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Rare earth–transition metal cooperativity in the ring-opening polymerisation of tetrahydrofuran

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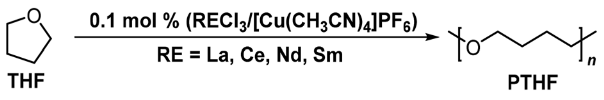
A synergistic $RECl_3/[Cu(CH_3CN)_4]PF_6$ catalyst system enables the controlled, ring-opening polymerisation of THF at room temperature without the need for any additional initiators. High-molecular-weight PTHF (M_n = 209 kDa, $Đ$ = 1.6) is obtained at low catalyst loadings, with tunable chain lengths *via* a targeted ligand addition.

Cyclic ethers are not only valuable model compounds for mechanistic investigations but also key monomers in the synthesis of industrially important polyethers. These polymers, known for their exceptional conformational flexibility and polarity, form the crucial soft, elastic segments in high-performance thermoplastic elastomers, including Hytrel® polyesters and Spandex polyurethanes.[1,2] Due to their industrial relevance and structural simplicity, cyclic ethers have long attracted interest as monomers for ring-opening polymerisations (ROPs). In this context, tetrahydrofuran (THF) has served as a model substrate for studying ROP mechanisms.[3,4] Since the pioneering work of Meerwein *et al.* on THF polymerisation using $[Et_3O]^+[BF_4]^-$ in 1937,[5] significant efforts have been directed towards the development of improved initiators for cationic ring-opening polymerisation (CROP). This continued interest stems from the limitations associated with conventional electrophilic initiators, such as Brønsted acids (*e.g.*, HCl, H_2SO_4),[6] Lewis acids (*e.g.*, $BF_3{\cdot}OEt_2$, $AlCl_3$),[7] silver[8] and iron[9] salts, which often suffer from slow initiation rates, corrosiveness, toxicity, and high costs. While BF_3-epichlorohydrin systems improve the initiation efficiency, they still exhibit suboptimal kinetics and premature chain termination.[10] Efforts to overcome these issues have focused on the use of more reactive Lewis acids, including PF_5 [11] and $NbCl_5$,[12] which enable the synthesis of polytetrahydrofuran (PTHF) with high number-average molecular weight, *i.e.* $M_n > 10$ kDa. However, these systems typically lead to broad molecular weight distributions ($Đ > 2$), limiting their applicability in precision polymer synthesis.

While lanthanide-based catalysts have been widely studied for cyclic ester polymerisations,[13,14] their application to cyclic ethers remains comparatively underexplored. Notably, lanthanide triflates can mediate the ROP of THF, but only in the presence of an epoxide initiator.[15] More recently, hydrated lanthanide chloride salts, $LnCl_3{\cdot}xH_2O$ (Ln = La, Ce, Nd, Sm, Gd, Y, Ho and Tm; $x = 6/7$), have been reported to facilitate the ring-opening copolymerisation of epoxides and cyclic anhydrides.[16] To the best of our knowledge, synergistic interactions between rare earth (RE) and transition metal (TM) centres in polymerization catalysis have only been investigated for ROP of L-lactide, predominantly employing Salen-type Schiff-base ligands.[17] Notably, there is no well-documented example in the literature of lanthanide-based heterobimetallic catalysts specifically applied to the ROP of THF.[18,19]

To advance lanthanide-based ROP of cyclic ethers, we present a heterobimetallic catalyst system combining $RECl_3$ (RE = La, Ce, Nd, Sm), and $[Cu(CH_3CN)_4]PF_6$, inspired by nature's paradigm of bimetallic synergy.[20,21] This cooperative pairing of a Lewis acidic RE and a soft TM enables the efficient bulk ROP of THF, yielding high-molecular-weight PTHF at low catalyst concentrations and without an additional initiator (Scheme 1). Given the complexity of multimetallic systems and the multifaceted roles of the metals involved, we use the term "catalyst" throughout, acknowledging the difficulty in distinguishing it from an initiator.[17]



Scheme 1 Reaction of the bulk ROP of THF using 0.1 mol% ($RECl_3/[Cu(CH_3CN)_4]PF_6$) as catalyst at room temperature.

