

Upcycling of polyvinyl chloride into polyalphaolefin lubricants

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Polyvinyl chloride (PVC) is a thermoplastic used ubiquitously in households and industry owing to its light weight, mechanical strength, durability, low cost and ultraviolet and fire resistance^{1,2}. With a production volume of about 60 million tonnes annually², post-consumer and post-industrial PVC waste pose marked environmental challenges, such as leaching chlorohydrocarbons and additives, which contaminate groundwater and soil^{1–4}. To address the formidable challenge of recycling PVC and achieving carbon circularity, valorization into high-value products is essential to mitigate the associated costs and offer high financial incentives for reusing plastic waste^{5–14}. Here we report a method for upcycling PVC into high-value lubricants with controllable viscosities. Using AlCl_3 at a mild temperature of 70 °C, PVC undergoes dechlorination, alkylation and chain scission, producing vinyl-derived polyalphaolefins (vPAO). PVC serves as an effective template for the alkylation of α -olefins of various chain lengths, producing vPAO with limited short branches in the backbone without the need for metallocene catalysts essential to current PAO technology. The PVC-derived lubricants exhibit tunable molar masses, kinematic viscosities at 100 °C ($\text{KV}_{100} \approx 14.9\text{--}26.3$ centistokes), a low coefficient of friction ($\text{COF} \approx 0.08\text{--}0.15$) and a high viscosity index (VI up to 130). This work highlights an economical approach to using PVC as a low-cost feedstock to synthesize high-value lubricants with superior tribological properties, meeting the demand for sustainability in both the plastic and lubricant industries.

Traditional mechanical recycling of polyvinyl chloride (PVC) is complicated by the presence of additives, such as plasticizers, stabilizers and flame retardants, which must be modulated before and during remanufacturing¹⁵. Moreover, the high chlorine content, which comprises about 57 wt% of PVC, releases corrosive acid and causes extensive damage to machinery during recycling^{5,6}. Apart from mechanical recycling, PVC can be chemically converted into fuels and carbonaceous materials¹⁶ through energy-intensive pyrolysis and aerobic photocatalytic processes¹⁷. Recently, pioneered by McNeil, strategies have been developed to use the chlorine content, redirecting it to produce valuable organic chlorides^{7,18}. The carbon content, however, is the focal point of PVC recycling. In this context, efforts have been made to convert PVC into polyethylene (PE)-like polymers and copolymers^{8,19}. The requirement of expensive catalysts and hydrogen sources, however, poses a challenge to economic viability²⁰. Alternatively, PVC is co-upcycled with polymers such as polyester⁶, polystyrene¹⁰, polyethylene and polypropylene^{9,21} to synergize chlorine removal and polymer backbone chain scission, producing organic chlorides, monomers and liquid hydrocarbons^{7,9}. Most of these products have values similar to the original polymer and

small market volumes for niche applications. Ideally, PVC and plastic upcycling, in general, should aim for high-volume, high-value chemicals and materials to ensure sufficient financial incentives for rapid industrial deployment^{14,22}. Preferably, these upcycling processes should avoid the use of expensive catalysts^{7,8}, ionic liquids^{6,23–25} and chlorine scavengers (for example, metal oxides and bases)^{26,27}.

With a strong market demand for sustainability, lubricants and greases²⁸ have enjoyed a steady growth in volume (about 42 million metric tonnes annually) comparable to that of PVC. More importantly, high-grade lubricants such as polyalphaolefins (PAO) have a typical market value of US\$3,000 per tonne and sometimes up to US\$6,000 per tonne (ref. 29) (Fig. 1a), representing an exceptionally lucrative product for PVC upcycling. Here, we report the upcycling of PVC into high-value PAO using a dehalogenation–alkylation approach. Our approach uses PVC as a template for grafting α -olefins at the halogen sites to synthesize vinyl-derived PAO (vPAO), which differs fundamentally from the synthesis of existing PAO (Fig. 1b). Conventional PAO (cPAO) is synthesized from monomers of α -olefins (for example, 1-octene and 1-decene) using Lewis-acid catalysts^{30,31}. Owing to chain walking issues, cPAO typically

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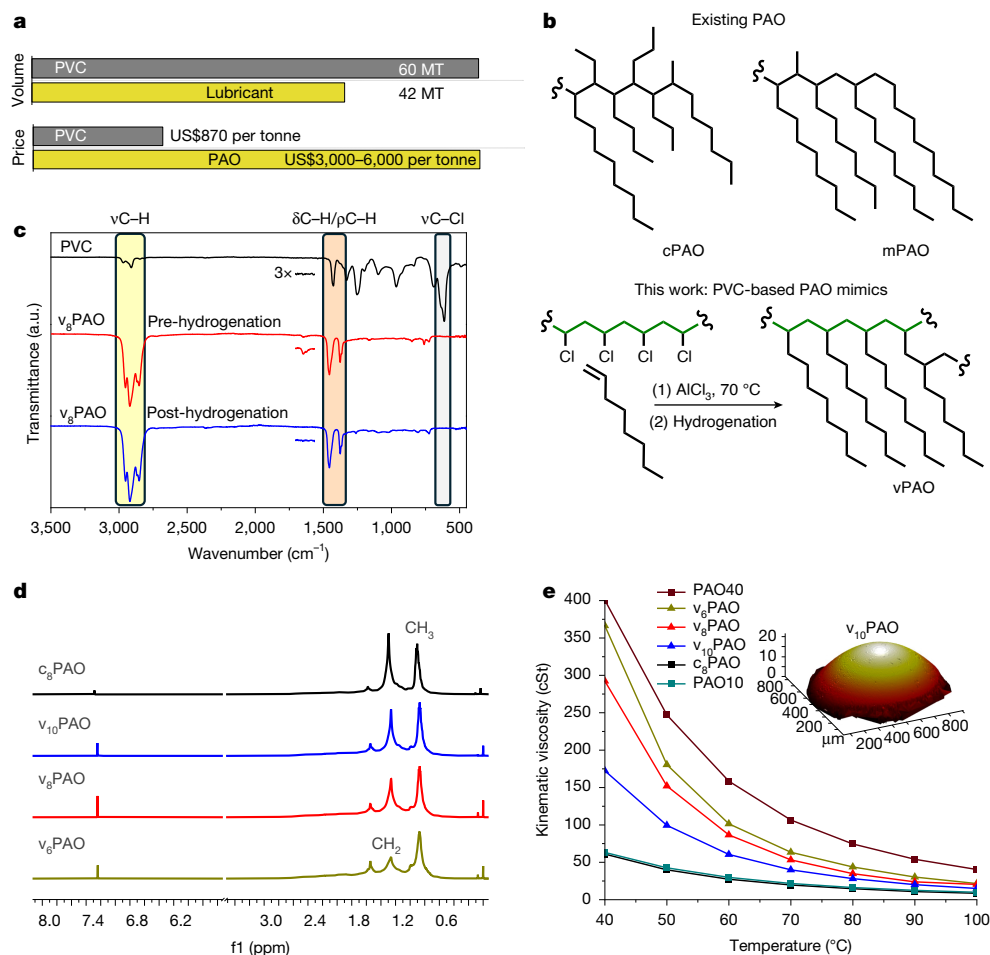


