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Polymeric bis(triphenylphosphine)iminium chloride as a recyclable catalyst†

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Metal-free catalysts have garnered considerable interest as an environmental and economical alternative to precious metal catalysts. Bis(triphenylphosphine)iminium chloride (PPNCl) has emerged as a prominent choice due to its air and thermal stability and broad reactivity, especially in applications where a bulky cation is needed. The high phosphorus content and synthetic effort required for catalyst synthesis increase environmental impact; the recyclability of PPNCl in catalytic processes remains largely unexplored. The potential development of a polymer-supported PPNCl catalysts therefore desirable to enable this recyclability. In this work, we synthesise polymeric PPNCl (**poly(PPNCl)**) for the first time. **Poly(PPNCl)** demonstrates a comparative catalytic reactivity to its small molecule variant when employed as a catalyst in halogen-exchange reactions and CO_2/epoxide coupling. For the latter the effect of catalyst loading, CO_2 pressure, reaction time and addition of co-catalyst on conversion and selectivity was investigated. **Poly(PPNCl)** was easily recovered from the crude product by simple precipitation and its catalytic reactivity was well-maintained over three reaction cycles, providing environmental and economic advantages for sustainable reaction development.

Introduction

Catalysts, often containing transition metals, are essential tools in chemical synthesis.[1–3] Challenges in metal extraction, complex toxicity, and economic cost frustrate the long-term sustainability of their industrial application.[4,5] Consequently, metal-free catalysts have been touted as environmentally friendly, economically viable, and less hazardous alternatives to metal-based catalysts.[6–9] An emerging class of metal-free catalysts are bis(triphenylphosphine)iminium salts,[10–12] thanks to their good solubility, stability at high temperatures and ease of handling.[11,13]

Bis(triphenylphosphine)iminium chloride (PPNCl) has been utilized in carbon dioxide (CO_2) valorisation[14–18] to affect the coupling of CO_2 and epoxides to form cyclic carbonates as key reagents for the pharmaceutical and fine chemical industry.[19–21] Wing *et al.* demonstrated that both the PPN^+ and Cl^- play important roles in the reaction mechanism.[22] PPNCl has also been explored as a co-catalyst in the ring-open co-polymerisation of CO_2 and epoxides to form polycarbonates.[23,24] Showing catalyst versatility, PPNCl can also be utilized to facilitate the hydrogenation of CO_2 to yield higher alcohols,[25] and in difficult halogen-exchange reactions to yield fluorinated aromatic compounds for pharmaceutical and agrochemical applications (Fig. 1a).[11]

The material-intensive, multi-step synthesis of PPNCl means that catalyst recovery would be important, however, the recycling of PPNCl has thus far not been explored. In recent years,

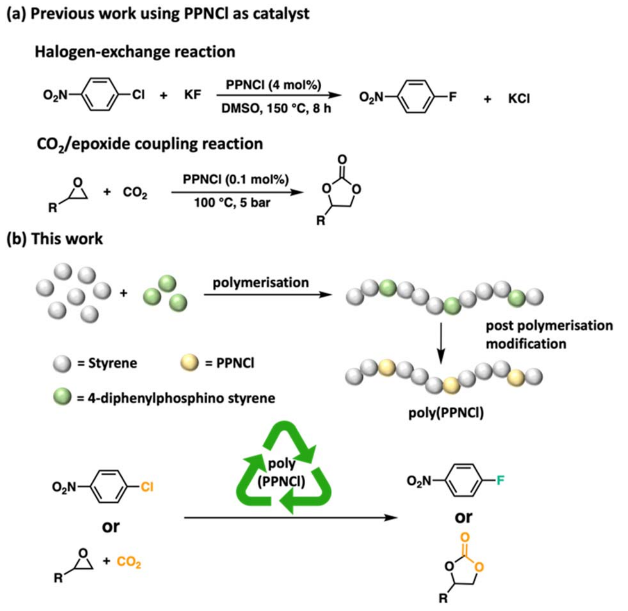

Fig. 1 (a) Previous work using PPNCl as catalysts; (b) **poly(PPNCl)** as a recyclable catalyst for halogen exchange and CO_2/epoxide coupling reactions.

