The Synthesis of Cyclic Phosphonates: Towards Stable and Recyclable Main Group Plastics

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March 2023

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Background

- Polysiloxanes [**Fig 1a**] are the most ubiquitous main group polymer
  - Used in sealants, biomaterials, elastomers, flexible electronics
  - ***New E-O (E = element) polymer families may yield new material properties***
- Polyphosphates $[PO_3^-]_n$ and polyphosphoesters $[RP(=O)\text{-}O\text{-}C_x\text{-}O]_n$ are isolobal to polysiloxanes [**Fig 1 b,c**]
- Most similar to polysiloxanes are the polyphosphonates $[RPO_2]_n$ [**Fig 1d**]
  - **Previously absent from the literature**

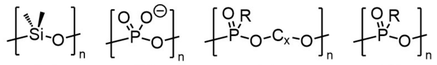


Fig 1: Polysiloxane (a) and isolobal polymers, polyphosphate (b), polyphosphoester (c), and polyphosphonates (d).

- We recently reported the synthesis of polyphosphonates through thermal ring opening polymerization (TROP) of *cyclic phosphonates* $[RPO_2]_3$ through the melt [**Fig 2i**] [1]
  - These recyclable phosphonate rings and polymers are under-explored
  - These polymers suffer from depolymerization when they are dissolved in solution
    - Adding steric bulk allows for better stability of polymers in solution [**Fig 2ii**]

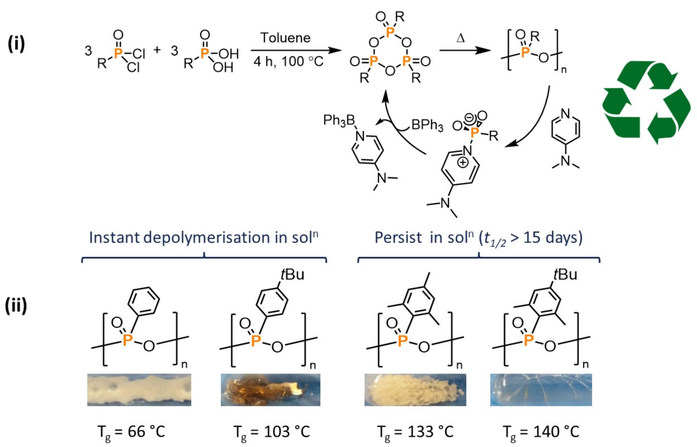
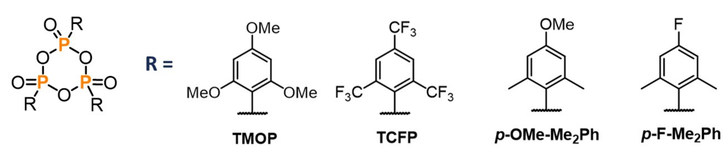


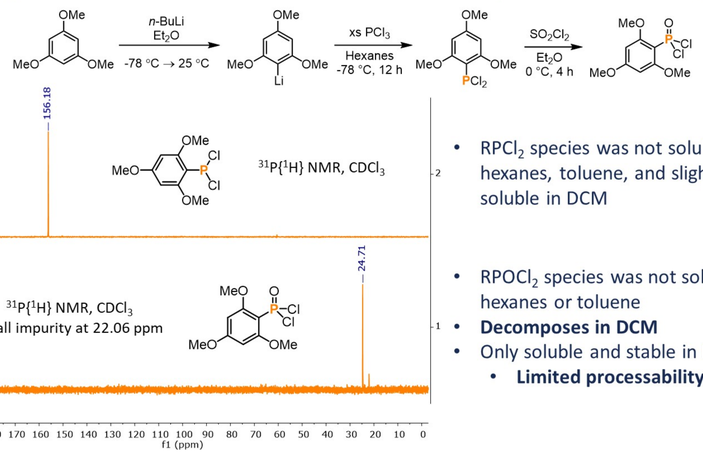
Fig 2: Cyclic phosphonate and polyphosphonates synthetic scheme (i); Pictures of Thermally robust polyphosphonate polymers and their Tg values (ii).

Hypothesis

- *If steric bulk improves stability towards depolymerization in polyphosphonates, can modifying the electronics further enhance the stability of these polymers?*
- Compare how **electron-withdrawing** (CF_3/ F groups) and **electron-donating** (MeO groups) affect the TROP of cyclic phosphonates and the stability of the polyphosphonates