Fig. 1 | Proof of concept and feasibility of upcycling PVC to lubricants.

a, Comparison of PVC and PAO market volumes and prices. MT, million tonnes. **b**, Molecular structures of existing PAO, including cPAO and mPAO, as well as the synthesis of vPAO using PVC as a template. **c**, FTIR of PVC and $v_8\text{PAO}$

before and after hydrogenation. **d**, ^1H NMR of vPAO and a control lubricant synthesized from 1-octene without using the PVC template. **e**, Kinematic viscosities of vPAO, the control lubricant and commercial PAO10 and PAO40. Inset, wear scar test of $v_{10}\text{PAO}$ at 25°C showing minimal to no wear.

has short branches. Alternatively, metallocene PAO (mPAO) is prepared from α -olefins using metallocene catalysts. Owing to the high cost of metallocene-catalysed reactions, mPAO is limited to niche applications in which high-temperature stability is needed. Although cPAO and mPAO expand the viscosity range of mineral oil lubricants, the conventional synthesis process inherently limits the accessible range of molar mass and viscosity. By contrast, the synthesis of vPAO using PVC as a template here, in principle, can provide tunable molar mass, depending on levels of chain scission along the PVC backbone, and thus enable a broad range of accessible molar masses and viscosities. Moreover, the synthesis of vPAO is versatile and can graft various chain-length α -olefins, which could be potentially produced from plastic waste^{11–13}. Structurally, vPAO intrinsically minimizes short-chain branches along the backbone, thus mimicking mPAO. Along the side chains, however, branches could occur on additional alkylation at the C2 position of the α -olefin, similar to cPAO. Thus, vPAO, in principle, has balanced properties of cPAO and mPAO (Fig. 1b).

To demonstrate the feasibility of vPAO synthesis, we used low-cost AlCl_3 to dechlorinate PVC under a mild reaction temperature of 70°C . We postulate that dechlorination generates backbone carbocations²¹, which induce chain scission and alkylation with α -olefins to produce vPAO with controlled viscosities. In a typical reaction, PVC powder and AlCl_3 (molar ratio, 1:0.5) were charged into a Schlenk tube and placed in an ice-water bath. While purging with nitrogen and stirring, a solvent (for example, dichloromethane (DCM)) was slowly added, followed by

the addition of 1.2 equivalents of α -olefin with respect to Cl atoms. The tube was then pressurized with nitrogen to about 3 bar and placed in an oil bath at 70°C for around 3 h. After the reaction was complete, the solvent and AlCl_3 were removed during work-up, yielding $v_x\text{PAO}$ lubricants featuring no detectable C–Cl bonds in Fourier transform infrared spectroscopy (FTIR) and ^1H NMR (Fig. 1c,d). In the nomenclature, v denotes vinyl or PVC, and the subscript x represents the α -olefin used for the synthesis (for example, $x = 6, 8$ and 10 for 1-hexene, 1-octene and 1-decene, respectively). The $v_x\text{PAO}$ notation is distinct from the industry convention of PAO_x , where x corresponds to the kinematic viscosity at 100°C in centistokes (cSt). A minor peak at $1,645\text{ cm}^{-1}$ is attributed to the small amount of alkene moieties formed by PVC β -scissions, as well as from carbocation and β -hydrogen elimination pathways^{6,23} similar to those in cPAO and mPAO syntheses. To eliminate the alkene groups and ensure lubricant stability, the lubricants were hydrogenated at 1 bar over Pd/C (8 wt% loading), producing saturated vPAO with good oxidative stability (Supplementary Fig. 1).

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 ^1H NMR spectra (Fig. 1d) and the branching ratio (BR) in ^{13}C NMR spectra (Supplementary Fig. 2), decreased with an increasing α -olefin chain length (Supplementary Table 1), 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 affected the