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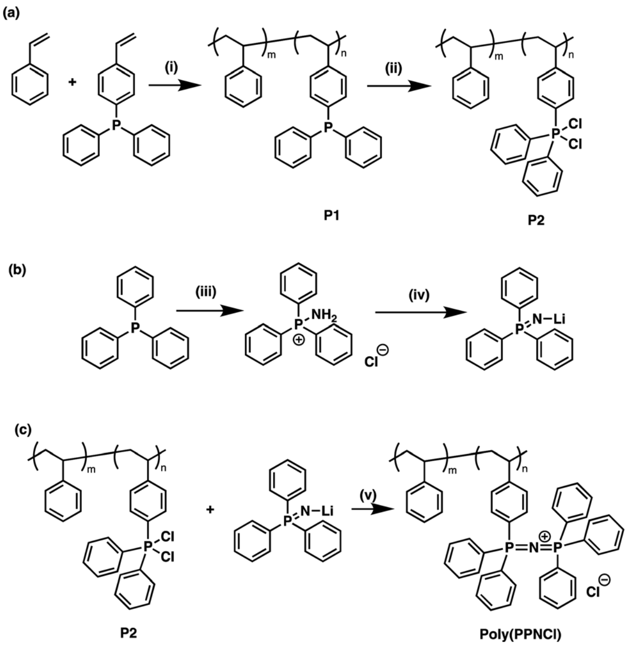
the recyclability of catalysts through incorporation into polymers has gained significant attention.[26–29] Previous work in our group showed that polymer-supported catalysts featuring main-group elements including phosphorus, can be easily recovered and achieve comparable catalytic efficiencies to their small molecule counterparts.[30–32]

Developing a polymeric variant of PPNCl could generate a catalyst capable of maintaining high activity and new recyclability. In this work, we report for the first time, the preparation of macromolecular **poly(PPNCl)**. We demonstrate the catalytic reactivity of **poly(PPNCl)** in catalyzing both halogen-exchange and CO_2/epoxide coupling reactions. The catalyst is readily recovered through post-reaction precipitation and serves as an important step in non-metal catalyst recycling (Fig. 1b).

Results and discussion

Synthesis of poly(PPNCl)

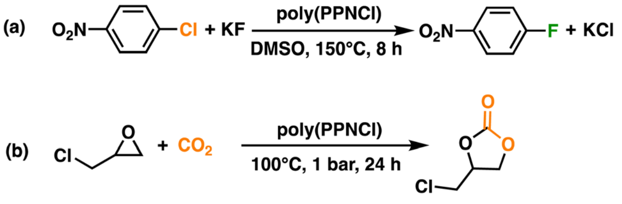
Macromolecular **poly(PPNCl)** was prepared through post-polymerisation modification of poly(styrene-*co*-diphenylphosphine styrene), **P1**, as shown in Scheme 1. **P1** was prepared by anionic co-polymerisation of styrene and *p*-(diphenylphosphino) styrene using *n*-butyllithium as the initiator in a methodology modified from our previous work on polymeric frustrated Lewis pairs.[30] The styrene co-monomer serves to provide inert spacers in the polymer chains, separating the active catalyst moieties, and improving solubility. The phosphorus groups incorporated into the polymer chains served as anchors for a modified small molecule synthesis.[11] As PPNCl is prepared by the reaction of a dichlorinated phosphine (Ph_3PCl_2), accessible in near quantitative conversion, and a lithiated amino(triphenylphosphine) (Ph_3PNLi) that forms unavoidable side-products, it is essential to dichlorinate the polymer first. The reaction of **P1** with C_2Cl_6 generates **P2** with full conversion and high purity, as shown by NMR spectroscopy (Scheme 1a and Fig. S1†). A broad resonance at 63.2 ppm in the ^{31}P NMR spectrum is comparable to the chemical shift for Ph_3PCl_2 (65.0 ppm).[33] Separately, amination of triphenylphosphine afforded amino(triphenyl)phosphonium chloride which was subsequently lithiated to afford lithium (triphenylphosphoranylidene)azanide (Scheme 1b). Finally, the targeted **poly(PPNCl)** was synthezised by the reaction between **P2** and lithium (triphenylphosphoranylidene)azanide (Scheme 1c). The obtained **poly(PPNCl)** was purified by dialysis to remove small molecule impurities. Analysis by ^{31}P NMR spectroscopy (Fig. S1†) showed a single resonance at 20.7 ppm, confirming the full conversion of **P2** to the desired product. Diffusion order spectroscopy (DOSY) showed a single diffusion coefficient, confirming that styrene and PPNCl moieties were distributed within the same polymer chains (Fig. S3†). This synthetic protocol was modified to prepare catalysts with 5 and 10 mol% PPNCl moieties (**poly(PPNCl)-5** and **poly(PPNCl)-10** respectively; Table S1†). For further characterisation of **poly(PPNCl)**, thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) showed that **poly(PPNCl)-5** has a lower degradation temperature and glass transition temperature compared to **poly(PPNCl)-10** due its lower PPNCl loading in the polymer chains (Fig. S4†). Importantly, the evident absorptions of Fourier-transform infrared spectroscopy (FTIR) in the region between 1100 and 1480 cm^{-1} correspond to the vibration of P═N bonds according to the literature,[34] further supporting the formation of **poly(PPNCl)**.