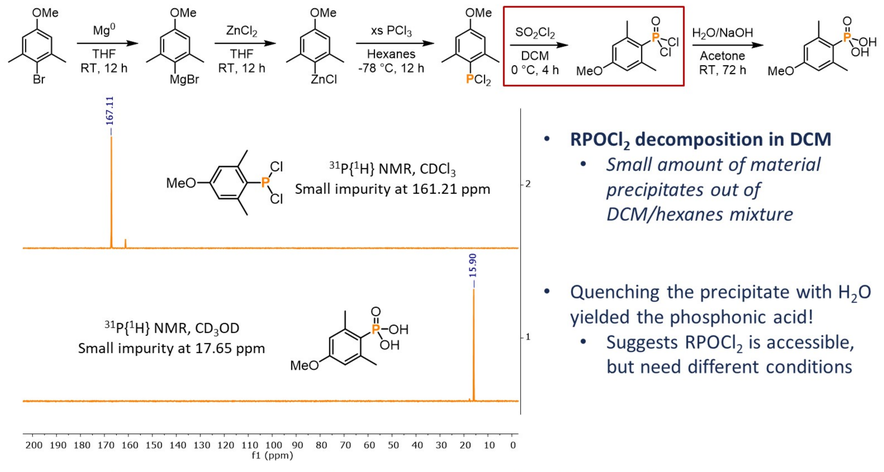


Synthesis Towards TMOP Phosphonate Ring



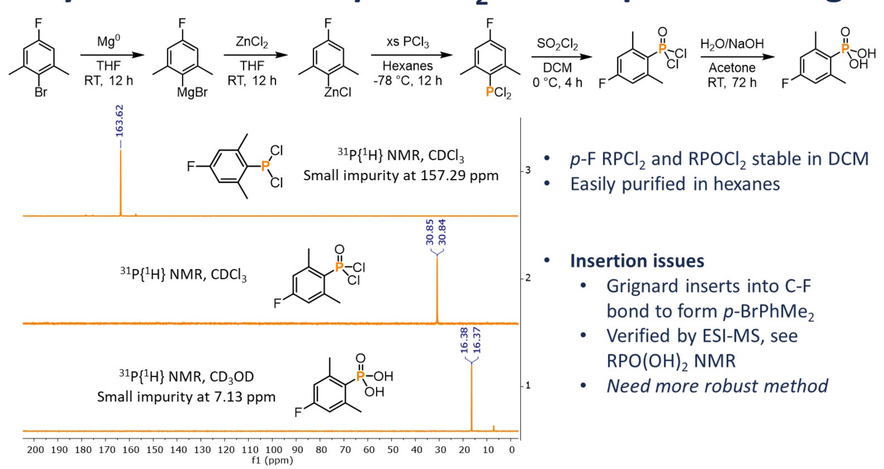
- $RPCl_2$ species was not soluble in hexanes, toluene, and slightly soluble in DCM
- $RPOCl_2$ species was not soluble in hexanes or toluene
- **Decomposes in DCM**
- Only soluble and stable in Et_2O
  - **Limited processability**

Synthesis Towards *p*-OMe-Me_2Ph Phosphonate Ring



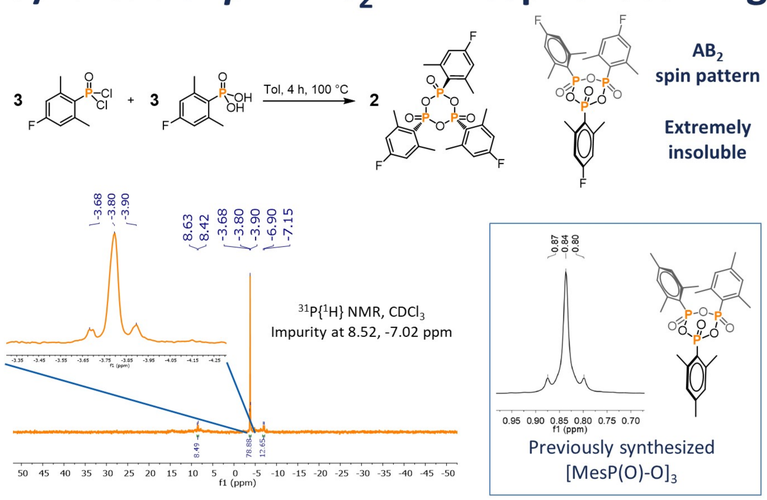
- **$RPOCl_2$ decomposition in DCM**
  - *Small amount of material precipitates out of DCM/hexanes mixture*
- Quenching the precipitate with H_2O yielded the phosphonic acid!
  - Suggests $RPOCl_2$ is accessible, but need different conditions

Synthesis Towards *p*-F-Me_2Ph Phosphonate Ring



- *p*-F $RPCl_2$ and $RPOCl_2$ stable in DCM
- Easily purified in hexanes
- **Insertion issues**
  - Grignard inserts into C-F bond to form *p*-$BrPhMe_2$
  - Verified by ESI-MS, see $RPO(OH)_2$ NMR
  - *Need more robust method*

Synthesis of *p*-F-Me_2Ph Phosphonate Ring



Summary and Future Work

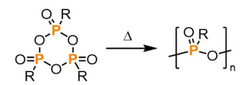
- Successfully synthesized $RPOCl_2$ and $RPO(OH)_2$ (R = *p*-F-Me_2Ph)
  - Test reaction shows evidence of $[RP(O)\text{-}O]_3$ cyclic phosphonate
- Able to access MeO-substituted $RPOCl_2$ and $RPO(OH)_2$
  - **Issue:** solvent compatibility and stability

Current studies

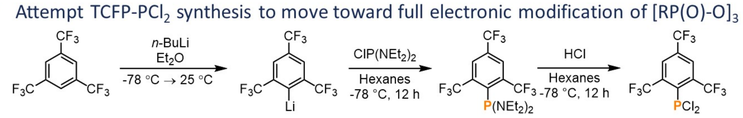
- Optimize purification of *p*-F-Me_2Ph $[RP(O)\text{-}O]_3$ cyclic phosphonate
  - Single crystals will verify formation
- Optimize solvent condition of *p*-MeO-Me_2Ph-$POCl_2$

Future Work

- ROP of new cyclic phosphonates



- Attempt TCFP-PCl_2 synthesis to move toward full electronic modification of $[RP(O)\text{-}O]_3$



Acknowledgements

This research was supported by the Jamie Cassels Undergraduate Research Awards University of Victoria. M.A.N. thanks NSERC for a CGS-D scholarship and UVic for a UVic Fellowship. I. M. thanks the NSERC for a C150 Research Chair.

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Reference(s)

[1] J. Am. Chem. Soc. 2019, 141 (7), 2894-2899.