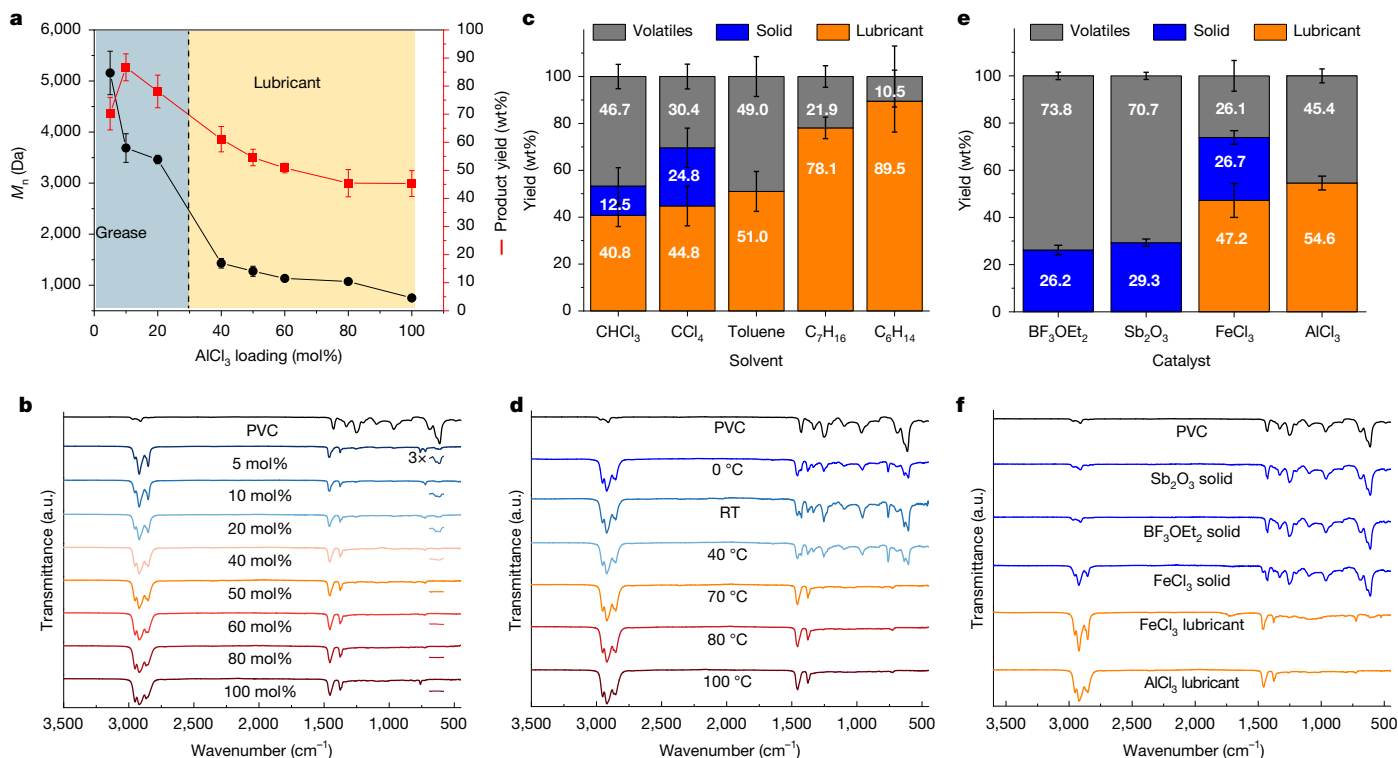


Fig. 2 | Reaction condition optimization. **a, b**, Molar mass and yield (**a**) and FTIR spectra (**b**) of v_8 PAO at various AlCl₃ loadings (70 °C, DCM). **c**, Upcycling reaction products in various solvents. **d**, FTIR spectra of v_8 PAO at various reaction temperatures (50 mol% AlCl₃, DCM). **e, f**, Upcycling products (**e**) and FTIR spectra (**f**) of the selected products in reactions with various Lewis acids

viscosity index (VI)^{32,33}. v_6 PAO with a BR of 65.2% exhibited a VI of 64, whereas v_{10} PAO with a BR of 38.5% showed a relatively high VI of 84. The highly branched v_6 PAO 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 (Supplementary Fig. 3), consistent with established trends between branching and viscosity^{34,35}. Similarly, v_6 PAO exhibited a high kinematic viscosity at 40 °C (KV₄₀) of 366.4 cSt compared with v_{10} PAO (KV₄₀ = 173.2 cSt). The KV₁₀₀ values of v_6 PAO, v_8 PAO and v_{10} PAO were 21.5 cSt, 20.4 cSt and 14.9 cSt, respectively. v_{10} PAO showed an almost unnoticeable wear scar in the wear test at 25 °C (Fig. 1e).

Control reactions confirmed the role of each component in the synthesis of v_x PAO. Without α -olefins, the reaction did not produce any lubricants (Supplementary Fig. 4). The product included a polyene from PVC dehydrochlorination, which gradually oxidized over time, consistent with previous studies³⁶. Moreover, 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 (Supplementary Figs. 5–7). Without PVC, the α -olefins underwent conventional oligomerization over AlCl₃, yielding branched cPAO, as confirmed by ¹H NMR and FTIR (Fig. 1d and Supplementary Figs. 8–10). Notably, a relatively weak CH₂ peak at 1.3 ppm implied a great extent of branching in the control sample c₈PAO compared with typical cPAO synthesized using about 10 times less AlCl₃ loading³⁷ (Supplementary Fig. 9c).

To determine the ideal reaction conditions for PVC upcycling into lubricants, we monitored the effects of AlCl₃ loading on the synthesis of v_x PAO. At 5–20 mol% of AlCl₃ loading, the reaction yielded a viscous Cl-containing grease with a number average molar mass (M_n) in the range of 3,500–5,200 g mol⁻¹, implying that the AlCl₃ loading was too

(1-octene, 50 mol% Lewis acids, DCM). The yield represents the ratio of the final product mass to the sum of PVC (including the mass of Cl) and α -olefin masses. All error bars are standard deviations from the means based on $n = 3$ independent experiments.

low to achieve complete dechlorination (Fig. 2a,b and Supplementary Fig. 11a) and ensure extensive chain scissions. An increased AlCl₃ loading of 40–50 mol% induced more PVC chain scission, resulting in a decrease in product molar mass and viscosity (Supplementary Table 2 and Supplementary Fig. 11b). AlCl₃ loadings of 50 mol% generated lubricants of low viscosities without any detectable C–Cl bands in the FTIR spectra. Ion chromatography studies showed trace levels of chlorine (<100 ppm), representing >99.98% dechlorination efficiency (Supplementary Fig. 12 and Supplementary Table 3). AlCl₃ loadings of above 50 mol% led to (1) extensive chain scission to produce low molar mass volatiles (Supplementary Table 2), thus decreasing the lubricant yield, and (2) promoted undesired side reactions (for example, isomerization and excessive branching). Therefore, we selected 50 mol% AlCl₃ loading for further investigation in this work.

We screened the reaction temperature and time to monitor the effects on dechlorination and v PAO structure. In the synthesis of v_8 PAO at 50 mol% of AlCl₃ loading, reactions at temperatures of 0–40 °C did not proceed to completion, and the resulting v PAO still retained Cl (Fig. 2d). Reactions at higher temperatures of 70–100 °C resulted in complete dechlorination, and the v PAOs synthesized at ≥ 80 °C showed high extent of branching (Supplementary Fig. 13). Regarding reaction time, v PAO collected after 1 h featured an M_n of 1,410 g mol⁻¹ and a noticeable C–Cl peak at 617 cm⁻¹ in the FTIR spectrum (Supplementary Fig. 14b). Extending the reaction time to ≥ 3 h resulted in complete PVC dechlorination and produced v PAO with reduced molar masses. The molar mass slightly increased after 3 h and then dropped at prolonged reaction times, probably because of a combination of oligomerization and fragmentation processes (Supplementary Fig. 14c).