Scheme 1 (a) Synthetic procedures of **P2** from phosphine-containing copolymer, $m:n = 95:5$ or $90:10$; (i) *n*-butyllithium, toluene, −78 °C, 3 h; (ii) C_2Cl_6, THF, r.t., 3 h; (b) Synthesis of Ph_3PNLi from triphenylphosphine; (iii) hydroxylamine-*O*-sulfonic acid, methanol/DCM, r.t., 1 h; (iv) *n*-butyllithium, THF, initiated at −50 °C, −15 °C 2 h; (c) synthesis of **poly(PPNCl)** (v) THF, r.t., 3 h.

Halogen-exchange reaction

Halogen-exchange reactions were performed with these novel catalyst systems, **poly(PPNCl)-5** and **10**. The conversion of 1-chloro-4-nitrobenzene (**CNB**) to 1-fluoro-4-nitrobenzene (**FNB**) by **poly(PPNCl)-10** (63%) was surprisingly lower than that of **poly(PPNCl)-5** (80%) (Scheme 2a, Table S2†). While the higher loading offered a higher catalyst concentration, the increased number of PPNCl groups led to poorer solubility of the catalyst, therefore lowering conversion. Similar phenomena have been observed in the literature.[35] The conversion catalysed by **poly(PPNCl)-5** is comparable to that facilitated by PPNCl (81%), suggesting similar efficiency for small and macromolecular systems. With its superior solubility and performance,



Scheme 2 (a) Halogen-exchange reaction from **CNB** to **FNB**; (b) coupling reaction of CO_2 with **GC**.

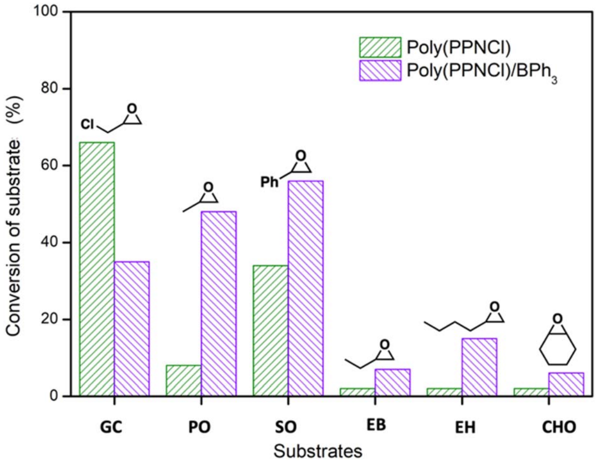


Fig. 2 CO_2/epoxides coupling reaction to yield cyclic carbonates. Conversions calculated by ^1H NMR spectroscopy. Conversions for **GC** and **PO** were taken from the average value of three trials; the rest substrates were conducted once. Reactions were performed in a sealed ampoule on a 12.8 mmol scale at 0.1 mol% **poly(PPNCl)** with or without 0.1 mol% BPh_3 (0.1 mol% as calculated from the number of expected active functional groups).

poly(PPNCl)-5 was chosen as the preferred catalyst for the rest of this work.

