relative thermodynamic energies of the intermediates? This should be clarified/corrected in the manuscript.

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Author response: We thank the reviewer for the insightful comment on the undesired reaction pathways, product purity, and stability. We have performed (i) comparative thermogravimetric analyses of the hydrogenated vPAO and the carbonaceous products from the control reaction, (ii) qualitative/quantitative analyses of the gas phase using GC-MS and SEC, and (iii) residual chlorine analysis using ion chromatography. We have updated the main text and supplementary materials accordingly.

1. Comparative thermogravimetric analysis of polyene solid residues and vPAO

Following the reviewer's recommendation, we performed TGA under air. The polyene product from the control reaction exhibited thermal stability with $T_{d5\%}$ of 262 °C and $T_{d50\%}$ of 464 °C in air, implying high thermal stability in agreement with the behaviors of typical carbonaceous materials. In contrast, v_8PAO exhibited a $T_{d5\%}$ of 203 °C and $T_{d50\%}$ of 397 °C in the air (**Fig. R1a**). In addition, only the polyene product generated a measurable char yield (~12 wt.%) after the TGA experiment, while v_8PAO completely degraded after 535 °C. Therefore, we revised the manuscript

to highlight the chemical (oxidation) stability of fully hydrogenated vPAO, in stark comparison with the unstable polyenes featuring reactive alkene groups.

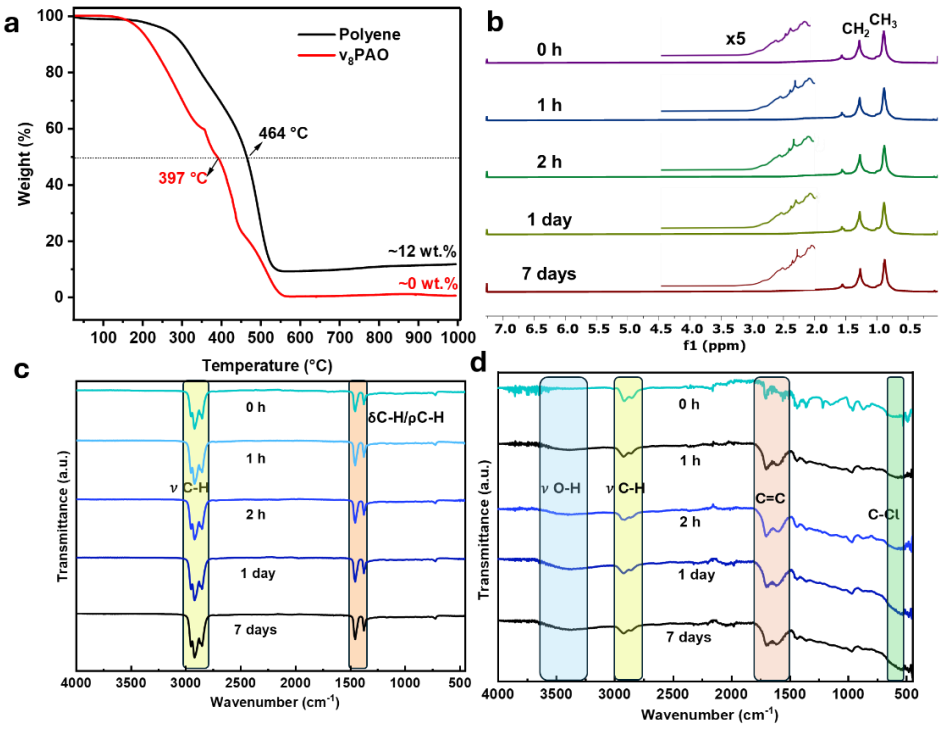


Figure R1. Comparative study on the oxidation stability of polyene versus v8PAO. a) In the air, thermogravimetric analysis of v8PAO and polyene generated in the control reaction. Polyene likely formed carbonaceous species and thus showed relatively higher thermal stability than v8PAO. b) Time-resolved ^{1}H NMR spectra of v8PAO left on a bench for 7 days. No noticeable changes were observed between 1.9 ppm and 4.5 ppm, indicating no oxidation occurred. c) Time-resolved FTIR of v8PAO exposed to air over a period of 7 days, revealing no evolution of oxidation peaks, such as O-H around 3500 cm^{-1}. d) Time-resolved FTIR of polyene exposed to air over a period of 7 days. Note the O-H stretch intensity at 3500 cm^{-1} increased and plateaued after 1 day.

2. Oxidative stability of polyene solid residues and vPAO

To further demonstrate the chemical stability of vPAO compared to polyenes, time-dependent FTIR studies were performed on polyene solid residues and v8PAO exposed to air for a period of up to seven days. The polyene solid residues underwent gradual oxidation as indicated by the broad O-H peak at ~3500 cm^{-1} in FTIR (**Fig. R1d**)[1]. The intensities of the O-H oxidation peak plateaued after ~ 1 day. In stark contrast, v8PAO displayed no oxidation peaks around 3500 cm^{-1} in FTIR and no signals pertinent to alcohols, ketones, and other oxygenates in the ^{1}H NMR spectra even after 7 days (**Figs. R1b and c,** 1.9-4.6 ppm region). These results align well with previously reported literature on the oxidative instability of polyacetylene and carbonaceous products derived from PVC[1,2].

3. Qualitative and quantitative analysis of the gas phase

We agree with the reviewer that evaluating the yield of gaseous products could provide insights into the extent of side reactions because a fraction of the hydrocarbons, especially highly volatile short-chain hydrocarbons, may end up in the gas phase. Based on the law of mass conservation in

a closed system, we estimated the weight of gases in the control reaction without α-olefins and the typical reactions with α-olefins in both hexanes and CH_2Cl_2. Because all our PVC reactions produced HCl, the gas phase was neutralized by passing the exhaust through a ZnO trap. The neutralized gases were sampled and injected into GC-MS for qualitative analysis. All upcycling reactions in the presence of α-olefins showed branched isoalkanes and no unsaturated products (**Figs. S5** and **S6**). Surprisingly, no hydrocarbon gaseous products were detected in the control reaction without α-olefins, implying that under Lewis-acidic conditions, the PVC degradation reaction preferentially generates HCl as the predominant gaseous product (**Fig. S7**). The low molar mass products, if any, from PVC degradation likely dissolved in the solvent and readily escaped on a rotary evaporator (**Fig. S4**). Minor chloroalkanes were detected, likely generated from addition reactions to alkenes from PVC β-scission degradation (**Fig. S4**).

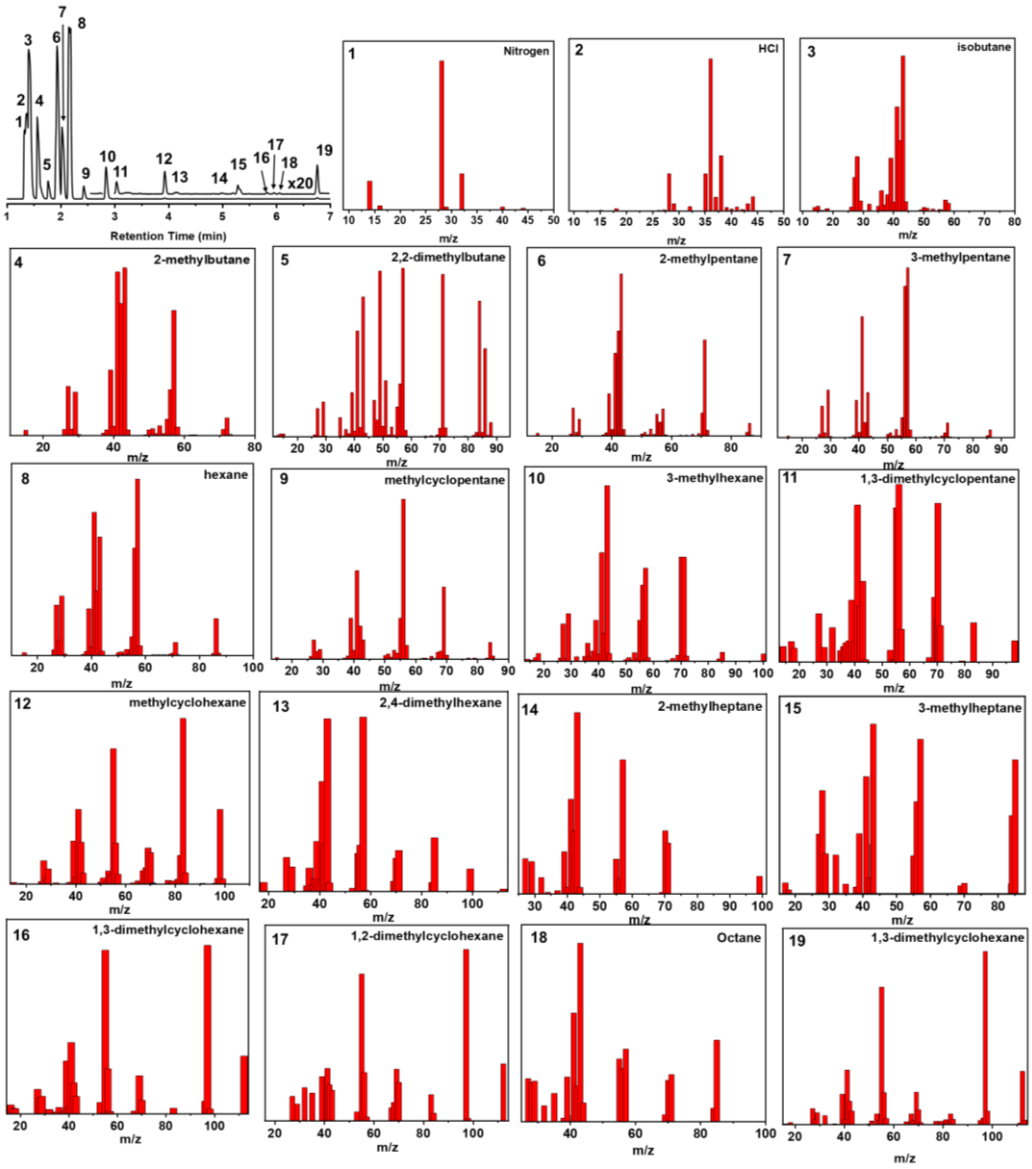


Figure S5. GC-MS analysis of the gas phase of v8PAO synthesis in hexanes. The product stream consisted mostly of isoalkanes and naphthenes. No unsaturated hydrocarbons were detected.

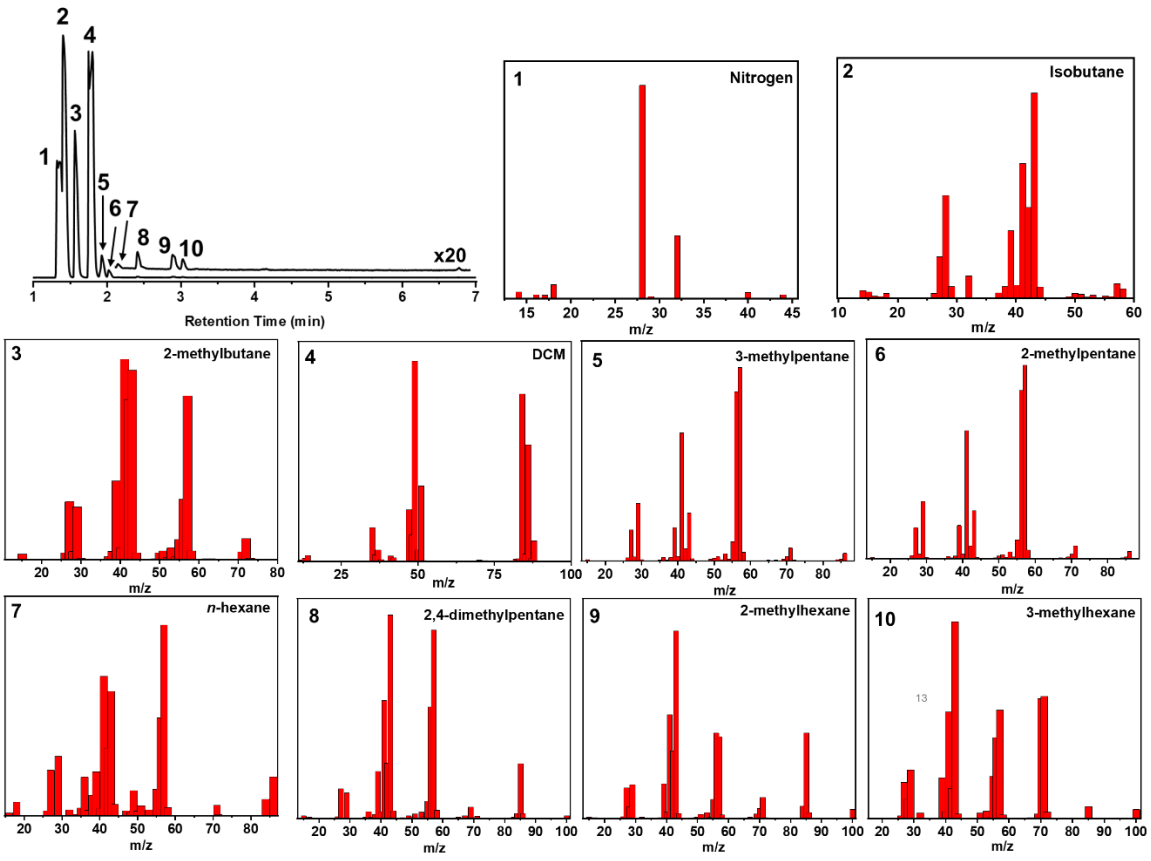


Figure S6. GC-MS analysis of the gas phase of v8PAO synthesis in DCM. The reaction generated mostly isoalkanes, similar to the upcycling reactions in hexanes.

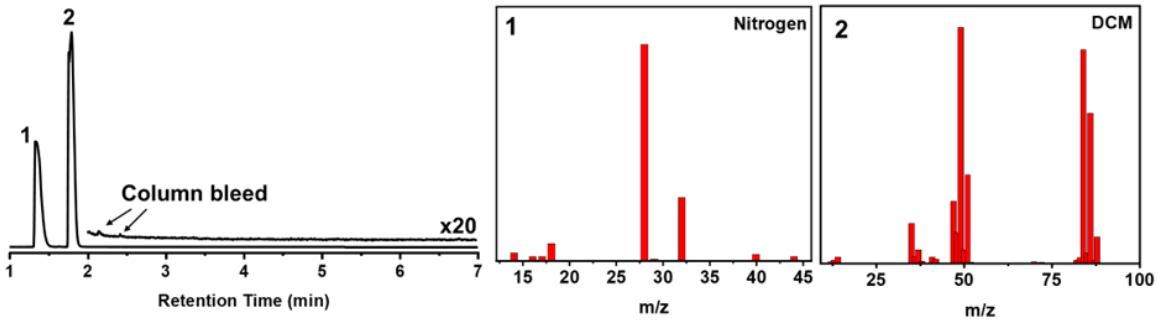


Figure S7. GC-MS analysis of the gas phase of the control reaction in DCM. No hydrocarbon gaseous products were observed. Low-molar-mass molecules from PVC degradation likely remained in the solvent DCM.

The gas yield was the highest in the control reaction without α-olefins, owing to unabetted dehydrochlorination and intramolecular alkylations to unsaturated cycloalkanes (**Figs. S7** and **S4**). The absence of hydrocarbons in GC-MS suggests that extensive dehydrochlorination generated a high concentration of gaseous HCl. The gas phase yield in CH_2Cl_2 was considerably low because alkylation reactions (i.e., formation of C-C bonds with olefins) suppress chain scissions and dehydrochlorination. Lastly, hexanes limited the extent of chain scission via hydrogen transfer to

carbenium and hindered undesired pathways (such as cyclization), accounting for the lowest gas and volatiles yield. The reduced chain scission was corroborated by SEC, which revealed a higher molar mass of v_8PAO prepared in hexanes than in CH_2Cl_2, because the hydrogen transfer to carbenium hampered unrestrained cleavages (**Fig. S33**). These results support that introducing α-olefins minimizes undesired reactions in a cationic reaction process that would otherwise lead to high gas production.

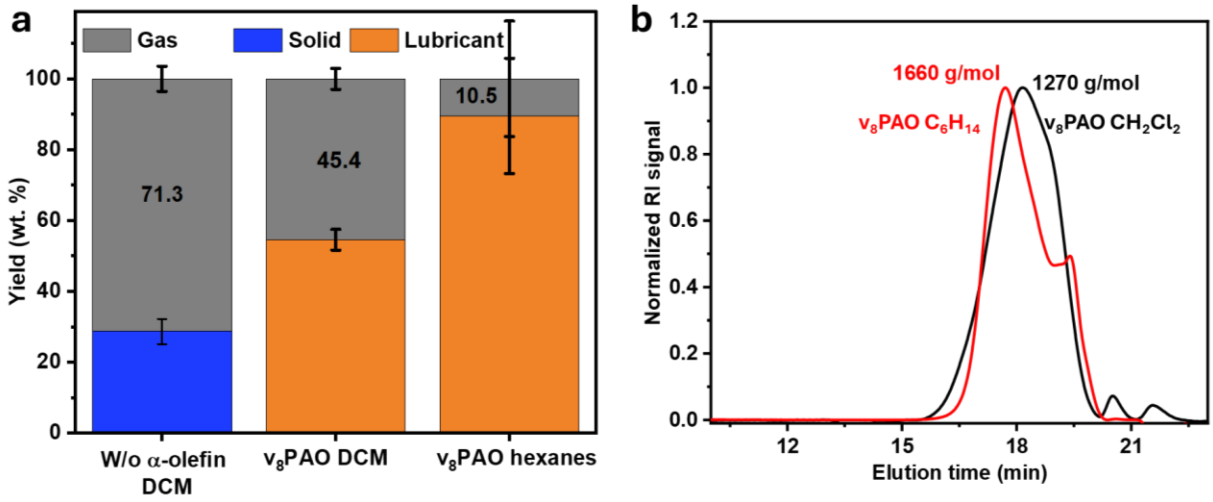


Figure S33. Effect of olefins and solvent on PVC chain degradation. a) Gas phase yield generated without α-olefin and with α-olefins under different solvent conditions. b) SEC chromatograms of v_8PAO in DCM and hexanes, revealing a high molar mass lubricant in the isoalkane solvent.