Inspired by the success with AlCl₃, we explored the use of other Lewis acids to synthesize v PAO. FeCl₃ yielded a liquid chlorinated lubricant (47.2 wt%) and a solid product of partially alkylated PVC (26.7 wt%)

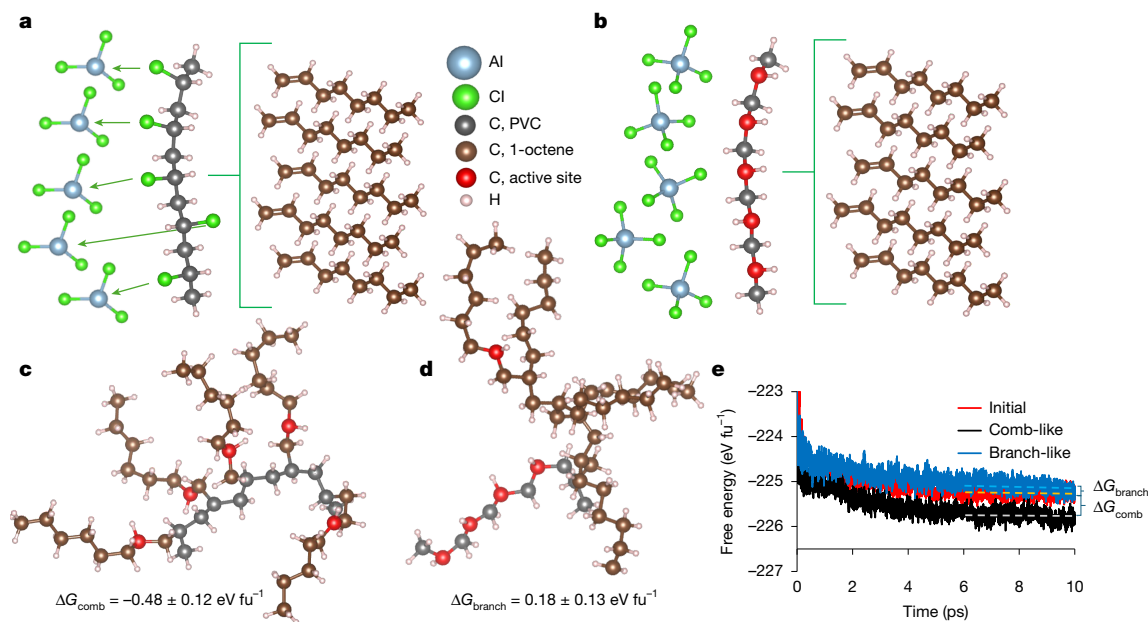


Fig. 3 | Predicted reaction mechanisms and free energies from molecular dynamics simulations. **a**, The initial molecular dynamics simulation system consists of an atactic PVC chain with five monomers (grey and brown, C; white, H; and light green, Cl), five AlCl_3 (light blue, Al; and light green, Cl), five 1-octene and 10 DCM (not shown here for clarity). **b**, (PVC chain)⁵⁺ with five active sites (shown in red) and five AlCl_4^- . **c**, Five 1-octene attached to each active site in parallel, forming a comb-like structure. Active sites are shown in red for easy

identification, which can facilitate further reactions. **d**, Five 1-octene oligomerized to form a branch-like structure attached to a single active site on PVC. For clarity, AlCl_4^- and DCM are omitted in **c** and **d**. Formation of free energies (eV fu⁻¹) are calculated per active site of carbon on the PVC chain or per formula unit. **e**, Comparison of the free energy for the initial state (**a**), comb-like structure (**c**) and branch-like structure (**d**) for a 10 ps quantum mechanical molecular dynamics simulation.

(Fig. 2e,f and Supplementary Fig. 15). Note that this yield is based on the total mass of PVC, including chlorine content. BF_3OEt_2 and Sb_2O_3 performed poorly and yielded no liquid lubricants but only slightly degraded PVC solids, probably because of the reduced electron deficiency at the boron centre and the weak Lewis acidity of Sb_2O_3 , respectively³⁸. The slight drop in solid product molar mass was attributed to minor decomposition of PVC under our reaction conditions (Supplementary Fig. 15d). Even at 50 mol% loading, there was no evidence of alkylation in the solid products from reactions using BF_3OEt_2 and Sb_2O_3 (Fig. 2f). The BF_3OEt_2 reaction was carried out at 40 °C to keep the reagent below its flash point of 48 °C.

The choice of solvent affected the vPAO yield and structures. The scope of tested solvents included chloroform, carbon tetrachloride, toluene, hexanes and heptane. Chlorinated CHCl_3 and CCl_4 solvents furnished dechlorinated lubricants with a yield of about 40.8 wt% and about 44.8 wt%, respectively (Fig. 2c), along with solid residual PVC (Supplementary Fig. 16d). The incomplete PVC conversion can be rationalized by the possible interactions between the chloromethanes and AlCl_3 (scheme S2). Given that the reactivity of chloromethanes with Lewis acids increases in the order of $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$ (ref. 39), the chloromethanes potentially diverted the Lewis acid from PVC dechlorination⁴⁰. Thus, PVC could not reach sufficient chain cleavage and complete dechlorination in highly substituted chloromethanes, resulting in an increasing amount of PVC residues (Fig. 2c, solid phase). The reactions in toluene yielded high-quality lubricants at a moderate yield of about 51.0 wt%. Aromatic moieties were observed in the product, probably because of Friedel–Crafts alkylation³⁷ (Supplementary Fig. 16b), suggesting the potential of synthesizing aromatic lubricants from PVC⁴¹. By contrast, non-aromatic hexanes generated the highest lubricant yield out of all tested solvents (about 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. The lack of C–Cl bonds in hexanes allowed for further reduction of the AlCl_3 loading to

28 mol%, marking an approximately 1.8 times increase in the efficiency (turnover number) relative to the reactions in DCM (Supplementary Fig. 17). vPAO produced in hexanes exhibited the least branching and isomerization, as indicated by a high CH_2/CH_3 integral ratio in ¹H NMR spectrum (Supplementary Fig. 16b and Supplementary Table 4).