Conversion of **CNB** with **poly(PPNCl)-5** was systematically optimized (Table S2†). Minor increases in conversion by increasing the molar ratio of potassium fluoride (KF) added and when lower concentrations of catalyst were observed (2 mol%, 89%), further improving reaction sustainability. While the reaction worked in DMSO, MeOH and DMF, the optimal solvent was DMSO which correlated with enhanced catalyst solubility. **CNB** concentration is also important, with both lower (0.5, 1 M) and higher (3, 4 M) concentrations giving decreased conversions. High concentrations of **CNB** impact catalyst solubility in DMSO, reducing resultant reactivity.

With an optimized system in hand, we investigated whether this substrate scope could be expanded using **poly(PPNCl)** as the catalyst. Electrophilic aromatic substitution is favoured by the inductive and resonance effects promoted by electron-withdrawing groups (EWGs); previously this reaction was only reported for nitro-substituted aromatics. Displacing the nitro group of **CNB** with other *para*-substituted EWGs or *meta*-substituted electron-donating groups (EDGs) (Fig. S6†) was challenging. Of the substrates tested, only 4-chlorobenzonitrile showed conversion by ^1H and ^{31}P NMR spectroscopy (Fig. S7†).

CO_2 and epoxide coupling reactions

The coupling of CO_2 and epoxides is an important reaction for CO_2 transformation, as the resultant cyclic carbonates are valuable intermediates for fuel additives,[36] polycarbonates,[37] and pharmaceuticals.[38] In previous reports, the PPNCl catalyst was usually paired with a Lewis acid co-catalyst such as triphenylborane (BPh_3) to enhance reactivity.[39,40] The catalytic reactivity of **poly(PPNCl)** for the insertion of CO_2 to epoxides in the absence of a solvent was investigated (Scheme 2b). Glycidyl chloride (**GC**) was selected as a model substrate, and the results summarized in Table S3† under standard conditions of 1 bar CO_2 for 24 h with 0.1 mol% **poly(PPNCl)-5**.

In the absence of **poly(PPNCl)**, no conversion to chloropropene carbonate was observed. With 0.1 mol% (by catalyst moiety) **poly(PPNCl)** without any borane co-catalyst, 66% conversion was achieved, increasing to 98% at 0.4 mol%. Conversions did not substantially change upon alteration of CO_2 pressure (1–5 bar) (Table S3,† entries 1 and 5–7), suggesting CO_2 is not involved in the rate-determining step. While the rate of epoxide activation is often enhanced through the addition of BPh_3, the conversion of **GC** surprisingly decreased to 48% when the Lewis acid is added to the system (Table S3,† entry 9).[30] No reaction was observed when employing BPh_3 alone. We hypothesize that the coordination of BPh_3 to a key intermediate (**I** in Fig. S9†) would slow the rate of CO_2 insertion and therefore decrease reaction rates. As the reaction works without the addition of an air-sensitive Lewis acid, we explored milder conditions under an air atmosphere (Table S3,† entry 16). However, **GC** conversion remained unchanged compared to inert atmosphere (Table S3,† entry 2).

