# **Ambient Cationic Ring-Opening** CHEMISTRY Homopolymerisation of a Thionolactone



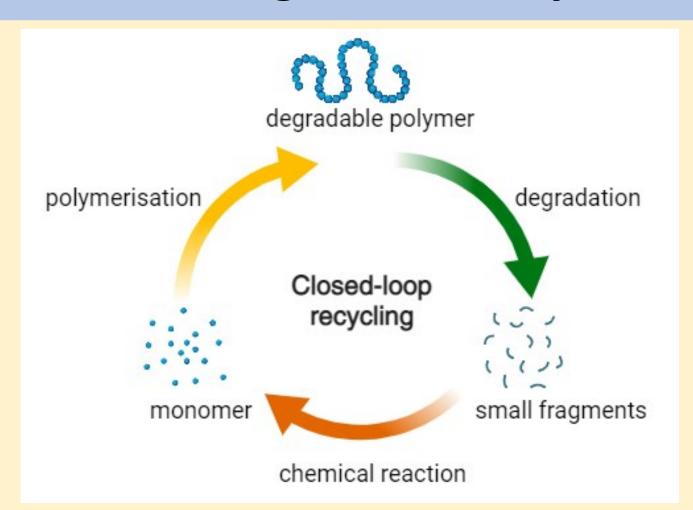
to Produce Recyclable Materials Swarnali Neogi, Qamar-un-Nisa, Rohani Abu Bakar, Nathaniel M. Bingham, Peter J. Roth

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# Introduction clothing packaging Vinyl polymers

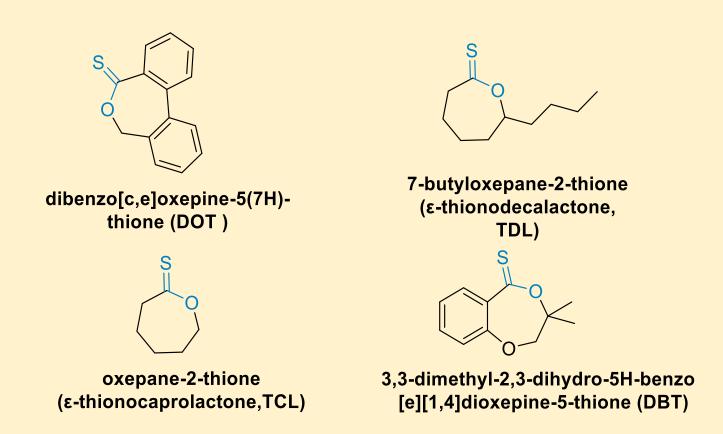
- The durability and versatility of vinyl polymers make them the most significant class of polymers.
- Their non-degradability limits their applications and imposes a global threat.

#### **Solution: Degradable Polymers!**



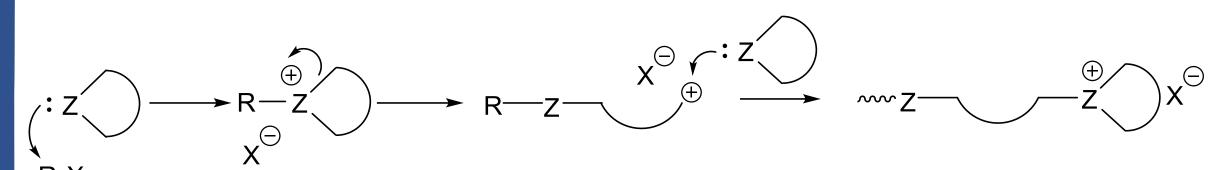
# Purpose of this work

- Polymers with groups like esters, thioesters in their backbones are degradable.
- Thionolactone monomers can install thioesters in polymers by Ring-Opening Polymerisation (ROP).
- Some of the existing thionolactones. [1], [2]



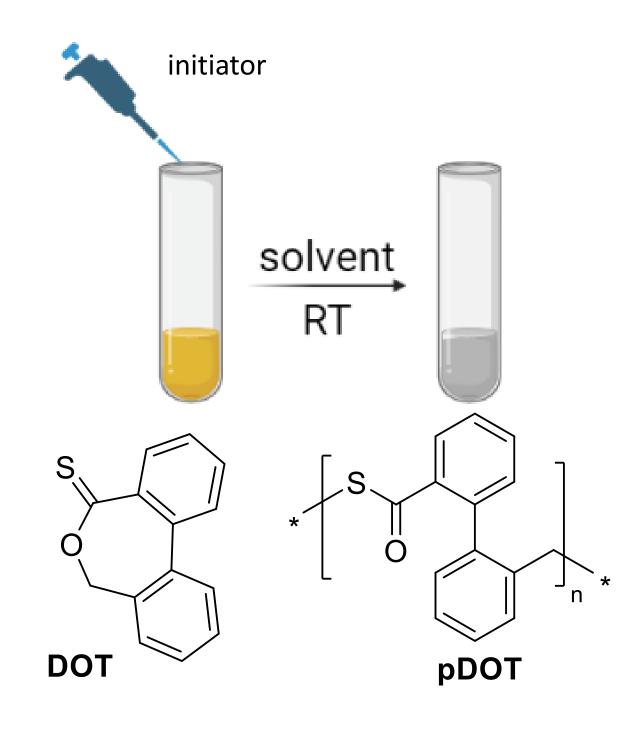
- DOT copolymerises radically with vinyl monomers but does not homopolymerize well by the established radical method.[3]
- A homopolymer of DOT (pDOT) will have cleavable linkages in every repeat unit and should be fully degraded to into small molecules.
- present **cationic** ring-opening Here homopolymerisation (CROP) of DOT.