We used molecular dynamics simulations to unveil the reaction mechanism and energy landscape. In the simulation, the initial configuration (Fig. 3a) comprised a pentamer PVC chain, five AlCl_3 , five 1-octene and 10 DCM. For clarity, the solvent DCM molecules are omitted in Fig. 3a but provided in Supplementary Fig. 18. During the simulation, AlCl_3 bonded to the Cl of C–Cl bonds in PVC, forming AlCl_4^- and activated C-sites on the polymer chain. Based on quantum mechanical calculations, the energy required for AlCl_3 to cleave the C–Cl bond in PVC was 95.9 ± 1.4 kcal mol⁻¹ (Supplementary Fig. 19). Owing to the concentration of AlCl_3 used here, we assumed that most of the C–Cl bonds were activated in parallel (Fig. 3b). The active sites, shown as red atoms, were surrounded by AlCl_4^- and 1-octene chains, and the alkylation reaction proceeded at the activated C-sites. We assessed two extreme scenarios: (1) the five 1-octene chains were attached to the PVC backbone in parallel to form a comb-like structure (Fig. 3c) and (2) one 1-octene chain was attached to the PVC active site; then the second carbon of the first 1-octene chain was activated to bind to another 1-octene chain, and the process repeated to form a branch-like structure (Fig. 3d). Quantum mechanical molecular dynamics simulation evaluated the free energies of these two extreme cases, which were compared against that of the initial state within a 10-ps time period (Fig. 3e). The free energies of comb-like and branch-like structures differed from that of the initial state by $\Delta G_{\text{comb}} = -0.48 \pm 0.12$ eV fu⁻¹ and $\Delta G_{\text{branch}} = 0.18 \pm 0.13$ eV fu⁻¹, respectively. The comb-like structure was energetically more favourable than the branch-like structure by 0.66 eV fu⁻¹, where fu stands for formula unit or per active site of carbon on the PVC chain.

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

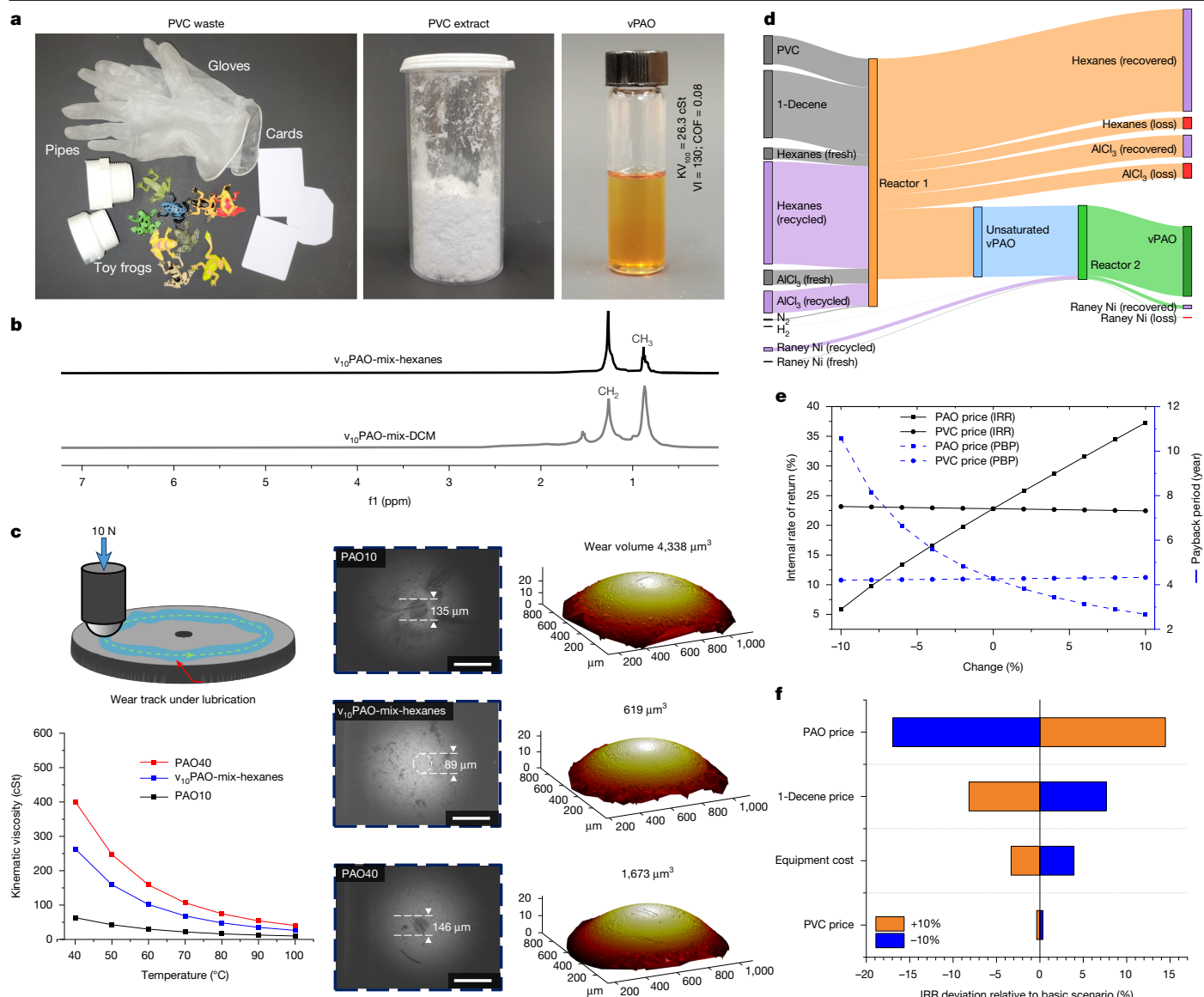


Fig. 4 | Extending upcycling to real-world PVC waste. **a**, Photographs of PVC waste (for example, pipes, gloves, credit cards and toy frogs), extracted PVC powder and the upcycled lubricant. **b**, ^1H NMR of mixed PVC waste-derived $v_{10}\text{PAO}$ showing structural differences in the hexanes and DCM systems. **c**, Tribology and kinematic test. Kinematic viscosities of waste-based $v_{10}\text{PAO}$ at 40–100 $^{\circ}\text{C}$ lie between those of PAO10 and PAO40. Wear test measurements showed that PVC-based $v_{10}\text{PAO}$ exhibited the lowest wear volume, despite its markedly lower

viscosity than PAO40; whereas PAO10, with the lowest viscosity, suffered the greatest wear. **d**, Sankey diagram illustrating the upcycling process of PVC to vPAO. **e**, TEA shows the sensitivity of profitability to the prices of PVC and PAO. **f**, Tornado diagram showing 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. Scale bar, 250 μm (c).

definitive. Free-energy contrasts of this magnitude are approaching the intrinsic uncertainty of the estimates based on density functional theory 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, favouring the formation of structures that resemble the comb-like topology. We note that this body of characterization and analysis, as well as computational results, albeit extensive and internally consistent, remains as indirect evidence. Future studies using isotopic labelling may further explain the composition of PVC-derived lubricants. Subsequent hydrogenation of these vPAO structures yields lubricants with the enhanced tribological performance observed experimentally.