4. Total chlorine analysis in vPAO

The reviewer is insightful to point out that low levels of chlorine can cause issues, including corrosion at elevated temperatures during operation. Using ion chromatography techniques, we performed total chlorine analyses of v_8PAO and v_{10}PAO-mix prepared in CH_2Cl_2 and hexanes. Although there is no available strict limit of halogen content in base oils, most modern oil products are marketed as chlorine-free. Hence, it is paramount to ensure that our lubricants contain only the lowest possible concentration of halogens.

Ion chromatography analysis showed that hydrogenated oils prepared in hexanes contained small amounts of chlorine (< 100 ppm), lower than the instrument's detection limit. The oils prepared in CH_2Cl_2 also exhibited < 100 ppm Cl, but they showed slightly larger areas under the curve of the chlorine signal, likely due to minor side reactions with the solvent (**Fig. S12** and **Table S3**). Thus, the upcycling strategy markedly decreased the chlorine content from ~5.7×10^5 ppm (56.7 wt.%) in PVC to <100 ppm in the oils. To reflect the elemental analysis results, we have updated the manuscript to clarify that chlorine was not detected in FTIR and $^1H/^{13}C$ NMR, but a small amount of chlorine (<100 ppm) was found in ion chromatography analysis.

We have updated the main text as follows:

Page 5: "After the reaction was complete, the solvent and $AlCl_3$ were removed during work-up, yielding v_xPAO lubricants featuring no detectable C-Cl bonds in FTIR and ^1H NMR (**Figs. 1d** and **e**)."

Page 6: "$AlCl_3$ loadings of 50 mol% generated lubricants of low viscosities without any detectable C-Cl bands in the FTIR spectra. However, ion chromatography studies revealed trace levels of chlorine (< 100 ppm), representing > 99.98% dechlorination efficiency (**Figs. S12** and **Table S3**)."

Page 5: "To eliminate the alkene groups and ensure lubricant stability, the lubricants were hydrogenated at 1 bar over Pd/C (7 wt.% loading), producing saturated vPAO exhibiting good oxidative stability **(Fig. S2)**.

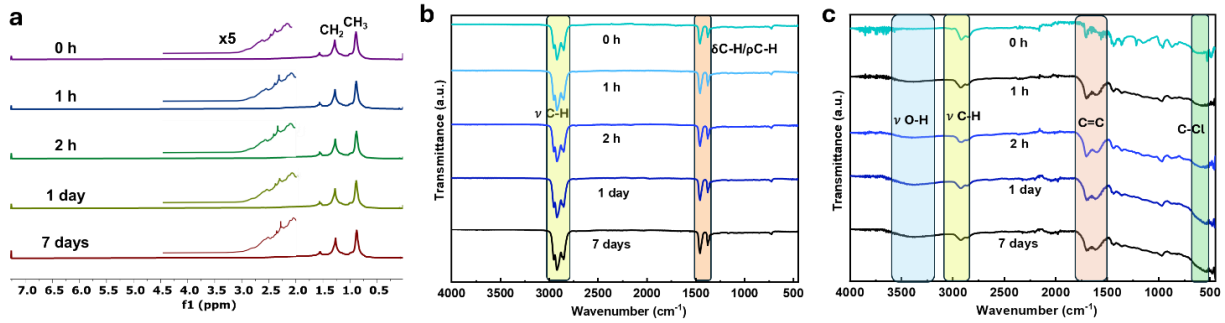


Figure S1. Comparative study on the oxidation stability of polyene versus v_8PAO. a) Time-resolved ^{1}H NMR spectra of v_8PAO left on a bench for 7 days. No noticeable changes were observed between 1.9 ppm and 4.5 ppm, indicating no oxidation occurred. b) Time-resolved FTIR of v_8PAO exposed to air over a period of 7 days, revealing no evolution of oxidation peaks, such as O-H around 3500 cm-1. c) Time-resolved FTIR of polyene exposed to air over a period of 7 days. Note the O-H stretch intensity at 3500 cm^{-1} increased and plateaued after 1 day.

Page 6: Control reactions confirmed the role of each component in the synthesis of v_xPAO. Without α-olefins, the reaction did not produce any lubricants (**Figs. S4a** and **S4c)**. The product included a polyene generated from PVC dehydrochlorination, which gradually oxidized over time in air, consistent with prior studies (**Fig. S4c**)[3]. In addition, low-molar-mass hydrocarbon products were detected in the reaction solvent, consisting primarily of *tert*-amyl chloride, isoparaffins, cyclopentadienes, and other conjugated hydrocarbons. Contrary to the upcycling reactions with α-olefins, few gaseous hydrocarbons were collected, implying that dehydrochlorination to HCl dominated PVC degradation (**Figs. S5-S7**).

Page 12: The key to successful PVC upcycling into PAO lies in the immediate alkylation with α-olefins, which suppresses the degradation into low-molar-mass gaseous products and the formation of oxidatively unstable polyenes and carbonaceous materials.

Page 19: GC and GC-MS analysis of gas phase.

To perform qualitative analysis of gaseous products, the contents of the Schlenk tube headspace were passed over ZnO to neutralize HCl before injection into GC and GC-MS. The analyses were performed using an Agilent 7890A Gas Chromatograph coupled with a 5975C Mass Selective Detector. The specific instrumental conditions used to analyze the gas samples were as follows:

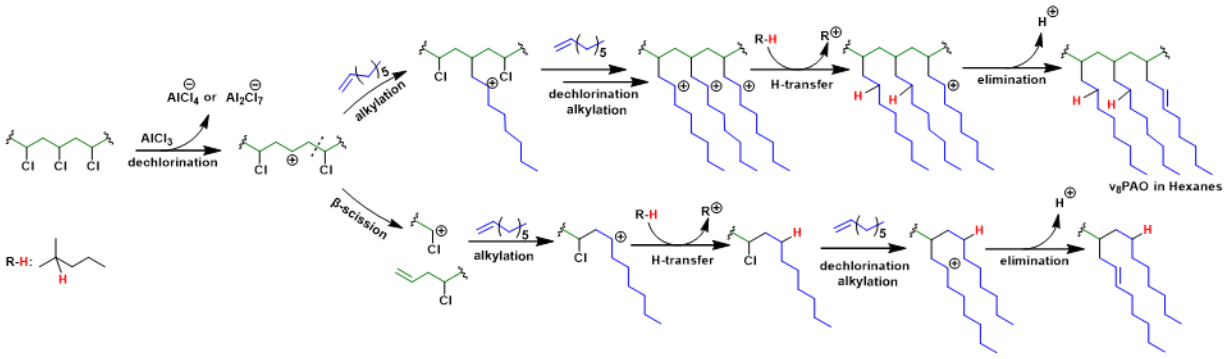
- Column: Agilent DB-5 MS (30 m x 250 µm, 0.25 µm film thickness)
- Injection Volume: 0.5 mL gas using a gas-tight syringe
- Injection Mode: Split 1:10
- Injection Temperature: 290°C

- Transfer Line Temperature: 250°C
- Oven Temperature Program: Initial temperature of 35°C (held for 3 min), ramped at 5°C/min to 100°C and finally ramped at 15°C/min to a final temperature of 290°C (held for 5 min)
- MS Mode: Scan mode (10-700 amu). No time delay in MS.
- Search Library : Wiley

Gas phase analysis and ion chromatography results were added to the supplementary materials as follows:

"4. Quantification of the gas phase and structure identification with GC-MS analysis

We estimated the gas fractions in the reactions based on mass conservation in a closed system. Without α-olefins, the control reaction generated the most gaseous products, due to unabetted dehydrochlorination to HCl (**Fig. S33a**). With α-olefins, the upcycling reaction in CH_2Cl_2 produced fewer gaseous products because the alkylation reaction between dechlorinated PVC and α-olefins attenuated backbone chain scissions. Furthermore, via hydrogen transfer to carbenium, the upcycling reaction in hexanes effectively reduced the extent of chain scission to produce short-chain hydrocarbons (**Scheme S3**), resulting in the least gas products. In addition, the SEC revealed a higher molar mass of vPAO prepared in hexanes than in CH_2Cl_2 (1660 kDa vs. 1270 kDa, respectively), further confirming that the hydrogen transfer to carbenium obstructed PVC chain cleavages (**Fig. S33b**).



Scheme S3. Proposed mechanism of PVC upcycling in hexanes. Carbocations are quenched via hydrogen transfer to limit chain scission and branching. Note: The H-transfer and elimination reaction do not necessarily proceed in sequence, and the scheme is to illustrate the possible reaction pathways. The hexane isomers include 2-methylpentane, 3-methylpentane, cyclohexane, and methylcyclopentane, in addition to n-hexane. Only one isomer is shown for illustration purposes

To perform qualitative analysis of gaseous products, the contents of the Schlenk tube headspace were passed over ZnO to neutralize HCl before injection into GC-MS. All reactions with α-olefins featured isoalkanes, mostly saturated and minor naphthene products. Almost no hydrocarbon gases were detected in the control reaction without α-olefins (**Fig S7**). The absence of hydrocarbons in GC-MS of the control reaction suggests that extensive dehydrochlorination generated a high concentration of gaseous HCl. However, isoalkanes and unsaturated products, along with minor chloroalkanes, were detected in the solution from the control reaction (**Figs. S4d and S4e)**."

5. Quantification of trace residual chlorine in lubricants

To determine the chlorine level in upcycled lubricants, we performed ion chromatography on lab-grade PVC-derived v_8PAO and mixed-waste-grade PVC-derived v_{10}PAO prepared in DCM and hexanes. The lubricants were first subjected to Schöniger oxidation to mineralize organic chlorine, and the products were dissolved in a hydrogen peroxide solution for further analysis. All lubricants contained <100 ppm chlorine, and v_{10}PAO mix hexanes showed the lowest levels of chlorine based on the area under the curve in the chromatogram (**Fig. S12** and **Table S3**). The oils prepared in DCM (v_8PAO and v_{10}PAO-mix-DCM) contained slightly higher chlorine, likely due to possible side reactions involving the solvent and Lewis acid (**Schemes S2** and **S4**). Therefore, the dechlorination and alkylation of PVC drastically decreases the concentration of chlorine to < 100 ppm in the lubricant, representing >99.98% chlorine reduction."

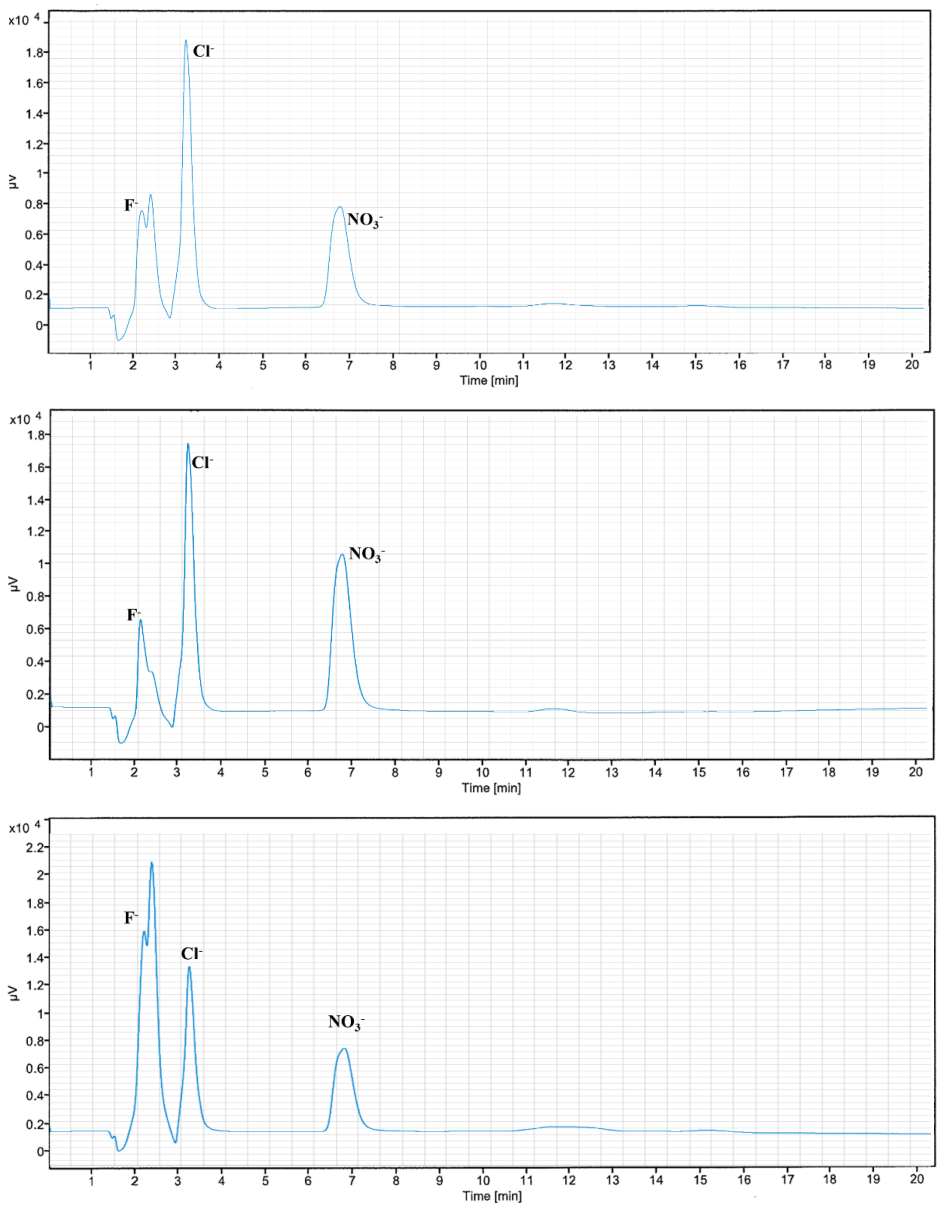
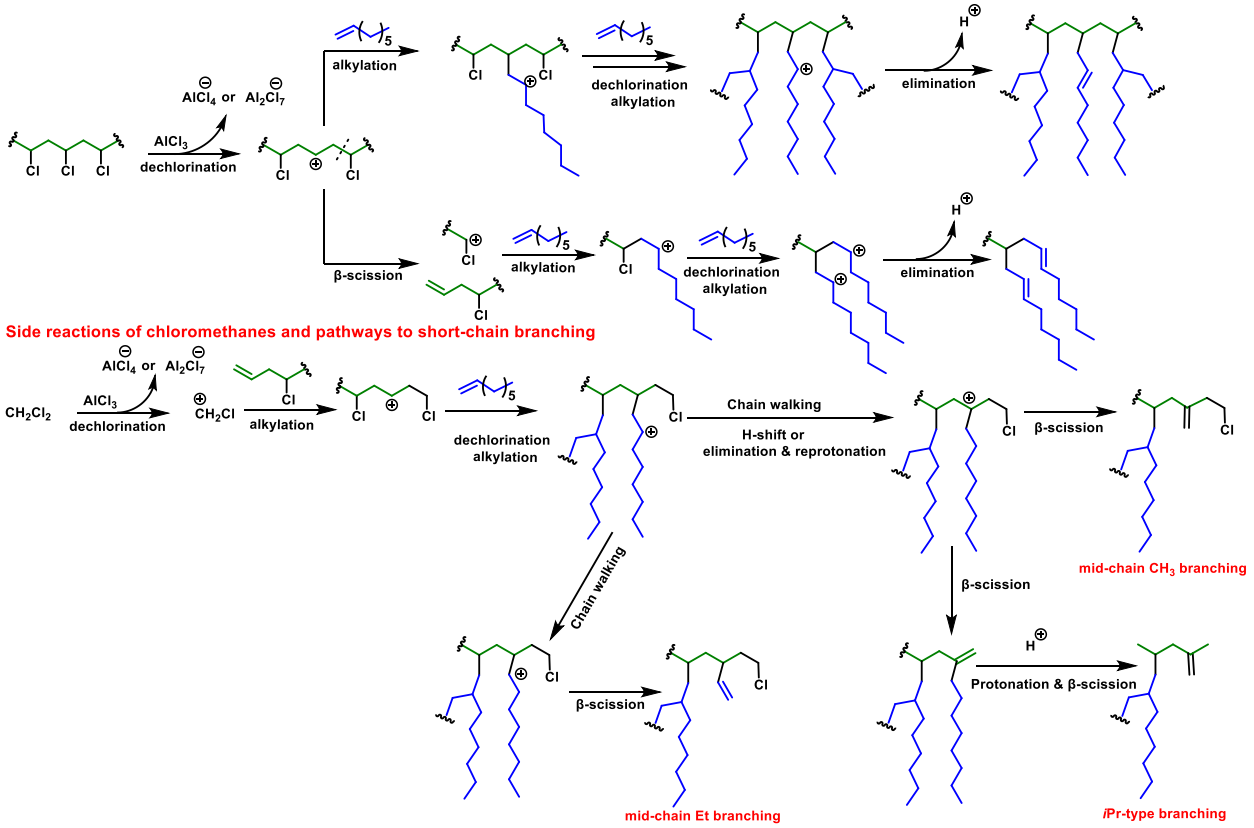


Figure S12. Ion chromatograms revealing chlorine detected in the oils. Top: v_8PAO; middle: v_{10}PAO-mix-DCM; bottom: v_{10}PAO-mix-hexanes. The concentration of chlorine in all oil samples was < 100 ppm.

Table S3. Results of ion chromatography analysis. All oils contained <100 ppm chlorine regardless of the PVC source and reaction solvent.