# **Cationic Ring-Opening Polymerisation (CROP)**

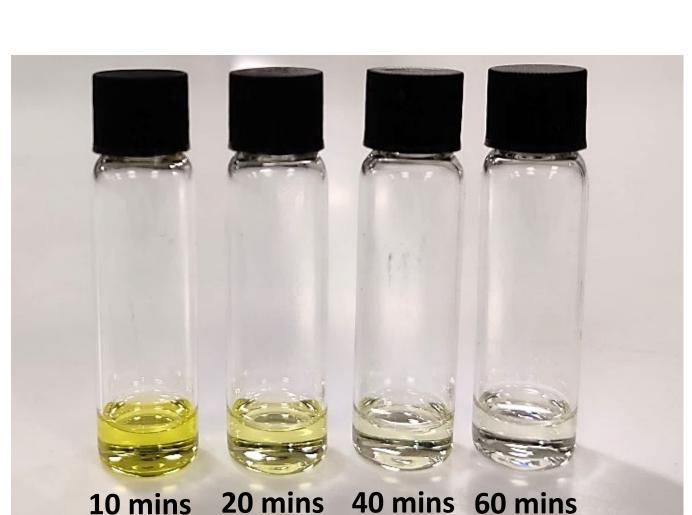


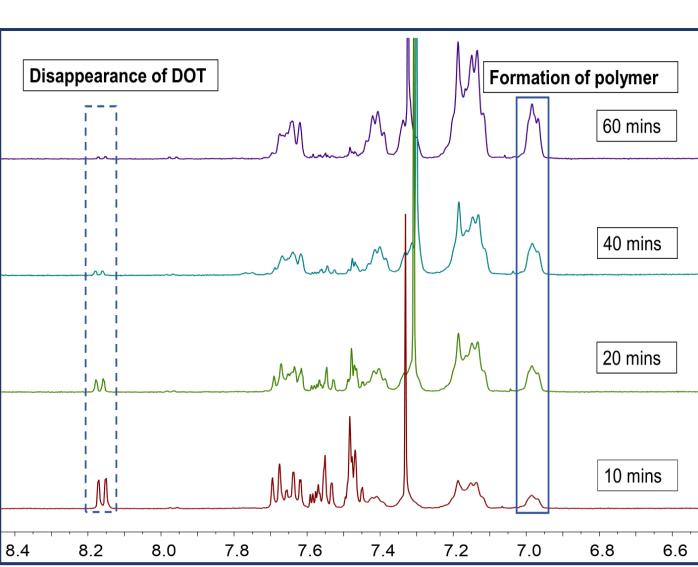
Heterocyclic monomers can cationically polymerised ring-opening cationic polymerisation (CROP).

# **Polymerisation Experimentation**



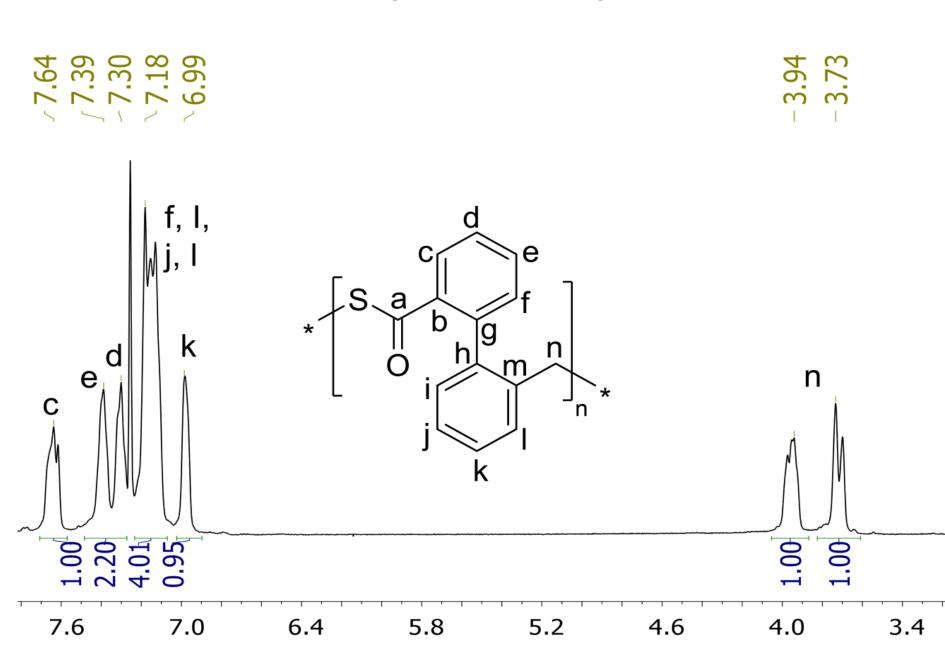
The homopolymerisation was rapid and proceeded with fading of the bright yellow colour of DOT.