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For the bulk polymerisation reactions, the metal precursors were homogeneously dispersed in a Schlenk flask under argon atmosphere prior to the addition of THF (Fig. S1). No external initiator was added. Reactions were conducted at room temperature (25 °C) and limited to a maximum duration of 5 hours for the ease of handling of the resulting product. Initial washing of the crude product with cold methanol has proven to be insufficient to fully remove residual copper species, as indicated by the yellow colour of the isolated polymer (Fig. S2a). To obtain a pure polymer, the crude PTHF had to be re-dissolved in THF and purified by column chromatography. The eluted product solution was subsequently re-precipitated in cold methanol to yield the pure, colourless polymer (Fig. S2c).

To further investigate rare earth–transition metal cooperativity in the ROP catalysis of THF, a range of metal and counterion combinations were screened to determine whether the observed activity arose from the metal centres themselves or from any associated counterions (Table 1). Neither Cu(I) nor RE(III) compounds alone exhibited any catalytic activity, underscoring the necessity of heterobimetallic cooperativity. Aside from the original $RECl_3/[Cu(MeCN)_4]PF_6$ (RE = La, Ce, Nd and Sm) systems, none of the tested combinations, including other rare earth chlorides (Sc, Y, Eu, Gd, Tb, Dy, Er, Yb, Lu) with $[Cu(MeCN)_4]PF_6$, showed any polymerisation activity.

Depending on the $RECl_3$ employed in combination with the Cu(I) precursor, analysis of the obtained PTHF by size exclusion chromatography (SEC) revealed M_n ranging from 137 kDa to 209 kDa, with narrow dispersities ($Đ \approx 1.6$). These results were achieved with just 0.1 mol% total catalyst loading (Table 2), comprising 0.05 mol% each of $RECl_3$ and $[Cu(MeCN)_4]PF_6$. This corresponds to a significantly lower catalyst concentration leading to a very high molecular weight PTHF compared to literature reports, which typically employ 0.07 to 0.5 mol% catalyst along with an additional initiator yielding M_n in the range of 1–60 kDa for the ROP of THF.[7,15] The high molecular weight of the resulting PTHF likely stems from THF pre-organization by the rare earth chlorides, which promotes propagation and limits multiple monomer activation. Additionally, the non-nucleophilic PF_6^- ion may stabilize the oxonium intermediate, favouring chain growth over termination.[22]

Table 1 Catalyst screening. AIBN = azobisisobutyronitrile. Reaction conditions: room temperature, 5 hours, 0.1 mol% total catalyst conc. No polymerisation activity could be detected in all of the cases during 5 h reaction time

Anion screening	Cation screening
$SmCl_3$	$SmCl_3$ + CuCl
$[Cu(MeCN)_4]PF_6$	$SmCl_3$ + $CuCl_2$
$Sc(OTf)_3$	$SmCl_3$ + NH_4PF_6
$ScCl_3$ + $[Cu(MeCN)_4]PF_6$	$SmCl_3$ + $[Cu(MeCN)_4]OTf$
$Sc(OTf)_3$ + $[Cu(MeCN)_4]PF_6$	$Sm(OAc)_3$ + CuCl
YCl_3 + $[Cu(MeCN)_4]PF_6$	$Sm(OAc)_3$ + $CuCl_2$
$SmCl_3$ + $[Ni(MeCN)_4](BF_4)_2$	$Sm(OAc)_3$ + $[Cu(MeCN)_4]PF_6$
$LaCl_3$ + $NaPF_6$	$Sm(OTf)_3$ + $[Cu(MeCN)_4]PF_6$
$La(BH_4)_3$ + $[Cu(CH_3CN)_4PF_6]$	$SmCl_3$ + AIBN
LaI_3 + $[Cu(CH_3CN)_4PF_6]$	

Table 2 M_n and dispersity ($Đ$) of PTHF using various RE chlorides in combination with $[Cu(CH_3CN)_4]PF_6$ as catalyst. Reaction conditions: room temperature, 5 hours, 0.1 mol% total catalyst conc.