Sample	Compound	Peak area	Peak height	Concentration (ppm)
v_8PAO	Cl^-	2.34×10^5	1.64×10^4	<100
v_{10}PAO-mix-DMC		2.27×10^5	1.58×10^4	<100
v_{10}PAO-mix-hexanes		2.08×10^5	1.29×10^4	<100



Scheme S4. Upcycling of PVC in DCM. The solvent can participate in the dechlorination and alkylation pathways, leading to residual chlorine in vPAO and increased branching.

Comment #2: Contextualizing the tribological performance: The wear performance of v_{10}PAO surpassing commercial PAO40 is remarkable. To make this claim even more powerful, please consider: Adding the wear volume or scar width data for PAO40 to Figure 4c for a direct visual comparison; discussing the potential scientific reason behind this superior performance despite the lower viscosity. Is it related to the unique "comb-like" structure and minimal short-chain

branching, which might facilitate the formation of a more resilient lubricating film? A sentence or two of speculation would intrigue the readers and point to future fundamental studies.

Author response: We thank the reviewer for the suggestion to include the wear volume of PAO40 in **Fig. 4c** and to elucidate the rationale for the remarkable tribological performance of the waste-based v_{10}PAO. In the revised Fig. 4c, we have now added the wear scar volume and width for visual comparison. Please note that the wear scar on the v_{10}PAO tested ball was difficult to discern. Therefore, we have back-calculated the wear width from the wear volume, as estimated by the white-light interferometry profilometer.

Explanation of the superior tribological performance of vPAO

Prior research on lubricants' tribology performance has established that variations in the molecular structure, including the degree of branching and branch length, greatly influence the lubricity of PAOs[4]. With respect to vPAO, we agree with the reviewer that a "comb-like" structure featuring a high proportion of long alkyl chains and ideally few short chains can lead to the formation of a robust film at the interface[5]. During testing, a resilient film is likely formed as a result of a more efficient packing of linear alkyl chains of "v_{10}PAO-mix-hexanes" at the interface between the ball and the rotating disk. Au contraire, a vPAO sample prepared in CH_2Cl_2 displayed poor lubrication performance, as measured by wear volume and coefficient of friction, probably because of branching at the alkyl chains (**Scheme S4** and **Fig. S26**). This increased short-chain branching hinders the alignment of alkyl chains along the shearing direction, effectively resulting in relatively high friction[6]. Therefore, to achieve efficient lubrication, it is paramount to reduce the degree of branching and short-chain branching of vPAO by curbing isomerization through hydrogen transfer and Lewis acid loading (**Scheme S3** and **Table S2**).

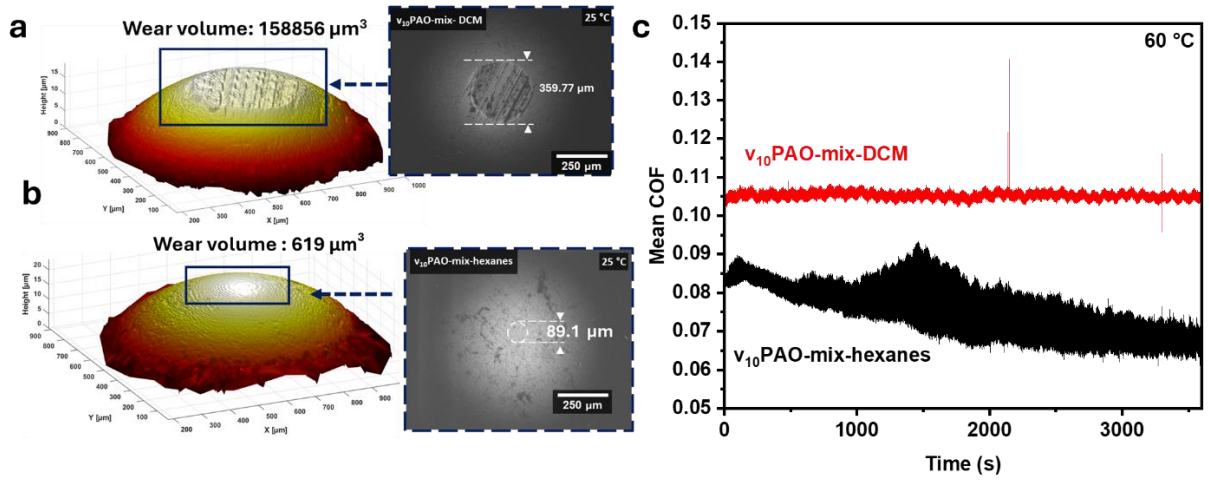


Figure S26. Comparative tribological performance of v_{10}PAO DCM and v_{10}PAO hexanes. 3D profiles of the steel ball after tribology test of oils: a) v_{10}PAO-DCM and b) v_{10}PAO-hexanes, showing the change in scar wear volume. The wear volume of the v_{10}PAO-DCM oil was higher than that of v_{10}PAO-hexanes, demonstrating the effect of the lubricant microstructure on tribological performance. c) Coefficient of friction of v_{10}PAO-DCM and v_{10}PAO-hexanes at 60°C.

With regard to the potential scientific reason behind this superior performance by v_{10}PAO, the following explanation is added in the manuscript to emphasize the importance of our "comb-like" structure and minimal short-chain branching.

Page 11: "While the exact molecular structure of vPAO is still being explored, we envision a comb-like architecture with a linear main chain and minimal short-chain branches. Such a molecular structure would most likely enhance tribological performance by enabling more efficient packing at the sliding surface and alignment of chains along the shearing direction, resulting in a resilient boundary film that prevents film rupture under high-pressure and shear conditions[5,6]. The effect of short-chain branching was evaluated by comparing the wear volume and COF of v_{10}PAO-mix-DCM and v_{10}PAO-mix-hexanes. The latter showed a 256 times lower wear volume (and a low COF) than the former oil prepared in DCM, due to the ability of hexanes to limit isomerization via hydrogen transfer (**Fig. S26**). Further analytical and computational studies are underway to validate these mechanisms.

Page 5: The highly branched v_6PAO resulted in the highest dynamic viscosity of 14.6 Pa·s at room temperature, an order of magnitude higher than that of v_{10}PAO (**Fig. S3**), consistent with established trends between branching and viscosity[5,7]."

We have added the wear volume values and scar width to all 3D profiles and photographs in **Fig. 4c**. Additionally, we labelled the methyl and methylene ^{1}H NMR peaks in **Fig. 4b**."

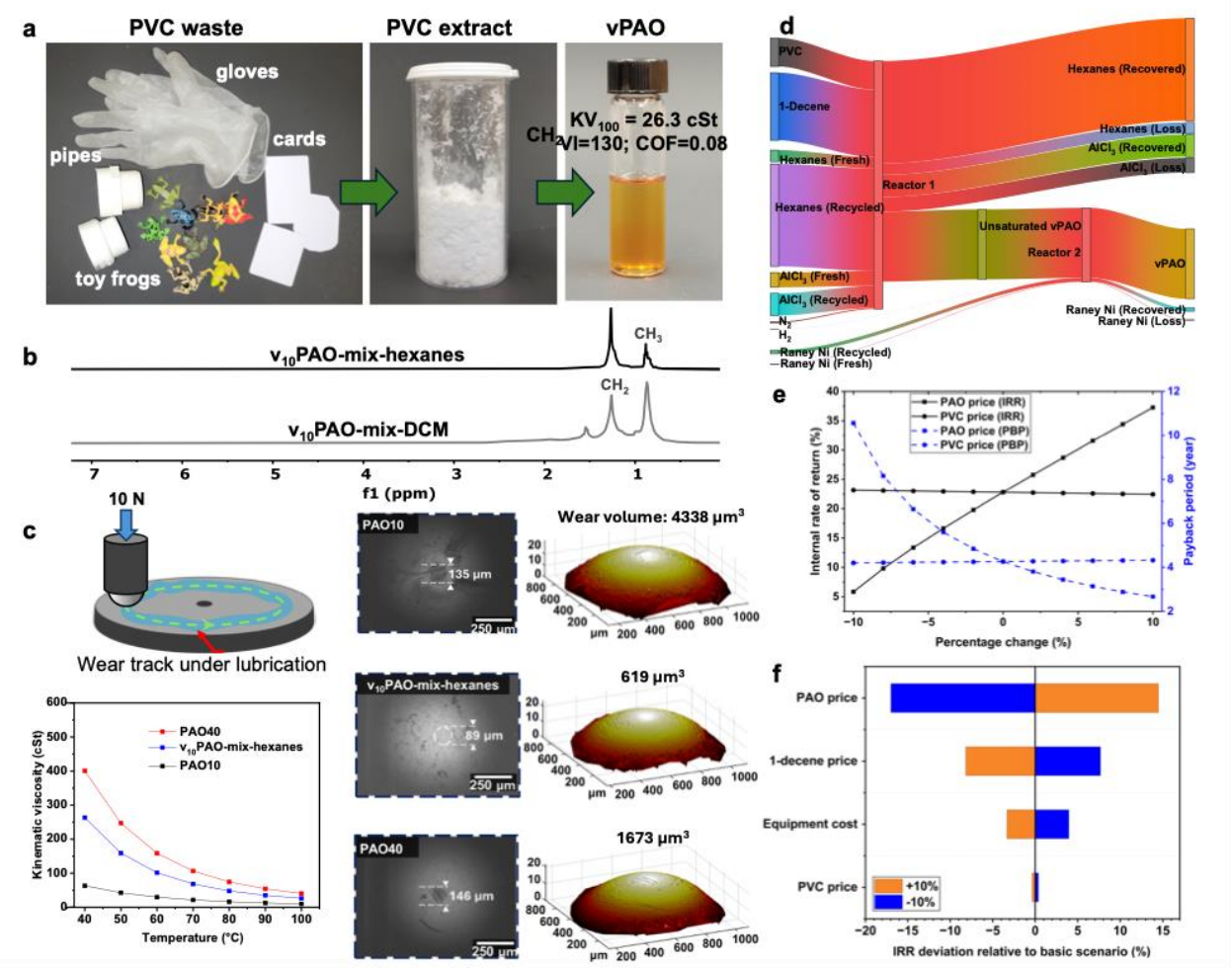


Figure 4. Extending upcycling to real-world PVC waste. a) Photographs of PVC waste (e.g., pipes, gloves, credit cards, and toy frogs), extracted PVC powder, and the upcycled lubricant. b) ^{1}H NMR of mixed PVC waste-derived v_{10}PAO showing structural differences in the hexanes and

DCM systems. c) Tribology and kinematic test. Kinematic viscosities of waste-based v_{10}PAO at 40-100 °C lie between those of PAO10 and PAO40. Wear test measurements revealed that PVC-based v_{10}PAO displayed the lowest wear volume, despite its markedly lower viscosity than PAO40; while PAO10, with the lowest viscosity, suffered the greatest wear. d) Sankey diagram illustrating the upcycling process of PVC to vPAO. e) Technoeconomic analysis reveals the sensitivity of profitability to the prices of PVC and PAO. f) Tornado diagram illustrates the sensitivity to the prices of PVC, PAO, 1-decene, and equipment costs. The horizontal bars show the deviation of the IRR from the basic case.

Comment #3: Robustness of the process with real-world waste: The application to mixed PVC waste is a major strength. To address potential scalability concerns, the authors should briefly comment on the fate of common additives (e.g., pigments, fillers like $CaCO_3$) during the dissolution/precipitation pre-treatment step. Were any significant challenges encountered? A sentence acknowledging this and stating that the insoluble residues were effectively removed by filtration would reassure readers about the process's robustness for heterogeneous feedstocks.

Author response: The authors thank the reviewer for the valuable recommendation to provide additional information on PVC waste purification and potential challenges related to the scalability of our process. We would like to share with the reviewer a detailed purification protocol and characterizations, which we adopted to ensure adequate purity of waste-based PVC powders.

1. Purification procedure and FTIR analysis of recovered powders

Additives in different PVC waste were removed through a combination of water extraction, THF dissolution, and filtration. In a typical experiment, PVC (1000 mg) was initially dissolved in THF (50 mL) and stirred until a uniform slurry was formed. The slurry was subsequently filtered to remove THF-insoluble additives, such as $CaCO_3$ fillers, followed by precipitation in water (250 mL) to isolate water-extractable compounds (Ca and Zn salts)[8,9]. The precipitate was air dried and redissolved in THF (50 mL), precipitated with isopropanol (250 mL), and filtered to remove organic additives, such as phthalates. This protocol ensured that most organic additives were separated, according to FTIR results (**Fig. S20**).

2. Detection of trace metals used in PVC additives

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis of the powders was performed to identify metals typically found in PVC products[2,10]. The purified powder from the four mixed PVC products showed 101 ppm Ti and 0 ppm Al, which are generally added to impart UV protection and flame retardancy, respectively[9,11-13]. Interestingly, the washed powders still contained substantial amounts of Ca from $CaCO_3$ (2232 ppm), which can generate CaO and poison $AlCl_3$. However, to effectively remove all $CaCO_3$, dilute HCl can be used in purification to neutralize the basic filler. Similar to virgin PVC, which was obtained from Sigma-Aldrich, no Fe or Cr was detected. On the contrary, if not subjected to the purification protocol, the PVC powders revealed high amounts of Ca, Mg, Ti, and Al (**Table S5**). Based on these findings, we concluded that the purification process effectively removed the majority of inorganic fillers and phthalate plasticizers, leaving behind a low concentration of metals. Notably, <10 ppm of the inorganic fillers and metals were detected in the final v_{10}PAO mix products (**Table S5**), suggesting their removal during downstream work-up of the upcycling and hydrogenation reactions.

Table S5. ICP-MS analysis of metals in PVC powders and upcycled oils.

	[Ca] (ppm)	[Mg] (ppm)	[Al] (ppm)	[Ti] (ppm)	[Cr] (ppm)	[Sn] (ppm)	[Fe] (ppm)	[Zn] (ppm)
Waste PVC	15958	299	227	259	0	94	0	117
Washed PVC	2232	0	0	101	0	61	0	68
Virgin PVC	0	0	0	5	0	0	0	0
v_8PAO	0	0	0	6	0	0	0	0
v_{10}PAO-mix-hexanes	0	0	0	7	0	0	0	0

Accordingly, we have updated the supplementary materials with the following clarification on page 8:

"To avoid the unfavorable interactions caused by additives and to synthesize high-quality lubricants, we dissolved the PVC waste in THF and filtered off the insoluble residues. The THF solution was then precipitated in water to remove water-soluble salts. The precipitate was redissolved in THF and precipitated in isopropanol to remove organic additives (e.g., phthalate plasticizers). ICP-MS was used to analyze the purity of PVC powder extracted from waste. Unpurified waste powders contained substantial amounts of Ca, Mg, Zn, Ti, and Al due to additives used in PVC products (**Table S5**). Ti is typically associated with UV protection, and Al is linked with flame retardancy[9,12,13]. In contrast, the purified PVC powders showed reduced concentrations of Ti (down to 101 ppm) and Al (down to 0 ppm). However, considerable amounts of Ca (2,232 ppm) were still detected in the purified powders, but their further removal can be accomplished by using dilute HCl during purification. Notably, < 10 ppm of Ti was found in the final vPAO, likely due to additional filtration steps after synthesis (e.g., passing through activated carbon of Pd/C catalyst)."

The main text is updated as per the reviewer's recommendation:

Page 10:

"To minimize the interference of plastic additives, we first dissolved the PVC waste in THF and filtered off the insoluble residues, such as $CaCO_3$ fillers and other metal-based additives (**Table S5**). The filtrate was then precipitated in water to remove water-extractable salts, including Zn, Mg, and Al compounds. The precipitate was redissolved in THF and crashed out in isopropanol to remove organic additives (e.g., phthalate plasticizers)[14], effectively reducing oxides and oxygenates that can poison $AlCl_3$."

The ICP-MS digestion protocol has been added to the methods section as follows:

"Approximately 100 mg of each sample was accurately weighed and transferred into Teflon microwave digestion vessels. To each vessel, 10 mL of concentrated nitric acid was added. The vessels were gently shaken for approximately 15 min to promote initial sample–acid interaction and improve digestion efficiency. The vessels were then sealed and subjected to microwave-assisted digestion. The temperature was ramped to 200 °C over 15 min and maintained at 200 °C for an additional 15 min. After completion of the digestion program, the vessels were allowed to

cool to ambient temperature before being carefully opened. The digested solutions were quantitatively transferred and diluted to a final volume of 250 mL with deionized water.

Analysis parameters:

ICP-MS analysis was conducted using Agilent 7900 ICP-MS operating on RF power of 1550 W and plasma gas flow rate of 15 L/min. Helium was used as the collision gas (5mL/min), and the analyte solutions in 2% HNO_3 were introduced via a MiraMist nebulizer and Quartz Scott double-pass spray chamber. Metal concentrations were quantified by external calibration against multi-element standards in the range of 0.001-1 ppm (1-1000 ppb)."

Comment #4: Techno-economic analysis assumptions: TEA is a welcome addition. Please briefly state the key assumptions for the 1-decene price in the base case scenario, given its identified sensitivity. Furthermore, the authors mentioned securing affordable α-olefins as a future goal. It would be beneficial to suggest one or two potential avenues, e.g., sourcing bio-derived or waste olefins, to demonstrate a forward-looking strategy for mitigating this cost factor.

Author response: We sincerely thank the reviewer for bringing up the sensitivity of the TEA to changes in the cost of α-olefins, such as 1-decene, and for inquiring further about alternative olefin sources. Below, we provide the relevant assumptions and historical trends in 1-decene prices. To address the reviewer's comment regarding the procurement of low-cost α-olefins for the dechlorination and alkylation of PVC, we draw on previous work from our group as well as studies reported by other researchers in the field.