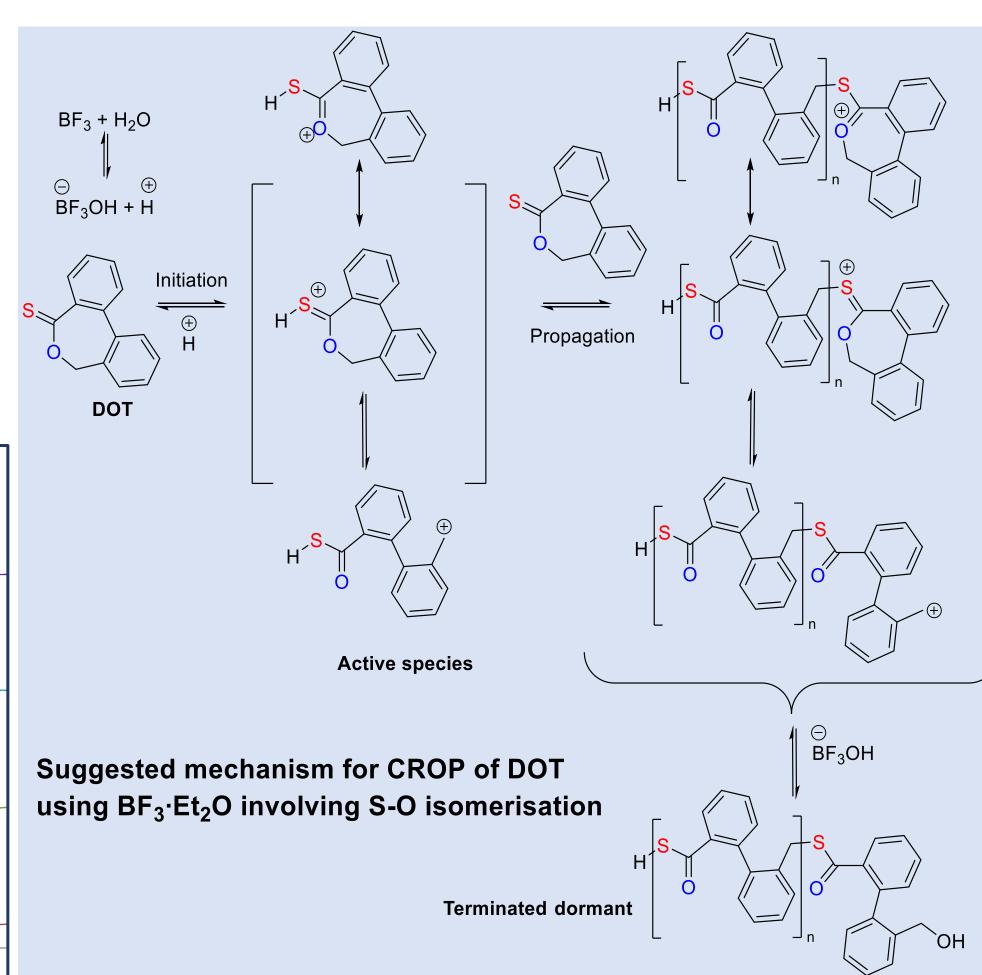




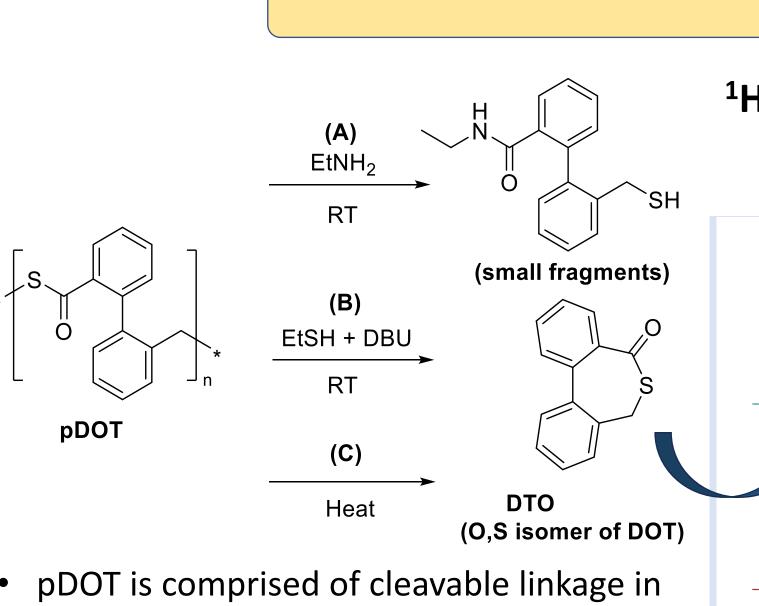
- DOT was polymerised using a cationic initiator in a selection of solvents at room temperature. [4]
- The propagation was believed to take place via the formation of a **benzylic cation**.
- Different cationic initiators (BF<sub>3</sub>·Et<sub>2</sub>O, MeOTf, TfOH, SnCl<sub>4</sub>) were found to successfully initiate the CROP of DOT.

#### <sup>1</sup>H NMR spectrum of pDOT



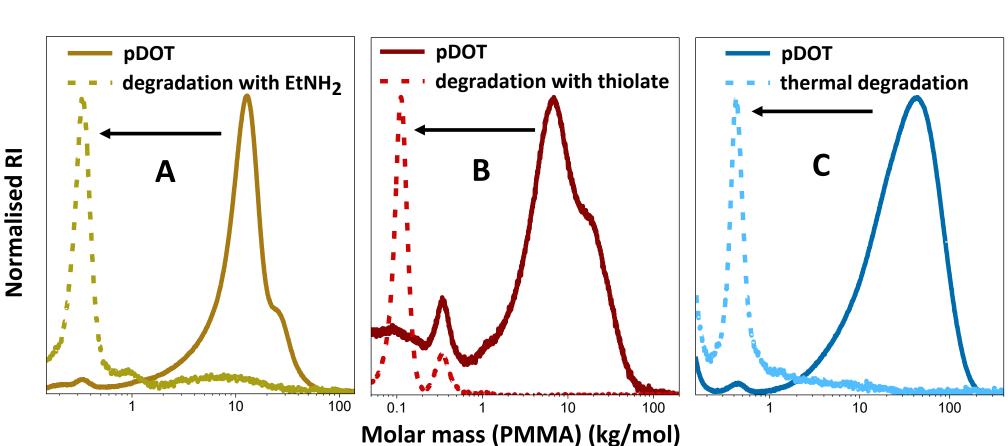


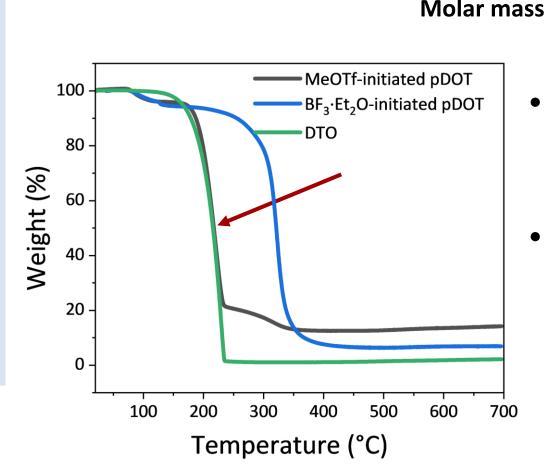
#### **Degradation Studies**



- every repeat unit.
- The successfully polymers were degraded completely by both aminolysis (A) and thiolysis (B) at RT and also under thermal conditions (C) [5], [6] as found in SEC chromatogram.
- <sup>1</sup>H NMR spectra showing the formation of DTO **(B) DTO** g'

Pathway (B) (treatment of pDOT with excess thiolate) and pathway (C) (heating) cause the pDOT chains to 'unzip' and form DTO





- **TGA** profile of **MeOTf-initiated** pDOT was like that of **DTO**.
- For thermal degradation at **140°C**, **MeOTf-initiated** pDOT depolymerised to DTO much **faster** as compared to BF<sub>3</sub>·Et<sub>2</sub>Oinitiated pDOT.

#### References and Acknowledgement

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- 4. Sanda, F.; Jirakanjana, D.; Hitomi, M.; Endo, T., *Polym. Sci. A* **2000,** *38* (22), 4057.
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### Conclusion

- Homopolymer of DOT has been synthesized quite rapidly under ambient conditions.
- The polymers are fully degradable into small molecules by different degradation methods.
- The choice of initiator had an influence on the thermal stability.
- The formation of DTO from degradation of pDOT is a step forward towards the **recyclability** of the polymer.