Entry	$RECl_3$	M_n (kDa)	$Đ$
1	$LaCl_3$	193	1.6
2	$LaCl_3$ + PPO	77	1.6
3	$CeCl_3$ [a]	176	1.6
4	$NdCl_3$	149	1.5
5	$SmCl_3$ [a]	171	1.6

[a] Average value, due to large experimental error.

Based on the rare earth ion screening, the bimetallic combination La(III)/Cu(I) was identified as an optimal catalyst combination, producing PTHF with consistent M_n (Fig. S14). This catalytic system exhibited significantly better reproducibility than the Ce(III) and Sm(III) (Fig. S15 and S17) analogues, which showed deviations of up to ±35 kDa. In contrast, the Nd(III) system yielded PTHF with notably lower molecular weights (Fig. S16). Additionally, La(III) offers a cost advantage over other lanthanides, making it both technically effective and economically favourable for catalytic applications. Beyond SEC characterisation, the resulting polymer was characterised by ^1H NMR spectroscopy (Fig. S9), confirming the formation of PTHF with characteristic peaks at 3.41 ppm (m) and at 1.61 ppm (m), which agree with literature reports.[23]

A monomer conversion study was performed gravimetrically and by ^1H NMR spectroscopy at room temperature using 0.1 mol% $LaCl_3/[Cu(CH_3CN)_4]PF_6$ (Fig. S4). The lower conversion observed gravimetrically can be attributed to polymer loss during the purification by column chromatography and precipitation. Nevertheless, in both cases, the results showed a steady increase in polymer yield over time, as illustrated in Fig. S3, which indicated a progressive monomer consumption. Consistent with this trend, the M_n of the resulting PTHF increased in a controlled manner with reaction times up to 7 h, supporting a chain-growth mechanism (Fig. 1).

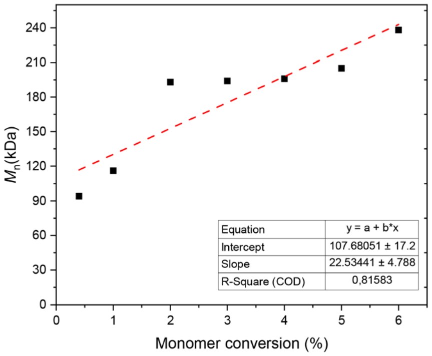


Fig. 1 Linear regression of M_n *vs.* monomer conversion determined by ^1HNMR spectroscopy at room temperature using 0.1 mol% ($LaCl_3/[Cu(CH_3CN)_4]PF_6$) as catalyst.

Simultaneously narrow dispersities are maintained. Beyond 7 h reaction time, however, M_n values became highly inconsistent (Table S5). This observation aligns with the established understanding that the "living" nature of THF polymerization diminishes at high conversions.[24–26] This behaviour is attributed to the dynamic equilibria between monomer, oligomers, and polymers, driven by THF's low ceiling temperature.

To further explore the $LaCl_3/[Cu(CH_3CN)_4]PF_6$ catalyst system, a design of experiments (DOE) approach was employed to investigate the effects of reaction time and catalyst concentration on the yield and M_n of the resulting PTHF.[27] In the context of ROP, the polymer yield provides insights into the extent of monomer consumption and the overall efficiency of the reaction. In contrast, the molecular weight of the resulting polymer is a critical parameter for assessing the material's physical and mechanical properties, as it directly influences the polymers characteristics, such as viscosity, elasticity, and processability. To evaluate the systems variability and detect potential curvature, a two-level full factorial design was performed, comprising four experiments at each factor combination and three independent centre point replicates (Table 3). Time and catalyst concentrations were chosen based on preliminary experiments to span a range with measurable effects on the catalytic performance. In addition to design-based replicates, multiple SEC measurements were performed, yielding an estimated M_n error of ~2%.