1. Assumptions about 1-decene in the TEA analysis

The sensitivity of our process to 1-decene arises from slight excess loading requirements (> 1 equivalent to Cl in PVC) and its higher procurement cost compared to other raw materials in the feedstock. In the unit reactor, the 1-decene feed was set to 1.05 equivalents of PVC Cl content, which is slightly lower than the 1.2 equivalents used in the laboratory-scale reaction. This reduction was considered feasible because several parameters that significantly affect the vPAO yield, such as the α-olefin feed rate, can be optimized at a larger scale but are less consequential in small-scale reactions. Furthermore, we assumed that all 1-decene in the feed reacts under highly cationic conditions, eliminating the need for additional costs associated with distilling unreacted olefins. Ultimately, careful calibration of olefin loading is critical to avoid unnecessary raw material expenditures as well as the formation of undesired products from olefin self-oligomerization in a Lewis acid-rich medium.

Similar to other feedstocks and vPAO products, the cost of 1-decene is treated as fixed in the base case scenario. This assumption is supported by market data indicating that the projected growth of the 1-decene market, approximately 5.7% annually from 2022 to 2030 according to Grand View Research[15], is primarily driven by increasing demand and capacity expansions rather than sustained price escalation. In addition, analyses from Imarc Group suggest that 1-decene prices in major markets, such as the United States and China, have remained relatively stable, with occasional downward trends observed in 2025[16]. These findings suggest that long-term price increases are expected to be modest, supporting the use of a constant price assumption in the base case. Nevertheless, we considered contingency plans in case 1-decene costs became prohibitively too high and compromised process profitability, as discussed below.

2. Alternative sources of α-olefins

Given the high sensitivity of the TEA to 1-decene, we considered whether α-olefins derived from the pyrolysis and thermolysis of polyethylene plastics could potentially substitute petrochemical α-olefins in the upcycling reaction. Previously, our group showed that olefin-rich hydrocarbons can be generated from plastic waste and further transformed through oxidation reactions to produce functional surfactants (*Science* 2023 and *Nat Sustainability* 2024). It was demonstrated that controlling the temperature gradient within thermolysis reactors is critical for regulating molar mass and carbon-number distribution, which in turn governs the oil-to-wax ratio. Using this approach, high oil yields with 54 wt. % alkenes and > 90 % selectivity to α-olefins were obtained from polyethylene. More recently, we extended temperature gradient thermolysis of polyolefins to highly contaminated plastic waste, such as detergent containers and plastic mulch, demonstrating that clean olefinic oil can be accessed from complex, low-cost waste streams through a non-catalytic process[17]. Other researchers have also demonstrated the efficacy of catalytic pyrolysis of polyethylene to produce oil containing olefins[18]. These precedents demonstrate that plastic waste, particularly polyethylene, can supplement petrochemical α-olefins in the proposed PVC upcycling strategy, thereby enabling a more sustainable methodology that relies on polyolefin and PVC waste to produce high-quality polyalphaolefins (PAOs). We have begun investigating polyethylene-derived α-olefins in alternative PAO synthesis and will report the results in a forthcoming paper.

Thus, we have updated the TEA section in the main text as follows:

"To enhance margins, it will be especially important to secure affordable and sustainable sources of α-olefins, which currently represent the largest contributor to raw material costs. We previously reported that α-olefins can be generated from low-cost contaminated plastic waste streams[17,19]. The synthesis of sustainable PAO from polyethylene-derived α-olefins is currently underway and will be reported in a forthcoming article."

Additional assumptions about 1-decene in TEA were included in Section 12.2.1. of the supplementary materials as follows:

"Key capital investment assumptions are presented in **Table S7**. Additional critical assumptions for the base case are detailed in **Tables S8** and **S9**, including project duration, salvage value, depreciation method and period, annual interest rate, fixed costs (such as raw material and product prices), operating labor, supervision, utilities, maintenance and repairs, operating supplies, laboratory expenses, royalties, plant overhead, and general expenses. In a 2-ton reactor, the 1-decene loading can be reduced by optimizing the α-olefin feed rate, an adjustment that is less consequential for small-scale reactions but can help minimize undesired oligomerization. Moreover, it is reasonable to assume that all 1-decene in the feed reacts under highly cationic conditions, eliminating the need for additional costs associated with distilling unreacted olefins. In the TEA, the plant is modeled with an annual production capacity of 50,000 tons, corresponding to 2,080 kg per batch."

Table S8. Other key assumptions and the prices of input and output

Assumptions	
Project length	20 years
Salvage value	0%

Depreciation method	Straight-line depreciation, under which equipment is depreciated at a constant annual rate of *1/n*, where *n* is the depreciation period in years
Loading of 1-decene	The optimal loading of 1-decene was assumed to be 1.05 equivalents to chlorine in PVC after optimizing the olefin feed rate
Depreciation period	10 years
Annual interest rate	3%
Fixed costs, raw material and product prices	Assumed to remain constant over time
PAO lubricant	$3,212/ton
PVC	$100/ton
1-Decene	$926/ton
$AlCl_3$	$329/ton
Dichloromethane	$348/ton
Nitrogen	$250/ton
Hydrogen	$1,280/ton
Raney Nickel	$16,680/ton
Operating labor	15% of the total product cost
Operating supervision	10% of the operating labor
Utilities	15% of the total product cost
Maintenance and repairs	5% of the fixed capital investment
Operating supplies	15% of maintenance and repair costs
Laboratory charges	15% of operating labor costs
Royalties	3% of the total product cost
Plant overhead costs	5% of the total product cost
General expenses	10% of the total product cost

Comment #5:

Minor Polishes:

i) The abbreviation "v_xPAO" is introduced but could be confusing. Consider using a more descriptive notation in the caption of Fig. 1d (e.g., "vPAO-6, vPAO-8, vPAO-10")

Author response: We thank the reviewer for the helpful suggestion and the opportunity to clarify our naming convention. In early drafts (before submission), we used the reviewer's proposed notation, but we ultimately adopted v_xPAO to emphasize that these materials were prepared from α-olefins with different carbon numbers.

We note that in the lubricants industry, the designation PAO*x* is commonly used to indicate a Group IV base oil with a kinematic viscosity of *x* cSt at 100 °C (e.g., PAO6 ≈ 6 cSt at 100 °C). Although not a formal standard, this convention is widely used by PAO producers. In our work, for example, we produced a waste-derived PAO with a viscosity of ~26 cSt at 100 °C from 1-decene. Under the industry convention, this material would be labeled vPAO26, not vPAO10.

However, the primary goal of our nomenclature in this manuscript is to clearly identify the olefin precursor chain length used to synthesize the PAO (e.g., PVC-derived precursor denoted by **v**, and a C6 α-olefin denoted by **6**). This approach helps highlight trends associated with varying olefin chain length and their effects on viscosity and tribological behavior. To avoid confusing expert readers who may interpret "PAO*x*" as a viscosity grade, we intentionally did not use a naming scheme that could be read as an industry viscosity designation.

Therefore, we use **v_xPAO**, where **v** indicates the vinyl (PVC-derived) origin and **x** denotes the α-olefin carbon number. If desired, the industry viscosity grade could be appended (e.g., **v_{10}PAO26**), but for clarity and simplicity, we omitted the viscosity suffix in the manuscript.

We hope this explanation clarifies our rationale and that the reviewer will find the revised notation acceptable.

We have added the sentence below to inform the readers about the reasoning behind the v_xPAO notation and updated the main text as follows:

"After the reaction was complete, the solvent and $AlCl_3$ were removed during work-up, yielding v_xPAO lubricants featuring no detectable C-Cl bonds in FTIR and ^{1}H NMR (**Figs. 1d** and **1e**). In the nomenclature, v denotes vinyl or PVC, and the subscript x represents the α-olefin used for the synthesis (e.g., x = 6, 8, and 10 for 1-hexene, 1-octene, and 1-decene, respectively). The v_xPAO notation is distinct from the industry convention of PAOx, where x corresponds to the kinematic viscosity at 100 °C in cSt."

For waste-based oils, we have changed the naming to v_{10}PAO-mix-hexanes and v_{10}PAO-mix-DCM for clarity.

ii) Please ensure all references to figures and tables in the text are correct (e.g., the reference to **Fig. S17** for viscosity index and friction coefficient).

Author response: We apologize for the incorrect figure reference and thank the reviewer for bringing it to our attention. We double-checked all figure and table references throughout the manuscript and ensured that they are correct. After including additional figures in the supplementary materials, the updated figure reference corresponding to the coefficient of friction and viscosity data is **Fig. S25**.

Final comment: In conclusion, recycling PVC is a huge challenge, the authors provide a competitive, practical way to use PVC waste as the resource. This is an outstanding piece of work that presents a transformative solution to chloride-containing plastic PVC pollution. This

reviewer is confident that addressing these minor points will elevate the manuscript to its fullest potential, ensuring it receives the high impact it deserves upon publication.

Author response: We are grateful for the supportive comments and suggestions to improve our manuscript.

Referee #2:

This manuscript reports a Lewis-acid-mediated strategy that combines PVC [de]chlorination with α-olefin oligomerization to produce chlorine-free, PAO-like lubricants with tunable viscosity and promising tribological performance. While each elementary transformation involved is individually well precedented, their integration into a single process explicitly aimed at generating lubricant-grade PAO analogues from PVC-containing feeds appears to be unprecedented. To my knowledge, no prior work has demonstrated the direct synthesis of PAO base-stock-like fluids via a one-pot Lewis-acid route starting from PVC. The work is conceptually appealing and potentially impactful.

Comment #1: The manuscript and SI rely primarily on the disappearance of the C–Cl FTIR band (~617 cm^{-1}) and of the ~4.4 ppm ^1H NMR signal as evidence for complete di[de]chlorination. While supportive, these techniques are not quantitative and may fail to detect residual organochlorides at ppm–0.1 wt% levels, which are highly relevant for lubricant applications. The lack of quantitative halogen analysis on the final vPAO (and ideally also on volatile fractions and aqueous work-up streams), for example, by ICP-based methods, therefore significantly weakens the claim of complete dechlorination.

Author response: We agree with the reviewer that FTIR and ^1H NMR are insufficient to detect low levels of chlorine in lubricants. It is paramount to quantify the residual chlorine in vPAO due to the potential corrosion of metal components during use. Following the great suggestion, we have complemented our analysis with additional ion chromatography data. In this context, ion chromatography technique can quantify a total chlorine content down to 0.01 wt.%.

We performed ion chromatography studies on lab-grade PVC-derived v_8PAO and waste-based v_{10}PAO-mix prepared in CH_2Cl_2 and hexanes. The lubricants were first subjected to Schöniger oxidation to mineralize organic chlorine. Oxidation products were subsequently captured in a hydrogen peroxide solution for further analysis. All lubricants contained < 100 ppm chlorine, and v_{10}PAO-mix hexanes showed the lowest levels of chlorine based on the area under the curve in the chromatogram (**Fig. S12** chromatograms and **Table S3**). The oils prepared in DCM (v_8PAO and v_{10}PAO-mix-DCM) contained slightly higher chlorine, likely due to possible side reactions involving solvent and $AlCl_3$ (**Scheme S4**). In addition, the residual chlorine content in waste-based oils can be attributed to leftover additives that can poison $AlCl_3$ (**Table S5**), effectively limiting the dechlorination. That being said, we decided not to increase the $AlCl_3$ loading past 50-60 mol% to avoid an undesired increase in branching and minimize additional cost for $AlCl_3$. Ultimately, the dechlorination and alkylation of PVC drastically decrease the concentration of chlorine to < 100 ppm, representing > 99.98% chlorine reduction.

Fortunately, the trace levels of chlorine and potential degradation products in the oils did not drastically affect the long-term tribological performance. To determine whether residual trace chlorine affects the long-term stability and reliability of the lubricants, we re-evaluated the friction and wear performance of a six-month-old vPAO-mix-hexanes sample. Wear tests revealed average wear loss volume (WLV) of approximately 1,391 μm^3, which was still lower than those of PAO10 (4,338 μm^3) and PAO40 (1,673 μm^3) (**Figs. 4c** and **S42**). Although the 3D non-contact profilometer suggested an increase in WLV from 619 μm^3, the 2D line-scans over the wear scars of both cases showed not much difference in the spherical contour of the wear scars, as shown in **Fig. S42.** Overall, the wear remained minimal with the steel ball showing no signs of wear, exhibiting only slight abrasive marks. The coefficient of friction remained almost unchanged (~ 0.08), signifying

tribological stability over an extended period of time. Therefore, it is reasonable to conclude that trace chlorine and its potential degradation products in the oils did not compromise the long-term rheological and tribological performance of v_{10}PAO.

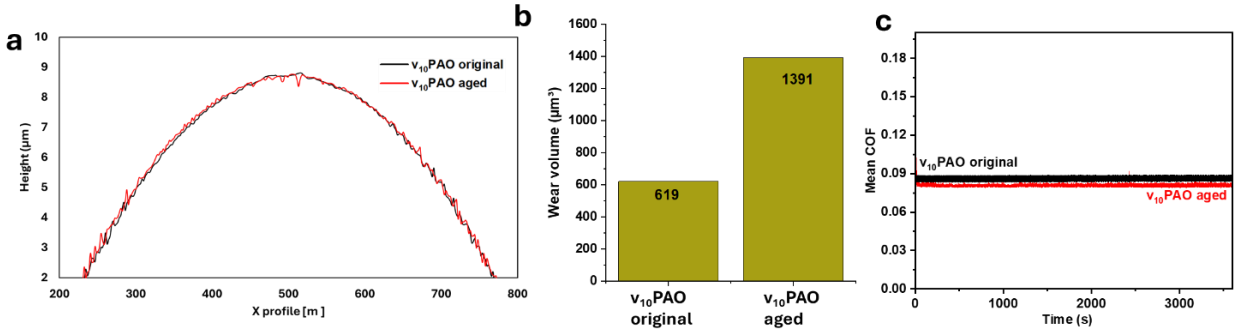


Figure S42. Effect of aging on tribological properties. a) 2D line scans over the wear scars of both the original and aged v_{10}PAO oils, showing negligible differences. b) Wear volume of original and aged v_{10}PAO-hexanes oil. c) COF revealing no substantial changes between the original and aged v_{10}PAO-hexanes oil.

We have updated the main text and supplementary materials, in consideration of the additional ion chromatography and lubricant stability results. Moreover, we clarified that residual chlorine in lubricants was below FTIR and NMR detection limit, and only a trace amount of chlorine was detected in ion chromatography.

The following changes are made in the main text:

Page 5: "After the reaction was complete, the solvent and $AlCl_3$ were removed during work-up, yielding v_xPAO lubricants featuring no detectable C-Cl bonds in FTIR and ^{1}H NMR (**Fig. 1d** and **1e**)."

Page 6: "$AlCl_3$ loadings of 50 mol% generated lubricants of low viscosities without any detectable C-Cl bands in the FTIR spectra. However, ion chromatography studies revealed trace levels of chlorine (<100 ppm), representing >99.98% dechlorination efficiency (**Fig. S12** and **Table S3**)."

Page 20: The experimental section is updated to include the ion chromatography protocol:

"**Ion chromatography**

Total chlorine content in the vPAO was evaluated using chloride ion chromatography on an Agilent 1100 HPLC with a Shimadzu CDD-6A Conductivity Detector. In a typical test, 5-50 mg of the lubricant was combusted in an oxygen combustion flask containing hydrogen peroxide. The solutions were injected and eluted through a polymeric anion exchange column using a sodium carbonate/sodium hydrogen carbonate mobile phase. In the column, the ions were separated as they exchanged between the mobile and stationary phases. Ions were then detected as they eluted from the end of the column by a conductivity detector. The detector measured the electrical conductivity of the solution eluting from the column and generated a response proportional to the ion concentration."

The following changes have been made in the Supplementary materials.

page 5:

"5. Quantification of trace residual chlorine in lubricants

To determine ppm-level chlorine content in upcycled lubricants, we performed ion chromatography on lab-grade PVC-derived v_8PAO and mixed-waste PVC-derived v_{10}PAO prepared in DCM and hexanes. The lubricants were first subjected to Schöniger oxidation to mineralize organic chlorine, and the products were dissolved in a hydrogen peroxide solution for further analysis. All lubricants contained < 100 ppm chlorine, and v_{10}PAO mix hexanes showed the lowest levels of chlorine based on the area under the curve in the chromatogram (**Fig. S12** and **Table S3**). The oils prepared in DCM (v_8PAO and v_{10}PAO-mix-DCM) contained slightly higher chlorine, likely due to possible side reactions involving the solvent and the Lewis acid (**Schemes S2** and **S4**). Therefore, the dechlorination and alkylation of PVC drastically decrease the concentration of chlorine to <100 ppm in the lubricant, representing >99.98% chlorine reduction.

11. Long-term stability of waste-derived lubricants

To determine whether residual trace chlorine affects the long-term stability of the lubricants, we evaluated the coefficient of friction and wear volume of a six-month-old v_{10}PAO-mix-hexanes lubricant. Wear tests revealed a wear loss volume (WLV) of ~1400 μm^3, which was lower than that of PAO10 and PAO40 (**Figs. 4c** and **S42**). Although the 3D non-contact profilometer suggested an increase in WLV from 619 μm^3, the 2D line-scans over the wear scars showed almost no differences in the spherical contour of the wear scars (**Fig. S42**). Overall, the wear remained minimal with the steel ball showing no signs of wear, exhibiting only slight abrasive marks. The coefficient of friction remained almost unchanged (~ 0.08), suggesting tribological stability over an extended period of time. Therefore, it is reasonable to conclude that the trace chlorine in vPAO did not drastically compromise the long-term rheological and tribological performance."

Comment #2: A key question is what fraction of the final lubricant carbon skeleton originates from PVC versus from α-olefin oligomerization. The process employs ~1.2 equivalents of α-olefin per PVC Cl. Under such conditions, it is plausible that a substantial fraction of the product is effectively a conventional PAO-like oligomer formed under unusually high $AlCl_3$ loading. At present, convincing evidence (for example, experiments using ^{13}C-enriched PVC followed by thorough microstructural characterization of the sample) that PVC-derived carbon is substantially incorporated into the oil phase is lacking.

