Rare Earth Triflates: Remarkable Catalysts for Ring Opening Homo/Copolymerization of Tetrahydrofuran and ε-caprolactone

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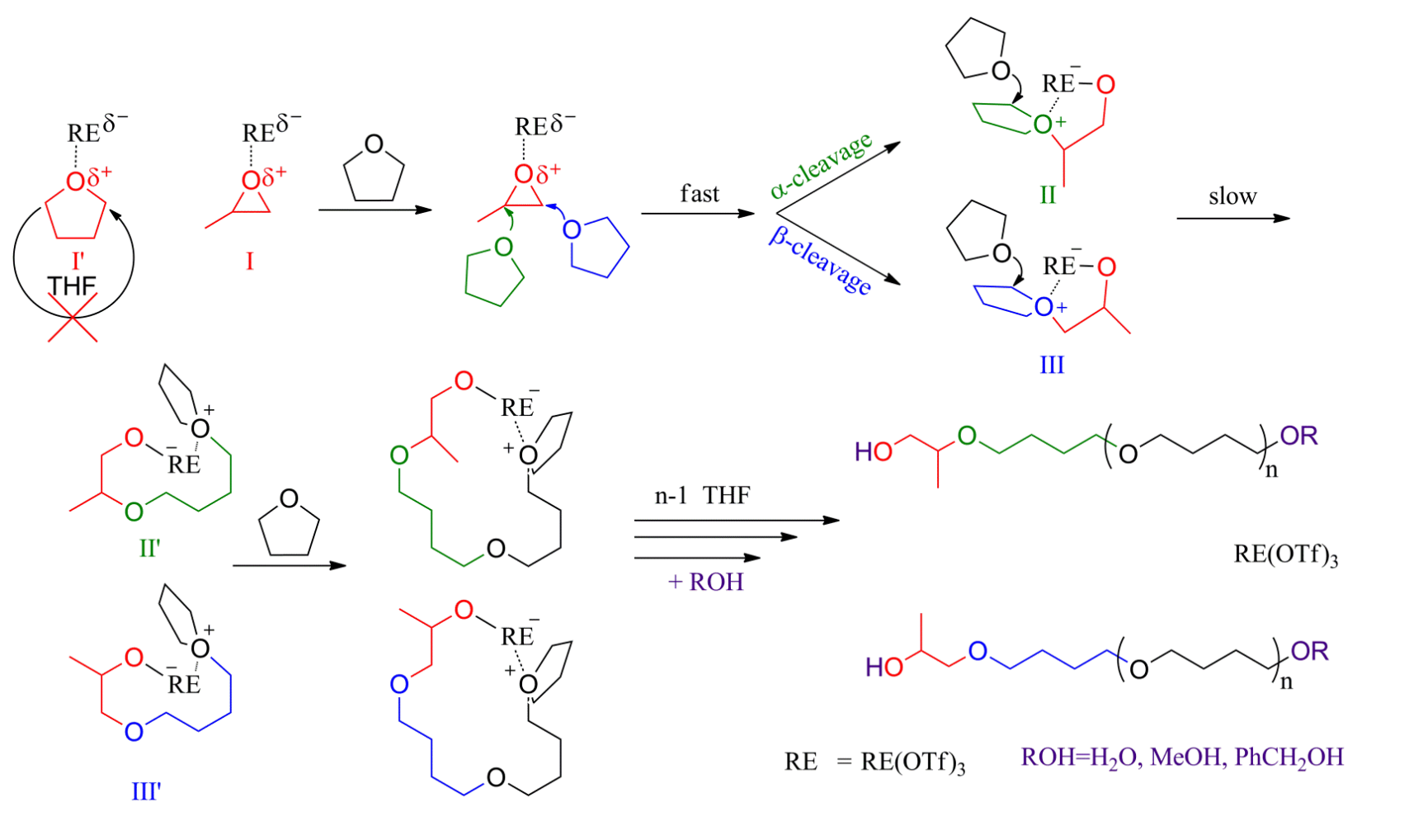
Introduction

Ether-ester copolymers, especially polytetrahydrofuran (PTHF) with poly(ε-caprolactone) (PCL) were synthesized *via* various catalysts. However, all these reported catalysts can only catalyze cationic ring-opening copolymerization of THF and CL, affording copolymers with uncontrolled molecular weights (MWs) and broad molecular weight distributions (MWDs). Long length of homo-PCL segment was absent in the copolymer as only random copolymerization took place. In this work, ring-opening polymerization (ROP) of tetrahydrofuran (THF) and its copolymerization with ε-caprolactone (CL) using lutetium triflates ($Lu(OTf)_3$) catalyst were carried out in the presence of propylene oxide (PO) at 25 °C. With the optimized $[Lu(OTf)_3]_0$:$[PO]_0$:$[THF]_0$:$[CL]_0$ ratio of 1:1.5:200:100, one-pot ROP produced poly(tetrahydrofuran-*co*-ε-caprolactone)-*b*-poly(ε-caprolactone) (P(THF-*co*-CL)-*b*-PCL) with controllable MWs and narrow molecular weight distributions (MWDs) as low as 1.14.