To showcase the feasibility of producing vPAO from real-world mixed PVC waste, we upcycled a quaternary mixture of pipes, cards, gloves and toy frogs into lubricants using α -olefins (Fig. 4a and Supplementary Figs. 20 and 21). To minimize interference from 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 (Supplementary Table 5). 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 (for example, phthalate plasticizers)⁴², effectively reducing oxides and oxygenates that can poison AlCl_3 . Similar to the upcycling of lab-grade PVC, hexanes afforded vPAO with less branching compared with the reaction in DCM, as evidenced by both ^1H NMR CH_2/CH_3 ratios and ^{13}C NMR branching ratios (Fig. 4b, Supplementary Fig. 2 and Supplementary Table 1). 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 spectrum at {0.9, 22.7} ppm, unlike the oils prepared in DCM (Supplementary Fig. 22). v_{10} PAO obtained from the reactions in hexanes exhibited a low glass transition temperature (T_g) and high thermogravimetric residual weight, per ASTM D5800 test, compared with polyolefin waste-derived lubricants by other means, such as hydrogenolysis^{43,44}, indicating a comparatively low pour point and good thermal stability (Supplementary Figs. 23 and 24 and Supplementary Table 6). Furthermore, v_{10} PAO products from hexanes showed a high viscosity index (VI) of 130 with a KV₁₀₀ of 26.3 cSt and a low coefficient of friction (about 0.08 at 25 °C) (Fig. 4c and Supplementary Fig. 25). Thus, v_{10} PAO obtained from the PVC waste mixture represents a strong candidate as a Group IV base oil⁴⁵. The high VI of v_{10} PAO prepared in hexanes was supported by dynamic viscosity tests, which revealed a relatively low temperature dependence of viscosity in contrast to the DCM counterparts (Supplementary Fig. 25c,d). It is notable that the PVC-based v_{10} PAO featured a low wear volume compared with commercial PAO10 and PAO40 at 25 °C (Fig. 4c). Although the exact molecular structure of v_{10} PAO is still being explored, we predict a comb-like architecture with a linear main chain and minimal short-chain branches. This 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^{35,46}. 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, because of the ability of hexanes to limit isomerization by hydrogen transfer (Supplementary Fig. 26). Further analytical and computational studies are underway to validate these mechanisms.

The economic viability was assessed using a technoeconomic analysis (TEA) for a system for an annual production capacity of 50,000 tonnes (Fig. 4d). Based on the system design, the total capital investment was estimated at US\$84 million, including US\$11 million in working capital. The system is projected to generate US\$160 million in annual revenue, with annual variable production costs, excluding depreciation, of US\$136 million. Under this scenario, the net annual profit is US\$19.6 million, corresponding to an internal rate of return (IRR) of 22.8%, a payback period of 4.26 years and an average return on investment of 23.45% (Fig. 4e). Notably, the proposed approach remains highly profitable even without government subsidies or tax incentives typically available to the recycling industry, highlighting its potential attractiveness for industrial investment. Although overall profitability is sensitive to fluctuations in PAO prices, it is relatively resilient to changes in PVC waste and other raw material costs, with the exception of 1-decene (Fig. 4f and Supplementary Figs. 27 and 28). Variations in equipment costs have only a minor effect on returns. According to recent market reports²⁹, the PAO prices have remained stable in recent years and are projected to increase in the North American market, further supporting long-term profitability. 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^{11,12}. The synthesis of sustainable PAO from polyethylene-derived α -olefins is at present underway and will be reported in a forthcoming article.

This work showcases a powerful and innovative strategy for synthesizing PAO lubricants through PVC dechlorination and alkylation. 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. The remarkable viscosity and tribological performance are fine-tunable by the α -olefin chain length, solvent and Lewis-acid loading. The method has been

applied to real-world PVC waste, generating high-VI lubricants with Cl content too low to be detectable spectroscopically. A TEA shows a short payback period and strong financial viability. We expect the dehalogenation-alkylation strategy to be generically applicable to other halogenated polymers, such as poly(vinylidene dichloride) and chlorinated polyethylene.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-026-10867-z>.

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Methods

Materials

Methylene chloride (99.9%; Fisher Scientific), chloroform (99.8%; Fisher Scientific), carbon tetrachloride (99.9%; Sigma-Aldrich), hexanes (98.5%; Fisher Scientific), heptanes (Spectro grade, Acros), toluene (99.8%; Fisher Chemical), 2-chloropropane ($\geq 99.7\%$, Fisher Scientific), 2-chloropropane (D_7) (98%, Cambridge Isotope Laboratories), deuterated chloroform (99.8%, Cambridge Isotope Laboratories), 1-hexene (98%; Thermo Fisher Scientific), 1-octene (99+%; Thermo Fisher Scientific), 1-decene (96%; Thermo Fisher Scientific), sodium sulfate (anhydrous, $\geq 99.0\%$; Fisher Scientific), Celite 545 (Oakwood Chemical), aluminium chloride (99%; Sigma-Aldrich), ferric chloride (anhydrous, 98%; Alfa Aesar), antimony (III) oxide (99%; Sigma-Aldrich), boron trifluoride diethyl etherate ($\geq 46.5\%$ BF_3 basis, Sigma-Aldrich), zinc oxide (99.9%; Fisher Scientific) and polyvinyl chloride (high molecular weight, 70,140 $g\ mol^{-1}$, Sigma-Aldrich) were purchased and used without further purification. Inductively coupled plasma mass spectrometry (ICP-MS) standard solution was purchased from Inorganic Ventures. Polyvinyl chloride pipe was collected from the authors' residence; polyvinyl chloride cards, toy frogs and gloves were purchased from Amazon, used locally and then recycled for this work.

vPAO synthesis

A representative synthesis is as follows: to an oven-dried Schlenk tube, PVC powder ($M_n = 70,140\ g\ mol^{-1}$, 0.5 g) and $AlCl_3$ (50 mol% with respect to chlorine atoms) were loaded. The mixture was chilled at 0 °C in an ice-water bath and purged with a steady stream of nitrogen. On initiating stirring, CH_2Cl_2 (10 ml) was added, followed by the dropwise addition of α -olefin (for example, 1.5 ml of 1-octene). The tube was pressurized with nitrogen gas (approximately 3 bar) and stirred in an oil bath at 70 °C for 3 h. After the reaction, the tube was cooled to room temperature and depressurized to ambient pressure by slowly unscrewing the cap. The products were transferred to a separatory funnel containing $CHCl_3$ (50 ml) and deionized water (100 ml), shaken to extract lubricants and quench residual $AlCl_3$. The organic layer was collected, washed twice with deionized water (100 ml each), dried over Na_2SO_4 and concentrated under vacuum.