The kinetics of the **GC**/CO_2 coupling reaction catalysed by **poly(PPNCl)** was explored (Table S3,† entries 10–15). Conversion of **GC** increased from 3 h to 48 h, indicating a long-lived catalyst (Fig. S11a†) and first-order kinetics for [**GC**] (Fig. S11b†). A catalytic mechanism for the **GC**/**poly(PPNCl)** system is proposed (Scheme S1†). Switching the substrate to propylene oxide (**PO**) showed remarkably different results: **PO** conversion was very low (9%) when using **poly(PPNCl)-5** while the introduction of a BPh_3 co-catalyst increased conversion to 48% (Table S4†). This reversion of the trends observed for **PO** suggests a significant change in the mechanism proposed in Scheme S2.† Increased reaction time resulted in a higher conversion (61%) suggesting catalyst death is not the reason for reduced yields. The effect of CO_2 pressure on **PO** conversion gave no significant change in conversion (1–5 bar). **PO** conversion was enhanced to 71% by increasing catalyst loading to

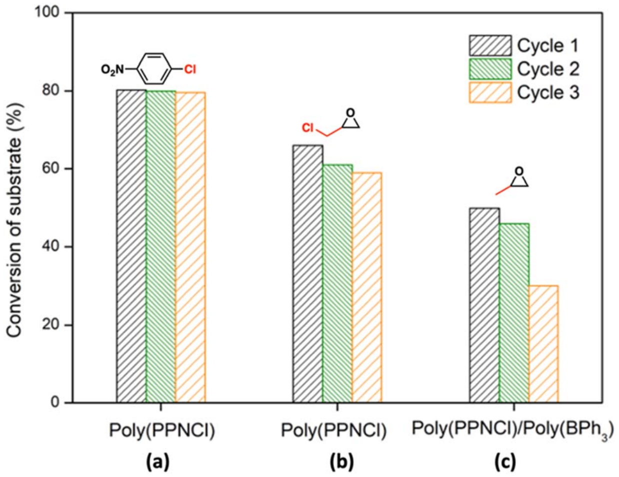
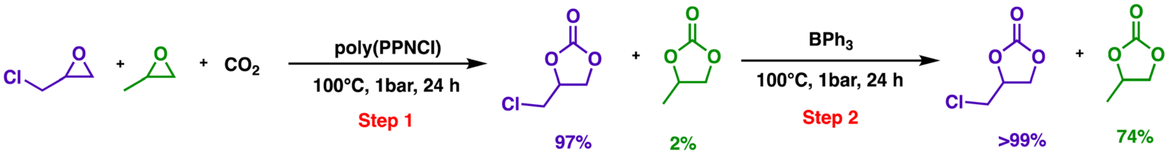


Fig. 3 Reaction conversions over three cycles (a) halogen-exchange, (b) CO_2/**GC** coupling, and (c) CO_2/**PO** coupling reactions. Conversion calculated by ^1H NMR spectroscopy. Conversions for recycled **poly(PPNCl)** were obtained from an average value of two trials.



Scheme 3 The selective one-pot, two-step reaction of epoxide conversion to cyclic carbonates. General conditions: the feed ratio of **GC** : **PO** : **poly(PPNCl)** : BPh_3 is 1000 : 1000 : 4 : 4.

0.2 mol%. The efficacy of the borane system also allowed us to test the poly(Lewis acid) variant previously developed in our group.[30] Poly(BPh_3), a co-polymer of styrene and 4-styryldiphenylborane, gave conversations comparable to poly(PPNCl)/BPh_3 system, demonstrating that both PPNCl and BPh_3 can be switched to recyclable polymeric systems while maintaining catalytic reactivity (Table S4,† entry 10).

Further expanding the substrate scope delineated two clear classes, evaluated by the overall catalytic reactivity of **poly(PPNCl)** *versus* poly(PPNCl)/BPh_3 under conditions that avoided reaching full conversion in order to probe structure/activity relationships (Fig. 2). Only the most reactive substrate, **GC**, favoured **poly(PPNCl)** as a lone catalyst and outperformed all other tested epoxides (66%). Styrene oxide achieved the second highest conversion (34%) using only **poly(PPNCl)**, supporting the theory that the electron-withdrawing nature of the substituents is key to ensuring reactivity. Interestingly, whilst the poly(PPNCl)/BPh_3 binary system resulted in a lower conversion of **GC** than for **poly(PPNCl)** alone, this trend was reversed for all other substrates screened. As the most reactive substrate, **GC** can be activated by both poly(PPN^+) and BPh_3, the two catalytic mechanisms may compete with each other to stall catalytic turnover. The sterically hindered cyclohexene oxide had the lowest conversion, attributed to its high steric hindrance preventing associative ring-opening.