Author response: We sincerely appreciate the thoughtful question by the reviewer. The reviewer is absolutely correct that direct evidence of PVC moieties incorporation is preferable to prove that the final lubricant skeleton originates from the PVC. We have attempted to procure ^{13}C-labelled PVC to synthesize ^{13}C-rich vPAO. Unfortunately, we could not find any available ^{13}C-labelled PVC. We considered synthesizing ^{13}C-labelled PVC; however, this will be beyond our expertise and our capability of safely handling carcinogenic vinyl chloride—you may have heard the disastrous vinyl chloride spill from the Norfolk Southern train derailed in East Palestine, Ohio, in 2023[20]. Therefore, we concluded that we could not access ^{13}C-labelled PVC within a reasonable timescale for the revisions.

As an alternative, we performed dechlorination on a deuterium-labelled small molecule (e.g., chloroalkane) as a model substrate and then conducted alkylation reactions using 1-hexene. We

monitored the products with GC-MS to track the differences in product structure and elution times of products synthesized with a non-deuterated substrate. Besides the model reaction, we have also compiled experimental data on structural analysis, rheology, thermal properties, and molar mass analysis of vPAO. Then we compared the properties of vPAO (with PVC carbon skeleton) side-by-side with those of cPAO (without PVC carbon skeleton) to show the clear differences in properties attributed to the incorporation of PVC carbon in the lubricant structure.

1. Comparative study of 2-chloropropane (D_7) and 2-chloropropane (H_7) reactions with 1-hexene to model the PVC reaction with α-olefins

To provide possible evidence for the integration of chloroalkane carbon moieties in the lubricant structure, we synthesized oils using 2-chloropropane-D_7 and 2-chloropropane-H_7 as the substrate. We reacted these substrates with 1-hexene under optimized conditions for vPAO synthesis. We attempted to delineate differences in the structures and retention time of both oils using GC-MS. The product stream consisted of alkanes, isoalkanes, alkenes, and cyclic compounds originating from isomerization and intramolecular alkylation. Both reactions produced monoalkylated hydrocarbons. Interestingly, the deuterium atom in the propyl methine group underwent H-D exchange under highly acidic conditions[21]. The small molecule model reactions confirmed the presence of molecules generated via C-C bond formation between the chloroalkane and α-olefins, but other products also formed through oligomerization and various isomerization pathways. That being said, we agree with the reviewer that ^{13}C-labelled PVC oligomers and/or α-olefins would be more suitable for providing direct evidence of chloroalkane moiety incorporation and enabling a more reliable estimation of cross-coupled feedstocks fraction vs. the self-oligomerized fraction.

2. Side-by-side comparison of α-olefin reactions with and without PVC

Given that ^{13}C-labelled PVC is difficult to obtain, it is extremely challenging to provide direct evidence for PVC dechlorination-alkylation. In light of these results, we decided to dedicate much effort to indirect evidence by highlighting the changes in the lubricant properties of upcycled oils and conventional oils prepared without PVC.

cPAO and vPAO showed starkly different molecular structures, properties, and performances, highlighting the impact of PVC on the synthesis of PAO. Mechanistically, vPAO contained vinyl-derived moieties in the lubricant structure, which were integrated through a new C-C bond between the PVC backbone and the olefins. First, the degradation of PVC under Lewis acid produces both unsaturated and saturated chlorocarbons (through β-scission) that can participate in alkylation reactions (**Scheme S4**), which generated a highly branched product (confirmed by the low I_{CH2}/I_{CH3} ratio in ^{1}H NMR, **Fig. S10a**). It is worth reiterating that branching was effectively minimized when the reaction solvent was switched to hexanes, owing to hydrogen transfer (**Fig. 4b** and **Table S1**). Moreover, the PVC template provides a platform for alkylation reactions with α-olefins, leading to a higher-molar-mass oil than that synthesized via simple oligomerization of α-olefins using 50 mol% $AlCl_3$ (**Fig. S10c**). Both molar mass and molecular structures (i.e., degree of branching) are two factors that greatly influence the lubricant's viscosity[22,23]. Indeed, vPAO showed a >30 times increase in dynamic viscosity and ~5 times increase in kinematic viscosity at 40 °C compared to cPAO (**Figs. S10d** and **S10e**). In addition, the more branched vPAO exhibited a T_g of -54°C (vs. -62 °C for cPAO) due to the high energy required to achieve long-range motion in branched chains (**Fig. S10f**)[24]. The negative effect of branching was further demonstrated through tribology studies, where PVC-derived lubricants led to a deep scar corresponding to a wear volume of 243000 μm^3 (**Figs. S10g and S10h**). The failure to effectively reduce friction can be ascribed to short-chain

branching caused by the introduction of PVC degradation moieties, which hinders the formation of a robust film at the interface during testing[4,5]. The totality of these results reveals clear structural differences in the oils (cPAO and vPAO) and vastly distinct material properties, thus reinforcing the thesis that PVC skeletal moieties become incorporated in the final molecular structure.

Unfortunately, we were unable to determine the fraction of PVC that was downcycled to gaseous and low-molar-mass volatiles due to the lack of ^{13}C-labelled PVC substrates. That said, it is evident that the overall yield of gases and volatiles drastically increases at high $AlCl_3$ loadings (**Fig. R3**). Therefore, the Lewis acid loading should be kept between 30-40 mol% to minimize excessive degradation. In the future, computational insights coupled with experimental validation can assist in evaluating the fraction of ^{13}C-PVC that ends up in the lubricant molecular structure as a function of $AlCl_3$ loading. In this manner, the amount of feedstocks and loading ratios can be further optimized to boost the profitability of large-scale PVC upcycling processes.

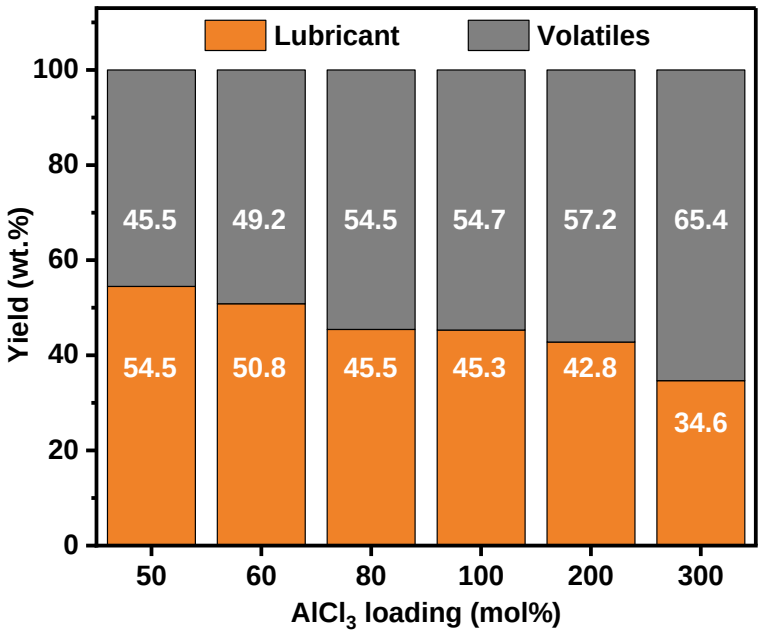


Figure R3. Upcycled products yield at varying $AlCl_3$ loading. A large fraction of feedstocks is converted to low-value volatiles under $AlCl_3$ overdose conditions.

We have added the following results to the supplementary materials to demonstrate the effect of introducing PVC-derived moieties on the lubricant performance:

9. Comparison of lubricant properties of α-olefin reactions with and without PVC

The introduction of PVC into the upcycling reactions leads to PAO with different molecular structures than those without PVC (**Fig. S10a**)[25]. Foremost, the PVC backbone template provides a platform for alkylation reactions with α-olefins, which afford vPAO with a relatively high molar mass of ~1270 g/mol, compared to ~870 g/mol for cPAO (**Fig. S10c**). In addition, side reactions may involve unsaturated and saturated chlorocarbons formed during PVC degradation, producing lubricants with different levels of branching (**Scheme S4**). Both molar mass and degree of

branching greatly influence lubricant properties, including viscosity and thermal properties[22,23]. For instance, vPAO showed over thirty times increase in dynamic viscosity and about five times increase in kinematic viscosity at 40 °C compared to cPAO (**Fig. S10d** and **S10e**). vPAO also exhibited a T_g of -54°C (vs. -62 °C for cPAO) due to restricted segmental mobility of branched chains (**Fig. S10f**)[24]. The effect of branching was further illustrated in tribology studies where PVC-derived vPAO synthesized in DCM led to a deep scar with a wear volume of 243,000 μm^3, in contrast to cPAO with about ten times less wear volume (24,900 μm^3, **Fig. S10g and S10h**). The relatively poor tribological performance is attributed to short-chain branching, as introduced via PVC degradation moieties in DCM solvent, which hinders the formation of a robust film at the interface during testing[4,5]. These results reveal clear structural differences in cPAO and vPAO, and the vastly distinct material properties reinforce that PVC skeletal moieties are incorporated into the final molecular structures.

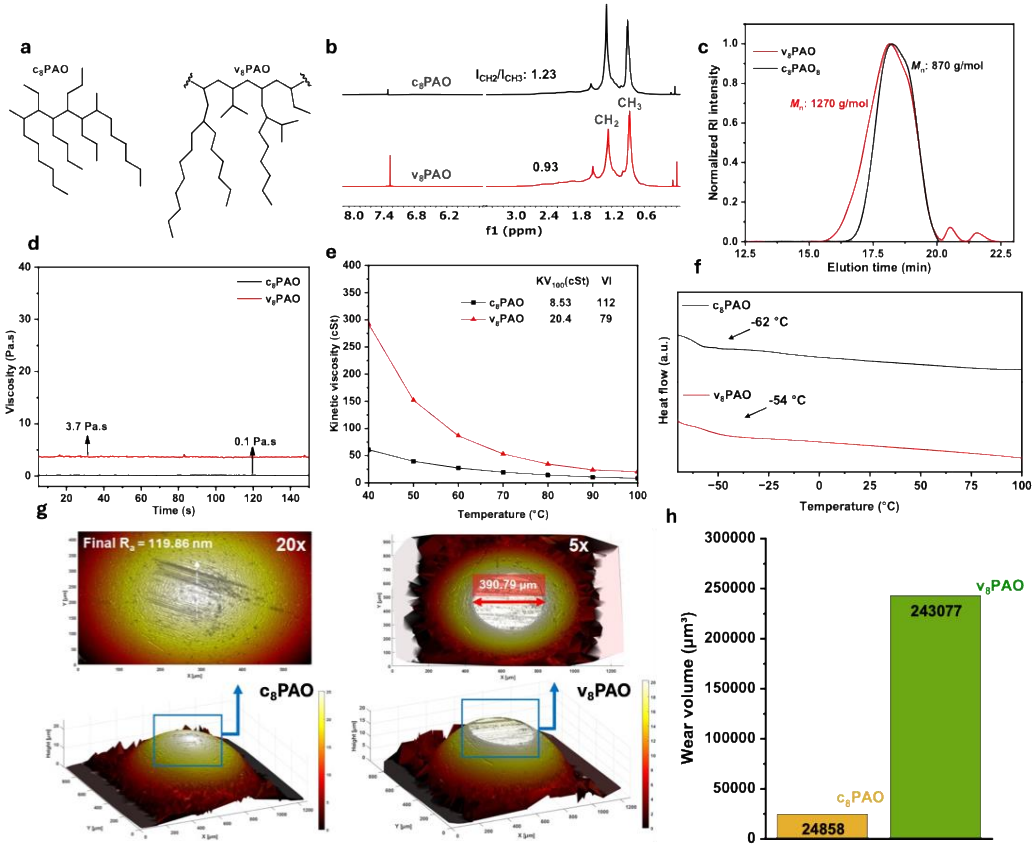


Figure S10. Lubricant properties of α-olefin reactions with and without PVC. a) Structures of c_8PAO and v_8PAO, comparing the extent of branching and branching chain lengths. b) ^{1}H NMR of c_8PAO and v_8PAO displaying the degree of branching determined through the I_{CH2}/I_{CH3} integral ratios. c) SEC chromatograms of c_8PAO and v_8PAO. d) dynamic viscosity and e) kinematic viscosity of c_8PAO and v_8PAO, revealing high viscosity for the more branched v_8PAO at low temperatures. f) DSC thermograms of c_8PAO and v_8PAO showing high T_g for the PVC-derived lubricant. g) 3D profiles of the ball's contour after tribology tests. v_8PAO resulted in a deep scar

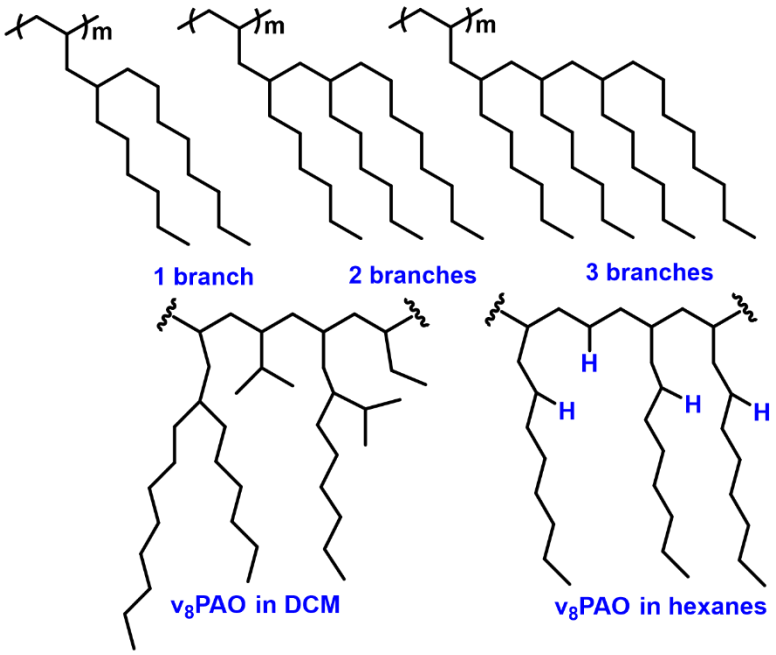
due to poor lubrication performance of short branch chains, whereas c_8PAO led mostly to abrasion marks. h) Wear volume of scars incurred in tribology experiments.

Comment #3: The branching structures proposed in Scheme 1 appear speculative and are not directly supported by spectroscopic evidence. Moreover, the branching ratio (BR) is estimated from ^{13}C NMR by integrating "methyl" versus "methylene" regions without reporting detailed peak assignments. This raises several concerns, among which: (i) methine carbons also resonate within the 18–44 ppm region; (ii) methyl groups resonances in long alkanes can appear in the 20–25 ppm range; (iii) chain-end methyl groups resonate in the 11–14 ppm region. Without explicit assignments, the BR values are difficult to assess.

Author response: We are grateful to the reviewer for raising these important questions, and we acknowledge that insufficient information regarding branching was provided in the first version of the manuscript. The reviewer makes a good argument to revisit the quantification of branching in the dechlorination and alkylation process, as well as the assignment of the peak chemical shifts. To address the reviewer's questions, we performed Distortionless Enhancement by Polarization Transfer 135 (DEPT 135) NMR and assigned CH, CH_2, and CH_3 resonance peaks. Heteronuclear single quantum coherence (HSQC) was also performed on four representative samples prepared in DCM and hexanes to further ascertain the chemical environment of carbon moieties. After assigning the peaks, we recalculated the branching ratios and updated the main text and the supplementary materials. Detailed responses to the reviewer's comment about branching are as follows.

1. Explanation of Scheme S1 branching structures

Due to the lack of experimental techniques to precisely determine the oligomer structures of vPAO, we resorted to molecular simulations to compare the free energies associated with the formation of "branched-like" structures vs. "comb-like" structures. In the simulation studies, we envisioned lubricants featuring different degrees of oligomerization at the C2 position of the mono-substituted product. As such, "branched-like" microstructures featuring 1 to 3 branches were shown to illustrate examples of branching scenarios. We would like to note that the structures shown in the first row of scheme S1 were not detected spectroscopically; instead, they were only intended to showcase the extent of olefin oligomerization, which is well known and established in polyalphaolefin synthesis using Lewis acids[26]. A plausible mechanism for the dechlorination and alkylation process, highlighting the role of CH_2Cl_2 and hexanes in branching, is also shown in the updated **Scheme S3** and **Scheme S4**. Possible structural variations that can arise from short-chain branching were omitted for clarity because short-chain branching was not considered in the molecular dynamics simulations. However, to further inform the readers about the role of solvents in regulating branching, we have provided plausible chemical structures featuring varying short-chain branching in the updated **Scheme S1.**



Scheme S1. Schematic illustration of **(Top)** PVC-initiated α-olefin oligomerization at one activated site to form "branch-like" structures and **(bottom)** α-olefin substitution at multiple activated sites. The solvent plays a role in the PAO chemical structure during the PVC-templated substitution of Cl with α-olefins. Compared to DCM, hexanes quench α-olefin oligomerization and minimizes short-branch formation, thus reducing the overall branching in PAO to form "comb-like" structures.

2. Identification of methine, methylene, methyl peaks, and associated trends in branching.

To ensure that the branching ratio values accurately reflected the ratio of CH_2/CH_3, we collected DEPT-135 spectra of the olefin series (v_6PAO, v_8PAO, and v_{10}PAO) synthesized using lab-grade PVC, in addition to mixed-waste-based v_{10}PAO prepared in DCM and hexanes (shown in **Fig. S1**). The integration was performed again, and we ensured that no methine peaks were included in the integration by considering only methyl peaks in the range of ~10.8-22.7 ppm and negative methylene peaks above 22.7 ppm[27,28]. According to previous ^{13}C NMR microstructure analysis of lubricants, methyl groups attached to short alkyl chains appear between 10.8 and 11.3 ppm, while terminal methyl groups on long chains resonate at ~14.3 ppm[29]. Lastly, methyl signals above 17 ppm are ascribed to CH_3 branching in the middle of the main chain (≥ four carbons away from the chain end) or isopropyl-type branching that appears at ~22.6 ppm (**Fig. S32**) [27,30]. Methylene groups in an α position to the chain end resonate at 22.7-22.9 ppm, and methylene signals β to a methyl branch are centered ~ 27.5 ppm[30,31]. CH_2 groups far from the chain end and branching positions (γ, δ, etc.) appear between 29.2-32.4 ppm, while CH_2 α to branched positions resonate around 32.5-40.4 ppm[30,31]. Typically, CH groups produce weak signals above 27.0 ppm that are difficult to detect. However, some CH signals were observed in highly branched oils between ~27.0 and 33.4 ppm (positive peaks in DEPT 135). After integration, the branching ratio values were updated and summarized in **Table S1** and the manuscript. In addition, we have noted that the structures displayed in **Scheme S1** are speculative based on the olefin oligomerization literature or spectroscopic characterization of lubricants.