The main and interaction effects were analysed, with the main effects being displayed in Fig. 2 and interaction plots being provided in the SI (Fig. S8).

In accordance with literature, the DOE approach has shown that the polymer yield depends on both time and catalyst concentration, where time had a more pronounced effect. Specifically, the yield increased from 3% to 40% between 4.5 h and 9.5 h, whereas the variation in catalyst concentration resulted in a smaller change, namely from 17% to 30%. Aouissi *et al.* reported similar trends, yet the significance was greater for the catalyst concentration than for the reaction time, opposite to what was observed in our system.[28] In contrast to the yield, the molecular weight exhibited a volcano-shaped dependence on both catalyst concentration and reaction time, reaching a maximum of 240 kDa at the centre point of the experimental design. This trend can be rationalised by considering the dual role of the catalyst concentration. At moderate concentrations, the catalytic efficiency increases, promoting effective monomer conversion and chain propagation. However, at higher concentrations, the elevated number of monomer units per active site facilitates side reactions, such as chain branching and backbiting, which ultimately reduce the molecular weight.[23] A similar pattern was observed in terms of reaction time. Initially, extended reaction times led to an increase in M_n, due to prolonged chain growth. Nevertheless, beyond 7 hours, the prevalence of side reactions intensified, resulting in a decline in M_n. Although interaction effects between catalyst concentration and reaction time were found to be slightly positive across all response variables, their influence was minimal compared to the dominant main effects.

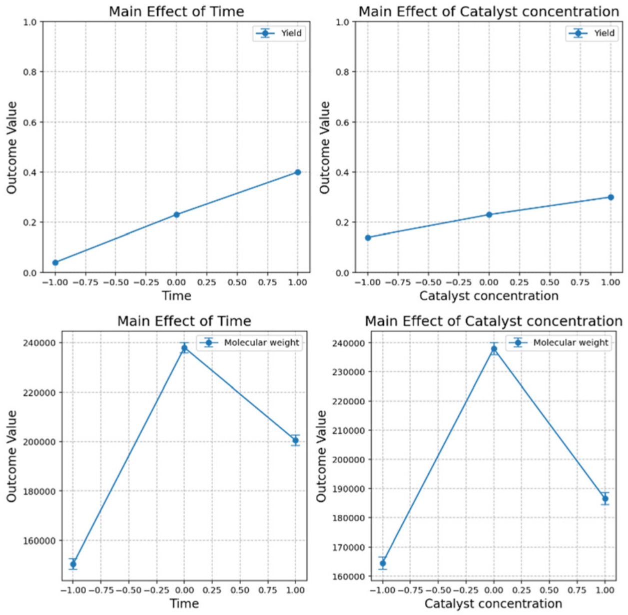


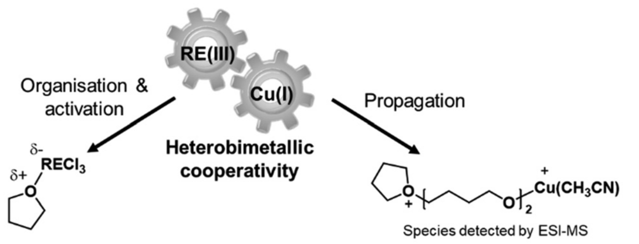
Fig. 2 The main effects of reaction time (left) and catalyst concentration (right) on yield (%) and M_n (kDa) of the resulting polymer, based on 2^2 full factorial design with three centre point replicates. Reaction conditions vary based on the factor levels.

Table 3 Factor levels and corresponding values for the factors time and catalyst amount. $LaCl_3/[Cu(MeCN)_4]PF_6$ was selected as catalytic system

Factor level	Time (h)	Catalyst conc. (mol%)
−1	4.5	0.05
0	7	0.1
+1	9.5	0.2

To reveal key insights into the ROP pathway, electrospray ionisation mass spectrometry (ESI-MS) analysis of a reaction aliquot taken at the start of the reaction using 0.1 mol% of the La(III)/Cu(I) catalyst system was conducted. These results strongly suggest a key role of Cu(I) in the tertiary oxonium ion formation. The fact that in the absence of rare earths, the polymerisation does not proceed, indicates the essential cooperative effect between Cu(I) and RE(III). Lanthanides may assist in pre-organising and activating[15] the THF monomer *via* RE–O (THF) coordination, effectively lowering the activation barrier for the Cu(I)–THF interaction and subsequent oxonium ion formation (Scheme 2).