Importantly, the selectivity of cyclic carbonates is 100% in nearly every case. Under no reaction conditions is polycarbonate and polyether generated in the presence of **poly(PPNCl)** alone. The good leaving group abilities of both poly(PPN^+) and Cl^- in the ring-closure step to form chloropropene carbonate likely facilitate this selectivity. For the **GC**/**poly(PPNCl)**/BPh_3 system, a secondary product was observed (^{1}H NMR: 4.7 ppm, Fig. S17 and S18†), identified as the carbonate anion adduct of BPh_3 following ring opening by Cl^-. This suggests that chlorine may attack the more substituted carbon to form an off-cycle product.

Finally, the catalytic selectivity and kinetic switch can be used in one-pot stepwise catalytic transformations. **GC** and **PO** could be sequentially converted into their cyclic carbonates as shown in Scheme 3. The epoxide mixture was first treated with **poly(PPNCl)** to yield chloropropene carbonate and propylene carbonate conversions of 97% and 2% respectively. The addition of BPh_3 to the reaction led to the conversion of the unreacted **PO** (74%), evidencing this epoxide selectivity.

Catalyst recycling

Polymer-supported catalysts are important additions to sustainable catalyst development as their ready isolation allows for recyclability.[31] We sought to explore the catalytic performance of both **poly(PPNCl)** and **poly(PPNCl)**/poly(BPh_3) after repeated recovery of the polymer-supported catalysts from crude products (Fig. 3). **Poly(PPNCl)** can be recovered easily from the product by precipitation from *n*-hexane and dried before reuse in subsequent reactions.

In the halogen-exchange reaction, the addition of *n*-hexane precipitated **poly(PPNCl)-5** which was recovered from the crude product by filtration and dried under vacuum prior to weighing between each cycle. Catalytic performance was well-maintained over three reuse cycles (1st cycle: 80%; 2nd: 79%; 3rd: 77%), demonstrating excellent recyclability. For CO_2/epoxide coupling, precipitation of the catalyst or catalysts from the crude chloropropene carbonate (**poly(PPNCl)-5**) and propylene carbonate (**poly(PPNCl)-5**/poly(BPh_3)) reactions was conducted in the reaction vessel. The catalytic reactivity of **poly(PPNCl)** drops slightly over three reaction cycles of **GC**/CO_2 coupling (1st cycle: 67%; 2nd: 61%; 3rd: 59%). A more precipitous decrease in substrate conversion is observed in the **poly(PPNCl)**/poly(BPh_3) binary catalyst system (1st cycle: 50%; 2nd: 46%; 3rd: 30%) likely due to the mass loss and partial deactivation of air-sensitive poly(BPh_3) during catalyst recovery.

Conclusions

In summary, we report the synthesis of **poly(PPNCl)** using post-polymerisation modification. **Poly(PPNCl)** can achieve high conversion at a low feeding ratio in the halogen-exchange reaction of chloroarenes to fluoroarenes, matching catalytic efficiency to the unrecoverable small molecule analogue, PPNCl. In CO_2/epoxides coupling, the selective formation of cyclic carbonates is catalysed by two mechanisms. Depending on epoxide reactivity, either air-stable **poly(PPNCl)** can be used on its own or with the addition of BPh_3 or poly(BPh_3) as a co-catalyst. The robust **poly(PPNCl)** can be recovered by simple precipitation and reused in further reactions, with both halogen-exchange and CO_2 coupling of reactive epoxides displaying excellent recyclability. The recovery and reuse of this key metal-free catalyst is an essential step to support sustainable chemical syntheses.

Data availability

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

Author contributions

Ziwei Xu and Meng Wang: investigation, methodology and manuscript writing. Michael P. Shaver: conceptualisation, manuscript writing – review and editing, supervision and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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