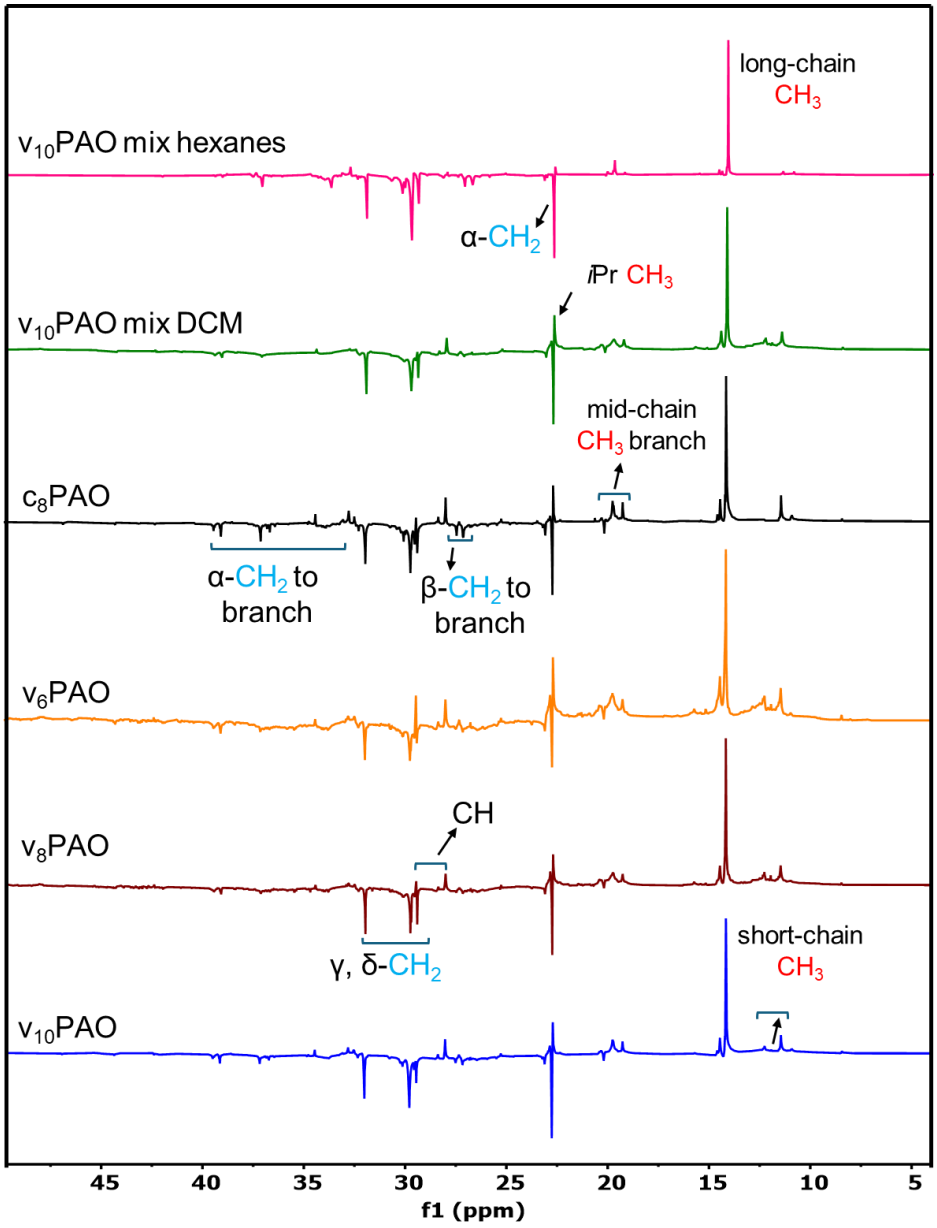


Figure S32. DEPT 135 NMR of upcycled PVC oils and cPAO to identify methine, methylene, and methyl signals. Methylene and methyl peaks were assigned based on prior literature on PAO microstructure. Methine peaks were assigned to positive signals above 27.0 ppm, which is outside the typical methyl group resonance range in saturated PAO structures[27,29-31].

The structures in the second row of **Scheme S1** were only meant to provide a comparative illustration of the branching levels in lubricants prepared in DCM and hexanes. To illustrate the ability of hexanes to minimize branching caused by chain walking and isomerization, we evaluated spectroscopic data from DEPT NMR and HSQC of two waste oil lubricants, focusing on the β-CH_2 and isopropyl type CH_3 signals at ~22.6-22.9 ppm in ^{13}C spectra. The DEPT 135 NMR of PVC mix waste-based v_{10}PAO synthesized in DCM exhibited an overlapping CH_3 and CH_2 peak at 22.6-22.9 ppm, which showed a correlation with both methylene and methyl ^1H NMR signals in HSQC (**Figs. S32** and **S22**). Conversely, v_{10}PAO synthesized in hexanes displayed mainly a

negative CH_2 peak at 22.7 ppm in DEPT 135 with a strong HSQC cross peak at {1.3, 22.7} ppm and a weak CH_3 cross peak at {0.9, 22.7} ppm compared to v_{10}PAO-mix-DCM (**Figs. S32** and **S22**). The weak intensity of the methyl group cross-peak stems from suppressed isomerization pathways through hydrogen transfer from the solvent. Therefore, hexanes promoted relatively low levels of branching, as indicated by minimal isopropyl groups in the upcycled oils.

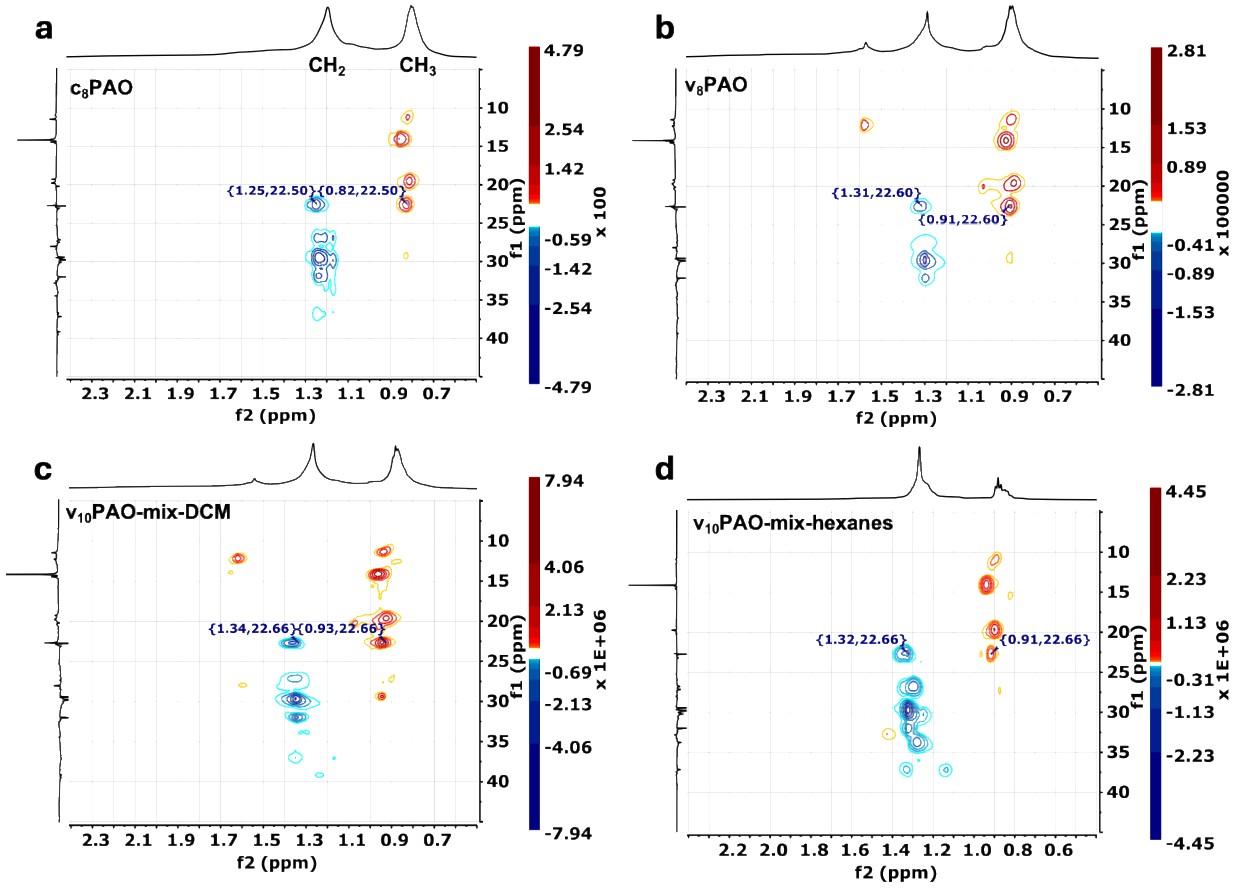


Figure S22. HSQC of the oils. a) HSQC of c_8PAO alkyl region, b) v_8PAO, c) waste-based v_{10}PAO-DCM, and d) waste-based v_{10}PAO-hexanes showing the correlation intensity map of β-CH_2 and isopropyl type CH_3 signals at ~22.6-22.9 ppm in ^{13}C NMR. The strength of the methyl group cross-peak showcases the difference in branching between oils prepared in DCM and hexanes.

The main text was updated as follows:

Page 5:

"vPAO exhibited controllable rheological and tribological properties as a lubricant. The level of branching, as determined by the CH_2/CH_3 integral ratios in the ^{1}H NMR spectrum (**Fig. 1e**) and the branching ratio (BR) in the ^{13}C NMR spectrum (**Fig. S1**), decreased with an increasing α-olefin chain length (**Table S1**), suggesting improved lubricity. This phenomenon can be rationalized by the diminished ability of long, bulky olefins to alkylate sterically hindered positions (**Scheme S1**). The α-olefin chain length and BR impacted the viscosity index (VI)[32,33]. v_6PAO with a BR of 65.2% exhibited a VI of 64, while v_{10}PAO with a BR of 38.5% showed a relatively high VI of 84. The highly branched v_6PAO resulted in the highest dynamic viscosity of 14.6 Pa·s at room

temperature, an order of magnitude higher than that of v_{10}PAO (**Fig. S3**), consistent with established trends between branching and viscosity[5,7].

Page 10:

"Similar to the upcycling of lab-grade PVC, hexanes afforded vPAO with less branching compared to the reaction in DCM, as evidenced by both ^{1}H NMR CH_2/CH_3 ratios and ^{13}C NMR branching ratios (**Figs. 4b**, **S2, and Table S1**). Moreover, the low degree of branching in the oils synthesized in hexanes was further validated by the presence of weak isopropyl C and H correlations in a heteronuclear single quantum coherence (HSQC) spectrum at {0.9, 22.7} ppm, unlike the oils prepared in DCM (**Fig. S22**)."

The supplementary materials are updated as follows:

"Additional factors demonstrated a substantial effect on branching in the PVC upcycling reaction, namely, solvent type (**Schemes S1**, **S3**, and **S4**) and α-olefin chain length. We should clarify that, in the current process, branching can result from α-olefin oligomerization at the side chains (i.e., the chains linked to the PVC backbone), as well as chain cleavage and isomerization under highly Lewis acidic conditions. The use of aromatic solvents, such as toluene, suppressed the α-olefin oligomerization at the side chain through Friedel-Crafts alkylation, which, in turn, minimized the degree of branching, as evidenced by the CH_2/CH_3 integral ratio from ^{1}H NMR (1.8 in toluene compared to 0.9 in DCM) (**Figs. S16** and **Table S4**). Similarly, non-chlorinated hydrocarbon solvents (e.g., hexanes) led to minimal branching in real-world PVC-derived lubricants (**Table S4**). To confirm that hexanes minimize branching caused by chain walking and isomerization, we evaluated spectroscopic data from DEPT NMR and HSQC of two waste-derived lubricants, focusing on the β-CH_2 and isopropyl-type CH_3 signals at 22.6-22.9 ppm in ^{13}C spectra. The DEPT 135 NMR of PVC waste-based v_{10}PAO synthesized in DCM featured overlapping CH_3 and CH_2 peaks at 22.6-22.9 ppm, which showed a correlation with both methylene and methyl ^{1}H NMR signals in HSQC (**Figs. S22** and **S32**). Conversely, v_{10}PAO synthesized in hexanes displayed mainly a negative CH_2 peak at 22.7 ppm in DEPT 135 with a strong HSQC cross peak at {1.3, 22.7} ppm and a weak CH_3 cross peak at {0.9, 22.7} ppm compared to v_{10}PAO-mix-DCM (**Fig. S22** and **S32**). The weak intensity of the methyl group cross-peak stems from suppressed isomerization pathways through hydrogen transfer from the solvent. Therefore, hexanes promoted relatively low levels of branching as indicated by minimal isopropyl groups in the upcycled oils. Lastly, ^{1}H NMR and ^{13}C NMR analyses revealed the least branching and isomerization in lubricants synthesized using long-chain α-olefins, as indicated by dynamic viscosity measurements. Lightly branched lubricant v_{10}PAO, synthesized from PVC and 1-decene, showed the lowest viscosity, in contrast to their highly branched counterparts synthesized from shorter-chain α-olefins (**Fig. S3**)[32,33]. Overall, to synthesize vPAO with a good viscosity index and tribological performance, it is crucial to minimize branching by judiciously selecting the α-olefin, the solvent, and the catalyst loading."

"The branching ratio (BR) of the lubricants was calculated according to the following equation,

$$BR = \frac{15 \int_{10.8\ ppm}^{22.7\ ppm} C13\ \ signal}{15 \int_{10.8\ ppm}^{22.7\ ppm} C13\ signal + 14 \int_{22.7\ ppm}^{44\ ppm} C13\ signal} \times 100\%$$

Generally, methine (CH) peaks are omitted in the integration due to their low intensities[27,28]. To ensure that the branching ratio values accurately reflect the mass ratio of CH_2/CH_3, we collected DEPT-315 spectra of v_6PAO, v_8PAO, and v_{10}PAO synthesized from lab-grade PVC, in addition to mixed-waste-based v_{10}PAO synthesized in DCM and hexanes to exclude methine signals from the integration."

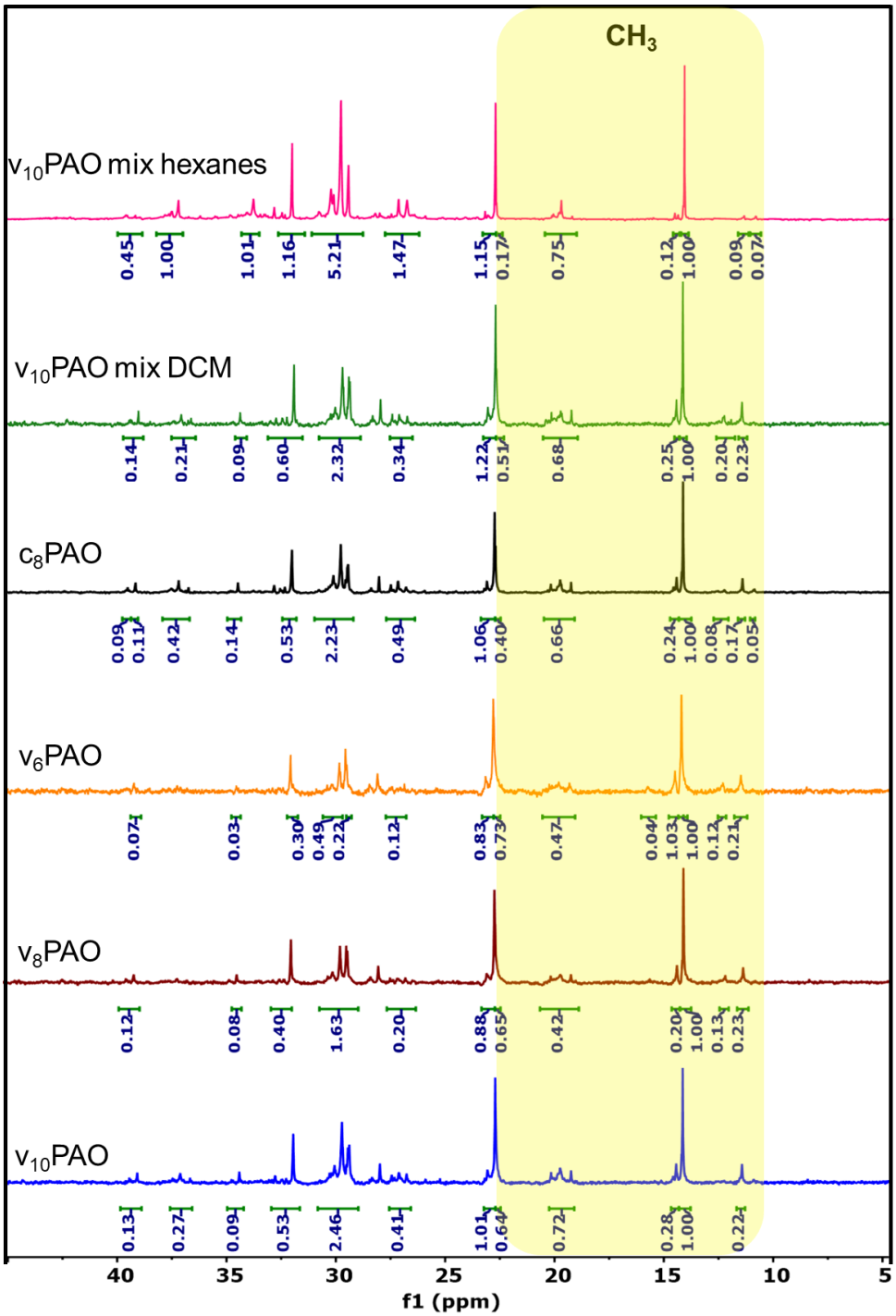


Figure S2. Integration of ^{13}C NMR peaks to evaluate the branching ratio in vPAO. All vPAO lubricants were synthesized in DCM except v_{10}PAO-mix-hexanes. CH_3 signals, 10.8-22.7 ppm;

CH_2 signals, 22.7-44 ppm (negative signals in DEPT 135). The mixed PVC waste consisted of cards, gloves, pipes, and toy frogs.