The following points should be noted. The solvent should be injected into a stirred mixture of PVC and $AlCl_3$ to prevent the formation of large solid chunks that are too difficult to disperse in the solvent. After adding the solvent, α -olefin should be introduced immediately to minimize undesired PVC side reactions (see Supplementary Fig. 29 and Supplementary Discussion), but slowly to avoid violent bubbling inside the reaction vessel.

To ensure long-term chemical stability, the recovered lubricants were hydrogenated over a Pd/C catalyst, similar to the industrial practice of PAO synthesis. Unsaturated vPAO (for example, 725 mg of vPAO₈) was diluted in CH_2Cl_2 (10 ml) and transferred to an oven-dried two-neck round-bottomed flask equipped with a magnetic stir bar. The flask was vacuumed and backfilled with nitrogen three times before introducing Pd/C (for example, 58 mg or 8 wt%). Additional CH_2Cl_2 (5 ml) was used to rinse Pd/C off the flask wall, and the flask was subjected to three vacuum-backfill cycles. A hydrogen balloon was fitted onto the reaction setup using a syringe needle, and the reaction was stirred overnight at room temperature. After hydrogenation, the mixture was filtered through Celite (5 g) to remove the catalyst. $CHCl_3$ (45 ml) was subsequently passed through the filter funnel to elute all lubricants from the filtration media. The combined filtrate was concentrated under vacuum, and the collected lubricant was dried in a vacuum oven at 90 °C for 16 h to ensure thorough solvent removal.

A similar synthesis protocol was adopted to prepare vPAO using other solvents ($CHCl_3$, CCl_4 , toluene and hexane). The synthesis of PVC waste in hexanes was performed at a 1 g scale using 20 ml of solvent.

All vPAO syntheses were performed at 70 °C except for the BF_3OEt_2 reaction, which was run at 40 °C to keep the boron compound below its flash point. The reaction conducted to determine the effect of concentration on product structure and viscosity was carried out with 5 ml of CH_2Cl_2 (Supplementary Fig. 30). 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 similarly to reactions without water and hydrogenated using 8 wt% Pd/C (Supplementary Fig. 31).

Control reactions

As control experiments to illustrate the importance of PVC in producing vPAO, an oven-dried Schlenk tube with a stir bar and $AlCl_3$ (533 mg) was placed in an ice-water bath at 0 °C and purged with nitrogen. CH_2Cl_2 (10 ml) was injected into the tube, followed by the addition of 1.5 ml of 1-octene (or 1.2 ml of 1-hexene or 3.6 ml of 1-decene). The tube was pressurized with 3 bar nitrogen and stirred in an oil bath at 70 °C for 3 h. The reaction product was worked up as described in the case of vPAO synthesis.

As control experiments to illustrate the effect of α -olefins, an oven-dried Schlenk tube with a magnetic stir bar was charged with PVC (500 mg) and $AlCl_3$ (50 mol% of monomer equivalence). A nitrogen inlet was fed into the tube, and the mixture was stirred at 0 °C. CH_2Cl_2 (10 ml) was injected into the Schlenk tube, and the reaction mixture was pressurized to 3 bar with nitrogen. Then, the Schlenk tube was transferred to a preheated oil bath at 70 °C and stirred for 3 h. After the reaction, the tube was cooled to room temperature, depressurized and filtered over cotton to isolate the solids, which were mostly polyenes and $AlCl_3$. The filtrate was collected in a 30 ml glass vial, washed three times with deionized water (10 ml each) and dried over Na_2SO_4 . The dried filtrate was analysed using gas chromatography–mass spectrometry (GC-MS) to explain the structures of low-molar-mass contents. The solids were washed three times with an acetone–water solution (10 ml each, volumetric mixing ratio 1:1) to remove any volatile organics and quench $AlCl_3$. The residual solid was washed with acetone (10 ml) and dried at 60 °C overnight in a vacuum oven. The experiment was repeated three times, giving an average solid yield of 28.7 wt% based on the weight of PVC.

Size-exclusion chromatography

The molar masses of lubricants were analysed using a multi-detector Shimadzu Ultra-Fast Liquid Chromatograph equipped with two MIXED-B Agilent PLgel 10 μm columns connected in series to a Wyatt Optilab Rex differential refractive index detector and a Wyatt Dawn Heleos 2 light scattering detector. Tetrahydrofuran containing 250 ppm butylated hydroxytoluene eluent was flowed at 1 $ml\ min^{-1}$ and 30 °C. To determine the dn/dc values of all hydrocarbon lubricants prepared in DCM, the refractive index response of five samples with concentrations ranging from 9 $mg\ ml^{-1}$ to 12 $mg\ ml^{-1}$ was recorded by assuming 100% mass elution from the columns, yielding an average dn/dc value of 0.058 $ml\ g^{-1}$. The dn/dc value of vPAO prepared in hexanes, obtained using a similar procedure, was 0.060 $ml\ g^{-1}$. The v₈PAO synthesized at a 40 mol% $AlCl_3$ loading was used to evaluate the dn/dc of Cl-containing lubricants using the same 100% mass recovery method for five separate samples (average $dn/dc = 0.070\ ml\ g^{-1}$). The dn/dc value of PVC in THF (0.110 $ml\ g^{-1}$) was adopted from the literature⁴⁷.

Rheological measurements

Dynamic viscosity measurements were conducted on a rheometer (AR-G2, TA Instruments) at specified temperatures in an oscillatory time sweep mode (frequency, 1 Hz) using stainless steel parallel plates (diameter, 25 mm; gap, 0.02 mm). The kinematic viscosity measurements were carried out using a Stabinger viscometer (SVM3001, Anton-Paar) at 40 °C and 100 °C.