Beyond the role of the metals, anions have found to have a profound impact on the polymerisation activity, since the oxonium ion intermediate can be stabilised by weakly coordinating counterions, such as PF_6^-,[22,29] BF_4^-,[30] or $CF_3SO_3^-$.[31] ESI-MS (Fig. S32) and $^{31}P\{^1H\}$ NMR spectroscopy (Fig. S5) showed PF_6^- signals, with slight degradation over time. The absence of detectable PF_5 species effectively rules out its participation in the initiation step.



Scheme 2 Heterobimetallic cooperativity in the ROP of THF *via* RE–O (THF) pre-assembly and Cu(I)-mediated chain propagation.

To tailor the outcome, meaning M_n and $Đ$, of the ROP of THF and therewith involved the properties of the resulting PTHF, equimolar amounts of selected ligands were added to the $LaCl_3/[Cu(CH_3CN)_4]PF_6$ catalyst system. As initial candidates, triphenylphosphine (PPh_3), diphenylphosphine oxide ($Ph_2P(O)H$), and 4,4′-bipyridine were chosen. These ligands span a broad spectrum of donor characteristics, from soft (PPh_3) to hard (4,4′-bipyridine), based on the Hard and Soft Acids and Bases principle.[32] This strategic selection was aimed to probe how ligand donor properties influence the activity and selectivity of the heterobimetallic catalyst. Interestingly, the introduction of these ligands to the rare earth/transition metal system, $LaCl_3$ and $[Cu(CH_3CN)_4]PF_6$, resulted in a complete suppression of polymerisation activity in the timeframe of 5 h, likely due to their strong coordination to either La(III) or Cu(I), which disrupts the synergistic interaction required for the effective monomer activation. When equimolar amounts of tetraphenyl-diphosphane monoxide (PPO) were added to the $LaCl_3/[Cu(CH_3CN)_4]PF_6$ system, the polymerisation was not entirely suppressed but significantly slowed down (Table 1). This was also evident from the lowered viscosity of the reaction mixture in the presence of PPO, and the reduced molecular weight of the polymer (77 kDa). Since PPO offers a hard (O) and a soft (P) donor side, it can be expected that both the metal centres are coordinated to one ligand molecule.[33,34] The partially retained activity highlights PPO's unique role as a modulating ligand, which enables the fine-tuning of the catalyst performance, while preserving the bimetallic cooperation.

We successfully demonstrated the bulk ROP of THF without any Brønsted acid or epoxide initiators by using a new heterobimetallic catalyst. Using only 0.1 mol% of commercially available TM and RE salts, the catalyst enables the formation of high molecular weight polymers with narrow dispersities, underscoring its potential for efficient and controlled polymerization. The reaction proceeds *via* a synergistic interaction between the RE and TM components, as neither species alone could initiate the polymerisation reaction. Conversion studies and a DOE approach support a living-type or at least a controlled polymerisation mechanism. The introduction of a ligand system, *i.e.* PPO, appeared to reduce the polymerisation rate, suggesting that metal coordination may limit the availability of the active metal sites.

Conflicts of interest

There are no conflicts to declare.

Data availability

Further information is available in the supplementary information (SI). Supplementary information: ESI-MS, SEC, ^1H, ^{13}C, COSY, HMQC, and HMBC NMR measurements. See DOI: **https://doi.org/10.1039/d5py00853k**.

Data in open file formats can be found on the NFDI4Cat repository Re-po4Cat (**https://hdl.handle.net/21.11165/4cat/7p68-kd7b**). A pre-print was published on ChemRxiv (**https://doi.org/10.26434/chemrxiv-2025-tcv7p**).

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