Table S1. Effect of α-olefin chain length and solvent type on the branching ratio and dynamic viscosity of vPAO

Lubricant	PVC feedstock	Solvent	I_{CH2}/I_{CH3}[†]	Branching Ratio (%)	Dynamic Viscosity[‡] (Pa·s)
c_8PAO	lab-grade	DCM	1.23	35.5	0.10
v_{10}PAO		DCM	1.00	38.5	2.20
v_8PAO		DCM	0.93	46.0	3.70
v_6PAO		DCM	0.63	65.2	16.40
v_{10}PAO mix[#]	real-life waste*	DCM	0.87	38.4	2.98
		hexanes	2.65	17.1	0.37

* Waste mixture consisted of PVC cards, gloves, pipes, and toy frogs.
[#] v_{10}PAO mix was synthesized using 60 mol% and 50 mol% of $AlCl_3$ loading in DCM and hexanes, respectively, affording Cl-free lubricants.
[†] The ratio of the CH_2 and CH_3 signal integration in ^1H NMR.
[‡] Dynamic viscosities were recorded at ~20 °C.

HSQC protocol

HSQC experiments were performed on a 500 MHz Bruker Avance III spectrometer at 298 K in $CDCl_3$, using a 2 s relaxation time, 32 scans, and a digitizing increment of 256.

Comment #4: The optimal conditions require ~50 mol% $AlCl_3$ relative to PVC Cl to achieve "complete dichlorination," which is a very large amount in practical terms and closer to stoichiometric reagent use than to catalysis, particularly if $AlCl_3$ is converted to $AlCl_4^-$ or hydrated aluminum salts upon quenching. As presented, this substantially weakens the manuscript's catalytic claims.

Author response: We thank the reviewer for highlighting the high $AlCl_3$ loading required for complete dechlorination and the choice of the word "catalysis" for these reactions. We agree that 0.5 equivalents of $AlCl_3$ loading is high. The word "catalysis" is an ongoing debate in the "Friedel-Crafts reaction" literature. We likely share a similar situation here, and it is fully debatable if "catalysis" is an appropriate term here. Thus, we have thoroughly gone through the manuscript and removed any wording related to "catalysis" in the manuscript.

In addition, prior researchers have identified that environmental factors, such as humidity and functional coordinating groups in the substrates, often impose close-to-stoichiometric loadings of $AlCl_3$ in many alkylation and acylation reactions[34]. Similarly, we have performed a systematic study to evaluate $AlCl_3$ dechlorination efficiency in a non-reacting solvent (i.e., hexanes) and compared the results with those in DCM. We have also added literature references to discuss typical challenges encountered in $AlCl_3$-assisted C-C bond-forming reactions.

1. Dechlorination efficiency under varied $AlCl_3$ loading in hexanes

As previously discussed, solvents can have a strong effect, and chloromethanes can react with $AlCl_3$, creating an equilibrium between chloromethyl cations and neutral chloromethanes[35]. To eliminate undesired pathways that divert $AlCl_3$ from dechlorinating PVC, we switched to hexanes without any C-Cl bonds. Under standard temperature, time, and concentration, PVC was dechlorinated and alkylated with 1-octene in hexanes using 10-50 mol% $AlCl_3$. $AlCl_3$ loadings of < 28 mol% generated lubricants and solids featuring discernible peaks associated with C-Cl in both FTIR and ^{1}H NMR (**Fig. S17**). However, complete dechlorination was observed at ≥28 mol% $AlCl_3$ loading, almost doubling the "catalytic" efficiency of Lewis acid achieved for reactions in DCM. These results show that solvents such as alkanes, despite their lower solubilities for PVC, are more effective and suitable for PVC dechlorination and alkylation. The benign nature of hydrocarbon solvents toward $AlCl_3$, in effect, further justifies our decision to select hexanes for technoeconomic analysis, in addition to their noted role in curbing excessive branching in vPAO.

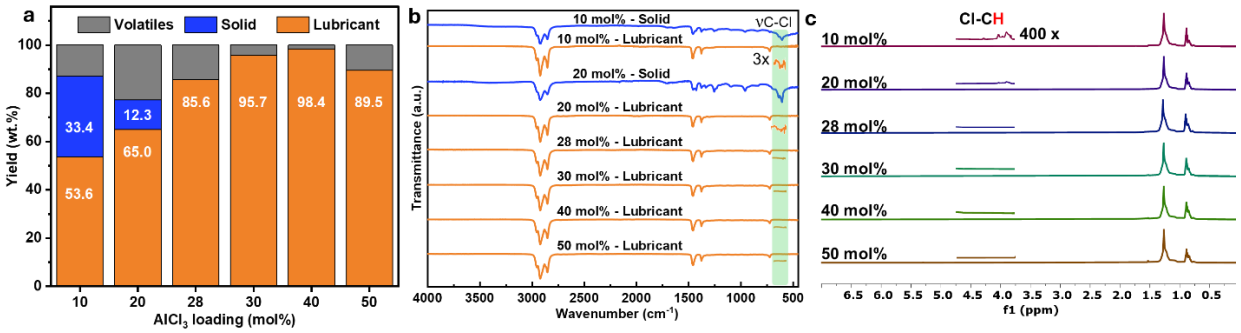


Figure S17. Optimization of $AlCl_3$ loading in PVC upcycling reactions in hexanes. a) Product yield at various $AlCl_3$ loadings. b) FTIR spectra of the lubricants and solids formed as the $AlCl_3$ loading varies. c) ^{1}H NMR spectra of the lubricants showing hydrogen signals at 4.0 ppm in the 10 mol% loading sample, likely corresponding to methine hydrogen near the Cl in low molar mass chlorohydrocarbons[36].

2. Effect of water on the upcycling reaction

Despite our best efforts, we could not reach a turnover number (TON) higher than 4, possibly due to additional factors that compromise the activity of $AlCl_3$. In principle, the dechlorination product of aluminum tetrachloride ion can react with a proton to turn over $AlCl_3$ and achieve a high TON[37,38]. However, given the high oxophilicity of the Al center, the potential presence of moisture in our reactions can reduce the activity of $AlCl_3$[39]. To confirm the effect of moisture, we added 2-10 wt.% water to $AlCl_3$ and then to the v_{10}PAO hexanes reaction, which resulted in solid byproducts with residual Cl, confirming the detrimental effect of excess water in the upcycling reaction (**Fig. S31**, FTIR and NMR). The loss of catalytic activity can also be attributed to the formation of aluminum chlorohydrates, which exhibit weaker Lewis acidity than $AlCl_3$. To minimize the effect of excess water in a large-scale process, $AlCl_3$ can be passed through a heated feeder before entering the main reactor. Additionally, the reaction produced HCl on site, which can be used to recover $AlCl_3$ from hydroxylates (**Scheme R1** and **Fig. S36**).

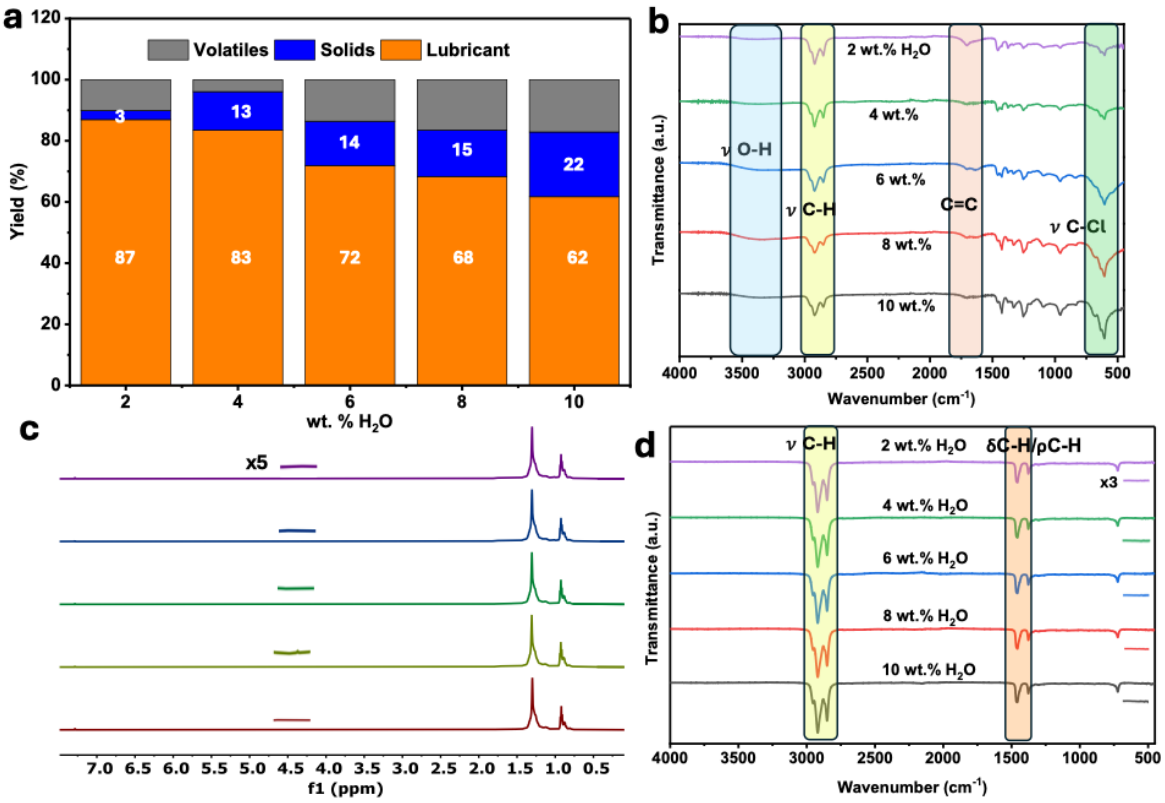


Figure S31. Influence of excess water on the PVC upcycling reaction. a) Product yield at various water contents in the reaction. The water content is based on the mass ratio of water to $AlCl_3$. The yield of solid byproducts increased with water loading, indicating decreased efficiency of $AlCl_3$. b) FTIR spectra of the solids featuring O-H, C=C, and C-Cl peaks as a result of partial dehydrochlorination and dechlorination. c) ^{1}H NMR and d) FTIR spectra of the lubricants showing no detectable C-Cl.

We have updated the main text and the supplementary materials as follows:

Main text

Page 8: "In contrast, non-aromatic hexanes generated the highest lubricant yield out of all tested solvents (~89.5 wt.%). The boosted yields are attributed to the absence of C-Cl bonds and the non-aromatic nature of hexanes, which eliminates the competing solvent-$AlCl_3$ interactions present in chloromethanes and aromatic solvents. In fact, the lack of C-Cl bonds in hexanes allowed for further reduction of the $AlCl_3$ loading to 28 mol%, marking a ~1.8 times increase in the efficiency (turnover number) relative to the reactions in DCM (**Fig. S17**). Interestingly, vPAO synthesized in hexanes exhibited the least branching and isomerization, as indicated by a high CH_2/CH_3 integral ratio in the ^{1}H NMR spectrum (**Fig. S10b** and **Table S3**), likely due to hydrogen transfer from the solvent.

Experimental section: "To investigate the role of water in the upcycling reaction, a controlled amount of water was added dropwise to a stirring mixture of $AlCl_3$ (28 mol% of monomer

equivalence) and hexanes (10 mL), followed by 1.5 mL of 1-decene. After 3 h, the reaction was worked-up similar to reactions without water and hydrogenated using 7 wt.% Pd/C."

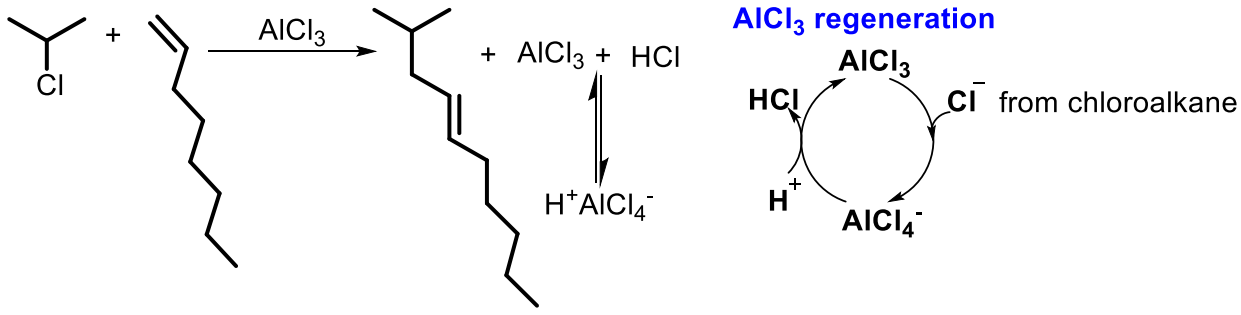
Supplementary materials:

6. $AlCl_3$ dechlorination efficiency in hexanes under dry and humid conditions

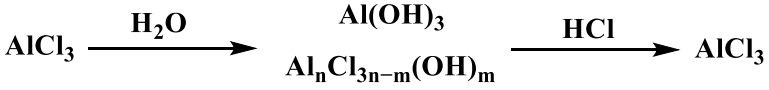
Previous work has established that chloromethanes can react with $AlCl_3$ to produce chloromethyl cations, diverting $AlCl_3$ from the PVC dechlorination reaction[35]. Therefore, we considered alternative solvents such as hexanes. To establish the effect of solvent on $AlCl_3$ loading, PVC was reacted with 1-octene in hexanes using 10-50 mol% $AlCl_3$. At low $AlCl_3$ loadings (<28 mol%), the lubricants and solid byproducts featured discernible residual chlorine as indicated by peaks associated with C-Cl in both FTIR and ^{1}H NMR (**Fig. S17**). Complete dechlorination was attained at ≥28 mol% $AlCl_3$ loading, representing a 1.8-times increase in efficiency compared to the reactions in DCM. Therefore, solvents such as alkanes, despite their lower solubilities for PVC, are effective and suitable for PVC dechlorination and alkylation. Attempts to lower $AlCl_3$ loadings in DCM reactions were unsuccessful, even after extending the duration to 48 h.

Page 6:

We further investigated additional factors that could lower the activity of $AlCl_3$. For example, the high oxophilicity of $AlCl_3$ could cause reactions with moisture, reducing the activity of $AlCl_3$[39]. Indeed, adding 2-10 wt.% water to $AlCl_3$ in the upcycling of PVC with 1-decene in hexanes resulted in decreased lubricant yield, leaving behind an increasing amount of residual solid, likely partially dehydrochlorinated PVC (**Fig. S31**). This reduced reactivity can be attributed to the formation of aluminum chlorohydrates, whose Lewis acidity was much weaker than that of $AlCl_3$. To minimize the effect of water in a large-scale process, $AlCl_3$ could be heated before feeding it into the main reactor. To ensure catalyst recyclability, the HCl produced during the reaction (**Fig. S5**) can also be used to convert chlorohydrates back to $AlCl_3$, as indicated in **Scheme S5** and the process flow diagram (PFD) (**Fig. S36**)."



Scheme S5. **Summarized dechlorination and alkylation reaction using model chloroalkane substrate**. In principle, $AlCl_3$ can turn over after dechlorination if free protons are present in the reaction solution.



Scheme R1. Formation of aluminum chlorohydrate and chlorination to aluminum trichloride under HCl flow generated from PVC upcycling.

Comment #5: The mechanism proposed by the authors assumes relatively selective C–Cl activation in PVC followed by controlled alkylation with α-olefins, with PVC acting as a structural "template". However, the authors did not provide enough experimental and computational evidence to support their claim. In particular, a key issue concerns the quantum mechanical molecular dynamics (QMMD) simulations: the calculated C–Cl bond cleavage energy (≈96 kcal/mol) assisted by AlCl3 is too high and completely inconsistent with the experimentally observed reactivity at 70 °C, thus questioning the soundness of the computational methodology. Additionally, the reported free-energy differences of the order of ~0.5 eV per site between the "comb-like" and "branch-like" structures are likely within the intrinsic uncertainty of such calculations and cannot be used to draw strong structural conclusions.

Author response: We thank the reviewer for this thoughtful and detailed assessment of our proposed mechanism and its computational support. Regarding C–Cl activation and the observed reactivity at 70 °C, we agree that interpreting the calculated 96 kcal/mol as a direct kinetic barrier for bond cleavage would be inconsistent with the measured rates at the reaction condition. In our original submission, this value corresponded to a high-energy, gas-phase–like dissociation limit at 0 K used as a reference benchmark, not the operative transition state along the catalytic pathway. Our objective was not to determine the absolute kinetic barrier under reaction conditions; rather, we used these calculations to compare thermodynamic barriers. The results showed that activating a single chlorinated site versus two sites on the PVC chain entails comparable thermodynamic barriers (**Fig. S19**). We have revised the text to clarify this interpretation and to frame these calculations as qualitative and supportive, rather than definitive.