Tribological studies

Tribological tests were performed under ASTM G99 conditions using a friction and wear test machine (TRB3, Anton-Paar) at room humidity (40%) and at temperatures of about 25 °C and 60 °C. The applied normal load was 10 N, resulting in a maximum Hertzian contact pressure of 1.08 GPa. The other test parameters are as follows: sliding speed 0.1 m s⁻¹, test duration 1 h and sliding distance 360 m. These parameters were selected to effectively create a boundary lubrication condition, thereby comparing the anti-friction and anti-wear properties of the tested lubricants. The ball and disk samples used during tests were made of AISI 52100 through-hardened bearing steels with a Rockwell C hardness of 60 and a surface roughness of 20 ± 10 nm. After the tests, a three-dimensional optical profiler (ContourGT, Bruker) was used to image and assess the wear loss volumes of the specimens.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was performed using a PerkinElmer ATR-FTIR (model Spectrum 100; 64 scans; scan range 4,000–400 cm⁻¹ and resolution 4 cm⁻¹) at room temperature.

Thermogravimetric analysis and differential scanning calorimetry

Thermogravimetric analysis was performed on a Discovery TGA5500 thermogravimetric analyser (TA Instruments) between 28 °C and 800 °C at a heating rate of 10 °C under a nitrogen atmosphere. ASTM D5800 experiments were conducted by heating the lubricants from 28 °C to 250 °C, followed by an isothermal hold at 250 °C for 60 min (ramp rate of 3.7 °C min⁻¹, under an air environment). Differential scanning calorimetry was performed on a Q2500 Discovery (TA Instruments) with a refrigerated cooling system (RCS90). Temperature range, -90 °C to 115 °C; ramp rate, 10 °C min⁻¹; sample loading, 5–10 mg.

NMR analysis

¹H NMR was performed on 500 MHz NEO-500 Oxford and 400 MHz NEO-400 HT spectrometers with 32 scans and a 1 s relaxation delay. ¹³C NMR was recorded on a 500 MHz NEO-500 (Oxford Instruments) spectrometer with a 2 s relaxation delay and 1,024 scans. All spectra were recorded in deuterated chloroform at room temperature. Heteronuclear single quantum coherence experiments were performed on a 500 MHz Bruker Avance III spectrometer at 298 K in CDCl₃, using a 2 s relaxation time, 32 scans and a digitizing increment of 256.

Gas chromatography–mass spectrometry

GC-MS spectra of the oils were collected on a Shimadzu QP2010 SE Single Quadrupole using an Rxi-5Sil MS column (length 30 m, diameter 0.25 mm and thickness 0.25 µm) under the following operating conditions:

- Injection port temperature: 280 °C
- Split valve: 1/20
- Purge flow: 3 ml min⁻¹
- Column flow: 1 ml min⁻¹
- Injection volume: 1 µl
- Column oven initial temperature: 50 °C
- Column initial time: 3 min
- Column oven ramp rate: 10 °C min⁻¹
- Column oven final time: 280 °C
- Mass spectrometry transfer line temperature: 250 °C
- Mass spectrometry database: Wiley
- Mass spectrometry scan mode range: 45–550 *m/z*

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/or GC-MS. The analyses were performed

using an Agilent 7890 A Gas Chromatograph coupled with a 5975C Mass Selective Detector. The specific instrumental conditions used to analyse the gas samples were as follows:

- Column: Agilent DB-5 MS (30 m × 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⁻¹ to 100 °C and finally ramped at 15 °C min⁻¹ to a final temperature of 290 °C (held for 5 min)
- Mass spectrometry mode: scan mode (10–700 amu). No time delay in mass spectrometry
- Search library: Wiley

Inductively coupled plasma mass spectrometry

Digestion protocol. Approximately 100 mg of each analyte 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 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 radiofrequency power of 1,550 W and plasma gas flow rate of 15 l min⁻¹. Helium was used as the collision gas (5 ml min⁻¹), and the analyte solutions in 2% HNO₃ were introduced using 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 (1–1,000 ppb).

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.

Technoeconomic analysis

A detailed description of the technoeconomic analysis methodology is provided in Supplementary Information section 12.

Computational methods

We constructed a simulation model comprising an atactic PVC chain with five monomer units, five molecules of AlCl₃ and an equimolar amount of 1-octene. The system also included 10 DCM molecules as a solvent. Activation of the PVC was achieved by dechlorinating PVC, forming AlCl₄⁻ and generating cationic sites on the polymer chain. Charge neutrality was maintained by balancing the number of cationic (C⁺) active sites with an equal number of AlCl₄⁻ anions.

Alkylated systems were modelled with five 1-octene molecules, resulting in either a comb-like structure through parallel alkylation (Fig. 3c) or a branch-like structure via sequential alkylation (Fig. 3d). Each system

contained 225 atoms. Initial structural relaxation was performed using the Universal Force Field^{48,49} and QEq⁵⁰ charge equilibration under NPT dynamics for 1 ns, followed by NVT dynamics for 2 ns.

Fully relaxed structures were then subjected to quantum mechanical molecular dynamics simulations using VASP v.6.4.2. Here, we used the Perdew-Burke-Ernzerhof flavour of density functional theory, including the Grimme's D3 dispersion correction with Becke-Johnson damping (D3(BJ)) for van der Waals interactions. These simulations were conducted under experimental conditions at 343 K using NPT dynamics for 10 ps to ensure convergence of the free energy. For energy comparisons, average free energies from the final 4 ps of each simulation were used.

Data availability

Additional data are provided in the Supplementary Information, and the raw files are available at Dryad (<https://doi.org/10.5061/dryad.xgxd254x8>).

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Author contributions G.L. conceived the idea, acquired funding and supervised the project. G.L. and E.M.N. implemented the idea and designed the research. E.M.N., C.T. and A.C. performed lubricant synthesis and characterization. C.T., A.C., A.D. and S.K. conducted reaction optimizations. E.M.N., C.T., A.C. and A.D. upcycled real-world PVC products. Y.Z. performed X-ray diffraction. J.B.M. and C.V. conducted size-exclusion chromatography experiments. X.C. and J.Z. evaluated financial viability through TEA. W.A.G. and T.D. performed computational studies. A.E., G.S. and S.L. explored the tribological performance of the lubricants. G.L., E.M.N., C.T., A.C., A.E., G.S., S.L., W.A.G., T.D., X.C. and J.Z. contributed to data interpretation and manuscript writing. All authors proofread the manuscript.

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Competing interests G.L., E.M.N., C.T. and A.C. have filed a provisional patent (application no. 63/922,666) based on this work. All other authors declare no competing interests. This work was completed before J.Z. joined Amazon.

Additional information

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