We have modified the caption to **Fig. S19** as follows:

"Figure. S19. Comparison of the thermodynamic energy barrier of a single Cl-site (left) and double Cl-sites (right) on PVC. $AlCl_3$ forms $AlCl_4^-$ after binding to Cl on PVC, and $AlCl_4^-$ is cleaved, forming an active carbon site on PVC in a gas phase reaction. The energy comparison plot shows the DFT calculated bond-breaking energy of ~96 kcal/mol in both simulated cases."

We also agree that free-energy differences on the order of ~0.5 eV per site between the "comb-like" and "branch-like" structures are approaching the intrinsic uncertainty of DFT-based free-energy estimates, particularly in heterogeneous disordered systems. Our intention was not to claim that such values alone are sufficient to unambiguously resolve the detailed topology of the grafted structures, but rather to show that the "comb-like" motifs are energetically accessible and consistent with the experimental trends. In the revised manuscript we have, therefore, toned down the strength of our structural claims based solely on these free-energy differences. Instead, we have emphasized that our structural conclusions emerge from the combined weight of computation, spectroscopic signatures, and macroscopic property changes, rather than from a single numerical free-energy contrast. We have modified the wording throughout (Results and Discussion sections) to reflect this more cautious interpretation and to clearly label these calculations as supportive and qualitative, rather than definitive.

The main text was updated accordingly:

“Although our calculations indicate that the “comb-like” motif is lower in free energy than the “branch-like” motif by approximately 0.66 eV per formula unit, we treat this difference as supportive rather than definitive. Free-energy contrasts of this magnitude are approaching the intrinsic uncertainty of DFT-based estimates in heterogeneous partially disordered systems. Nevertheless, the result demonstrates that “comb-like” configurations are energetically accessible under the reaction conditions and are consistent with the experimentally observed trends. Along with spectroscopic signatures and macroscopic property changes, the computational results suggest that the optimized $AlCl_3$ loading promotes more parallel site activation and alkylation pathways, favoring the formation of structures that resemble the “comb-like” topology. Subsequent hydrogenation of these vPAO structures yields lubricants with the enhanced tribological performance observed experimentally.”

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Referee #1:

General Comments: I am very pleased to see that the author has effectively addressed the questions raised by myself and the other reviewers, and has revised the manuscript accordingly. The revised paper is logically perfect, and I believe this work offers a practical pathway for the recycling and high-value utilization of PVC.

Author response: We sincerely thank the reviewer for the thorough and constructive comments and suggestions throughout the revision of this work. These invaluable comments and suggestions have substantially helped us improve the quality of this work. We are delighted that the revised manuscript is logically sound and that the reaction pathway is attractive for future PVC valorization.

Referee #2:

General Comments: I thank the authors for their detailed response and for the substantial additional work included in the revised manuscript. I have also considered the comments of Reviewer 1 and the authors' responses to them. I agree that the revised manuscript is significantly improved. The additional analyses of oxidative stability, gas-phase products, residual chlorine, waste-PVC purification, additive/metal content, tribological performance, and techno-economic assumptions strengthen the practical and application-oriented aspects of the work.

I also appreciate that the authors have moderated several claims in the revised manuscript. In particular, the discussion of residual chlorine is now more cautious, the structural interpretation of the "comb-like" motif is presented less definitively, and the computational results are described as supportive rather than conclusive. These changes improve the balance and credibility of the manuscript.

My remaining concern relates to the nature of the evidence supporting the central claim. I agree that the revised manuscript now provides a very large and internally consistent body of indirect evidence that PVC affects the reaction pathway and the properties of the final oil fraction. This evidence includes the comparison between cPAO and vPAO, differences in molar mass, viscosity, Tg, branching indices, tribological performance, and the additional NMR and control experiments. Taken together, these data make the authors' interpretation plausible.

However, these data remain indirect. They do not provide direct or quantitative proof of the extent to which PVC-derived carbon is incorporated into the final lubricant carbon skeleton. This distinction is important because the central framing of the manuscript is that PVC is upcycled into vinyl-derived PAO lubricants through a PVC-templated dichlorination/alkylation process.

The revised manuscript has addressed several of my original concerns, and I recognize that the remaining issue is primarily one of interpretation and framing. I therefore leave the final editorial judgement to the Editor, particularly in light of the strong conceptual and application-oriented aspects of the work and the positive assessment by Reviewer 1. If the manuscript is accepted, I recommend that the authors explicitly acknowledge that the evidence for PVC-derived carbon incorporation is extensive and coherent, but indirect rather than direct or quantitative.

Author response: We sincerely thank the reviewer for the insightful reassessment of the revised manuscript. We appreciate the reviewer for recognizing the substantial additional work and the moderation of initial claims. We agree with the reviewer about the distinction between direct and indirect evidence of PVC-derived carbon incorporation in vPAO products, and this nuance warrants explicit acknowledgment in the manuscript. Accordingly, we have added the following statement to the discussion part of the manuscript.

Page 10: "We note that this body of characterization and analysis, as well as computational results, albeit extensive and internally consistent, remains indirect evidence. Future studies employing isotopic labeling may further elucidate the composition of PVC-derived lubricants."

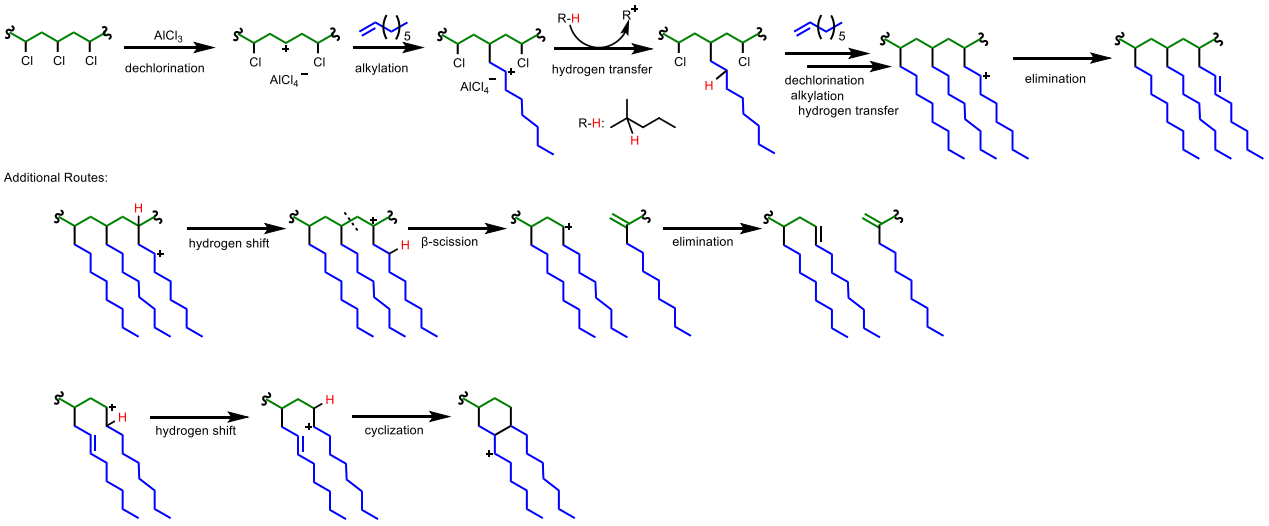
Referee #3:

General Comments: Liu and coworkers report a novel method for upcycling PVC to lubricants using a lewis acid mediated alkylation/scission of the PVC backbone. They demonstrate that using AlCl3 and an alpha olefin they can effectively dechlorinate and alkylate the backbone to give a branched structure. The authors showed that these materials were excellent lubricants. Overall, this is a well-written manuscript and a high-impact study that would be of interest to the readership of Nature. I also went through the other reviewer comments and the authors responses. I believe they have adequately addressed the concerns raised by the reviewers. My main concern with the current manuscript is the proposed mechanism in the supporting information. The mechanisms drawn in Scheme S3 and S4 show unreasonably high energy intermediates and should be revised or removed. Please take the following comments about these schemes into consideration:

Author response: We thank the reviewer for the positive assessment and kind suggestions, which greatly help us further improve the quality of our work. We have modified Schemes S3 and S4 according to the following comments.

Comment #1: After alkylation, the authors show an oligomer with 3 adjacent carbocations. This structure would be unreasonably high in energy. While I understand the authors were trying to streamline their mechanism and show multiple alkylations, the formation of this intermediate is unreasonable. They should show single alkylations and termination of the carbocation at a time.

Author response: We thank the reviewer for understanding our intent behind our scheme. We agree that the chemical structure with three adjacent carbocations is a potentially unreasonable intermediate, and we have revised Scheme S3. In the revised scheme, we have replaced this intermediate step with a much more reasonable chemical structure as follows.



Scheme S3. Proposed mechanism of PVC upcycling in hexanes. Carbocations shift or are quenched via either intramolecular hydrogen shift or intermolecular hydrogen transfer with solvent. Note: The H-transfer and elimination reactions do not necessarily proceed in sequence, and the scheme is to illustrate the possible reaction pathways such as alkylation, β-scission, and cyclization.

Comment #2: The authors show hydride transfer reactions to give the saturated product. Are they saying the hydride transfer occurs from solvent? Intramolecular hydride transfers would be more favorable. For example, a 1,6-hydride shift would give a tertiary carbocation. (or chain walking with 1,2-hdyride shifts)

Author response: The authors thank the reviewer for this insightful comment. Herein, we meant to suggest that hydride transfer can come from both the solvent of hexanes and intramolecular hydride shifts. We agree with the reviewer that intramolecular hydrogen transfers leading to tertiary carbocations are likely because of the thermodynamic stability. Hydride transfer, however, can also occur from the solvent, generating tertiary carbocations (Scheme S3), which has been reported in the literature[1, 2]. As we revise this manuscript, we are conducting an in-depth study of the solvent role, especially the isomers, in the upcycling of PVC. We found that hydrogen transfer from the hexane isomers play a significant role in the reaction. We plan to report our more detailed findings in a forthcoming manuscript.

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Comment #3: The beta-scission reaction shown is not the most reasonable pathway. The formation of a carbocation on a carbon attached to a chloride would be likely higher in energy than the secondary carbocation. From the authors results, it appears that more beta-scission occurs when the alpha-olefin is present, which suggests this reagent helps promote breaking of the PVC backbone. On this basis, please consider scission beta to a site that has already been alkylated. This would lead to a much more reasonable secondary carbocation. Additionally, if the first alkylation underwent elimination to the olefin the beta-scission reaction would lead to a much more stable allylic carbocation.

Author response: The reviewer is insightful in suggesting the β-scission pathway in Scheme S3. We agree that β-scission is more plausible once the PVC is alkylated by α-olefin, as our results suggest that the presence of α-olefin leads to a lower molecular weight. However, we could not rule out the possibility of β-scission before alkylation. In the interest of simplification, we have modified Scheme S3 and highlighted the β-scission after alkylation, following the reviewer's suggestion.

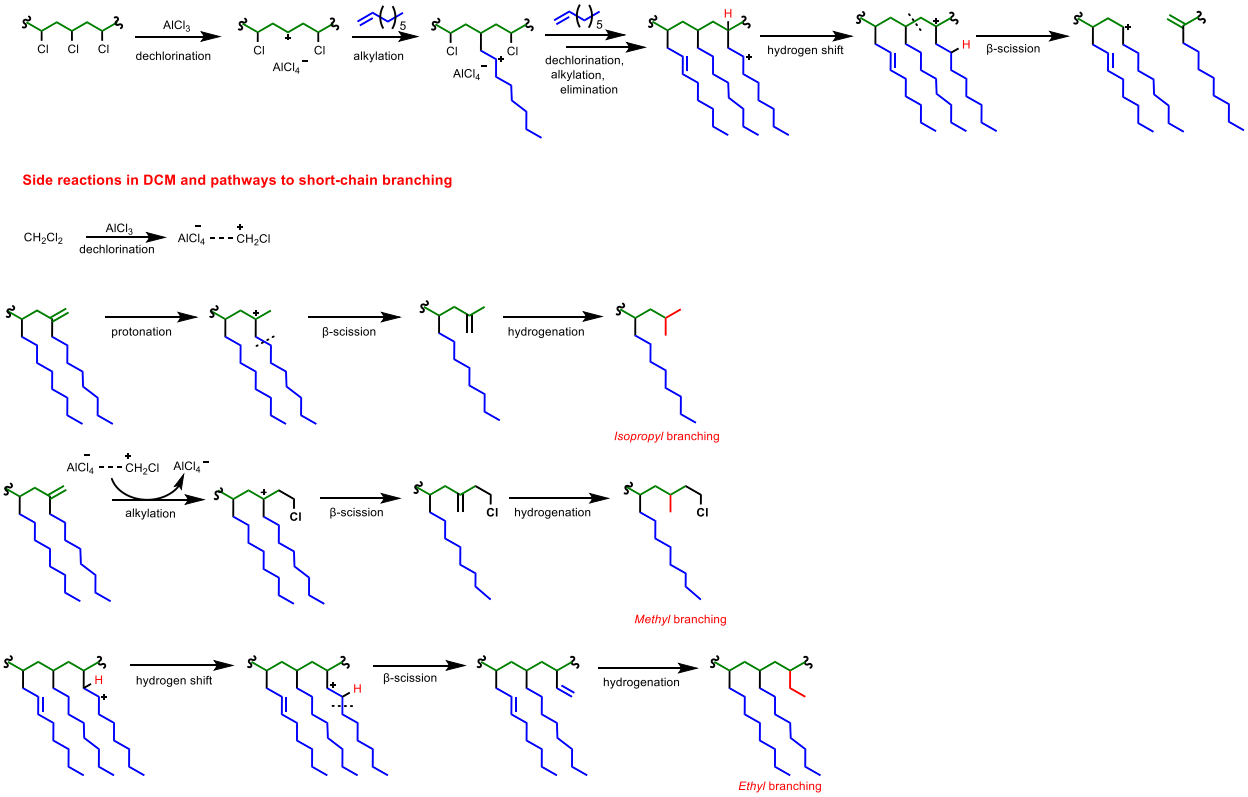
Comment #4: There also could be cyclization reactions occurring. This should also be considered.

Author response: We thank the reviewer for pointing out the possibility of cyclization in the PVC alkylation process. We agree that this is a possibility, and we have modified Scheme S3 to include this pathway.

Comment #5: Scheme S4 has many of the same issues and should be revised. Additionally, in Scheme S4 the authors show a beta-scission to give a primary carbocation. This would be unreasonably high in energy (some scientists would argue that primary carbocations do not exist).

These beta-scission events should be removed. Significantly more thought should be put into the mechanistic figures in the SI if they are kept.

Author response: We sincerely thank the reviewer for the comment on Scheme S4. We acknowledge that a primary carbocation is energetically unfavorable. We intended to demonstrate that the solvent DCM can undergo dechlorination and interact with $AlCl_3$ to form intermediates of cation-anion pairs. These intermediates could participate in the reaction, introducing more branching in the products than those in hexanes. Accordingly, we have modified Scheme S4 as follows.



Scheme S4. Upcycling of PVC in DCM. The solvent can participate in the dechlorination and alkylation pathways, leading to residual chlorine in vPAO and increased branching.

Comment #6: As an additional sidenote: when the authors were responding to one of the reviewers, they discussed "thermodynamic energy barriers." I do not understand what they mean by this, as energy barriers are related to the kinetics of the reaction. Do they mean the relative thermodynamic energies of the intermediates? This should be clarified/corrected in the manuscript.

Author response: We agree that the phrase "thermodynamic energy barrier" used in our original response was imprecise and could lead to confusion, since energy barriers are kinetic quantities associated with transition states and reaction rates, whereas thermodynamic quantities refer to the relative stabilities or free energies of reactants, intermediates, and products. What we intended to describe was the relative free-energy cost associated with different activation states or

intermediates, rather than a true kinetic barrier. We have corrected this terminology throughout the revised manuscript and Supporting Information to avoid ambiguity.

Accordingly, we would revise our response to Referee 2 comment 5 in the first round of revision, as follows:

We thank the reviewer for this thoughtful and detailed assessment of our proposed mechanism and its computational support. Regarding C–Cl activation and the observed reactivity at 70 °C, we agree that interpreting the calculated value of ~96 kcal/mol as a direct kinetic barrier for C–Cl cleavage would be inconsistent with the experimentally observed reaction under these conditions. In our original submission, this value refers to a high-energy dissociation limit in an idealized model, rather than the actual transition-state barrier along the catalytic reaction pathway. Accordingly, this value should not be taken as the operative activation energy under the experimental conditions.

Our objective was not to determine the absolute kinetic barrier under reaction conditions; rather, we used these calculations to provide a qualitative comparison of the relative energetics of different possible activation scenarios. In particular, the calculations suggest that activation involving a single chlorinated site and that involving two chlorinated sites on the PVC chain have similar relative free-energy requirements (Fig. S19), which supports the plausibility of multiple accessible activation motifs. We agree, however, that these results should be interpreted cautiously and not as definitive proof of the detailed reaction pathway.

Similarly, with respect to the calculated free-energy differences between the "comb-like" and "branch-like" structures, we acknowledge that differences on the order of ~0.5 eV per site may fall within the intrinsic uncertainty of this level of calculation. We therefore do not intend these results to serve as conclusive structural evidence, but only as qualitative computational support consistent with the experimentally inferred trends. To reflect this limitation, we have revised the text to explicitly present the computational analysis as supportive and suggestive, rather than definitive.

We have modified the caption to Fig. S19 as follows:

"Figure. S19. Comparison of the relative energetics of a single Cl-site (left) and double Cl-sites (right) on PVC. $AlCl_3$ forms $AlCl_4^-$ after binding to Cl on PVC, and $AlCl_4^-$ is cleaved, forming an active carbon site on PVC in a gas phase reaction. The energy comparison plot shows the DFT calculated bond-breaking energy of ~96 kcal/mol in both simulated cases."