Results and Discussion

Part I. Cationic ring-opening polymerization of THF



Scheme 1. Mechanism of cationic ring-opening polymerization of THF catalyzed by $RE(OTf)_3$/PO, where OTf ligands are omitted for clarity.

Polymerization kinetics

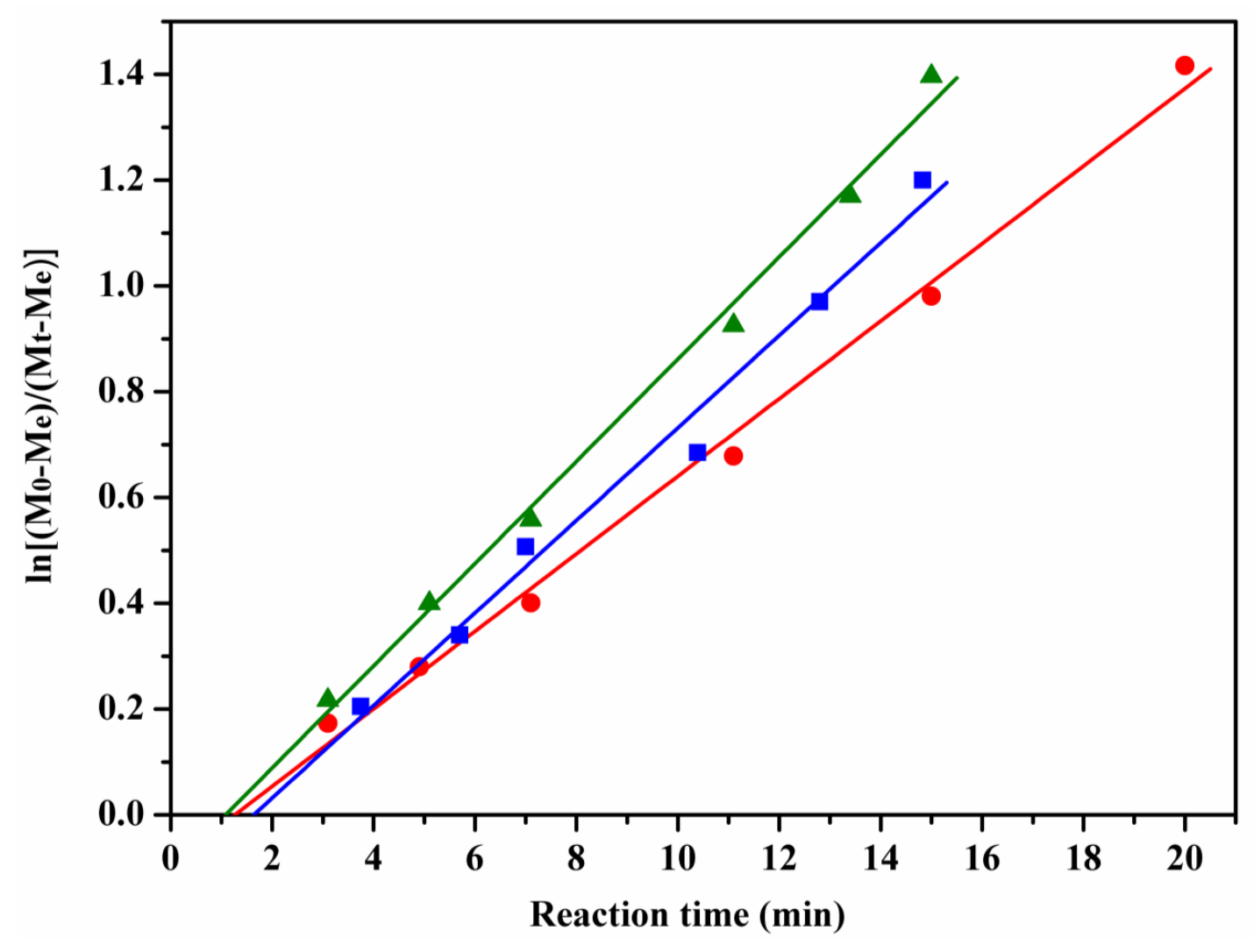
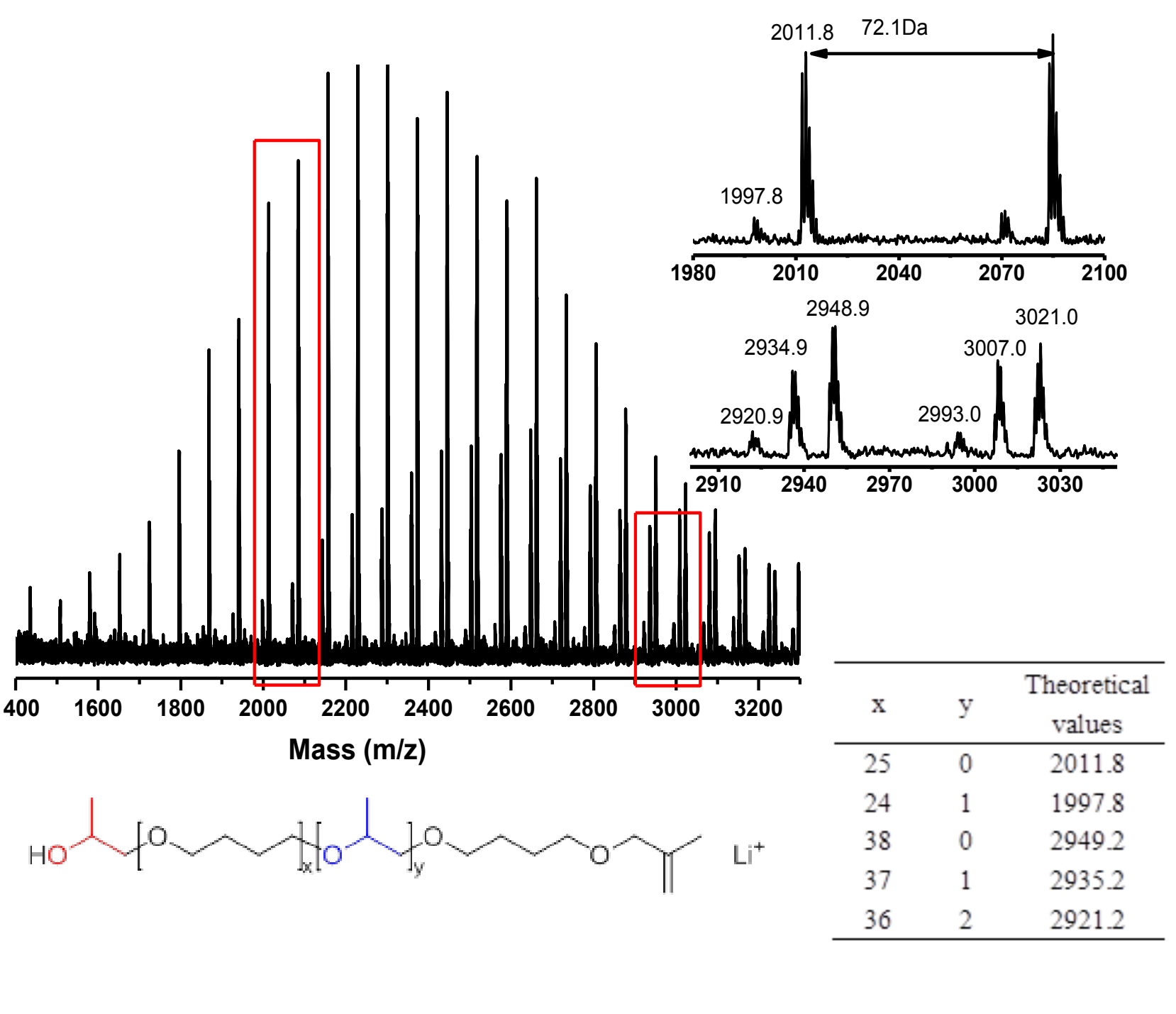


Figure 2. First order kinetic plots of ROP of THF at 25 °C catalyzed by $RE(OTf)_3$ in the presence of PO ([PO]/[RE]=5) in bulk, (▲)$Lu(OTf)_3$; (■)$Y(OTf)_3$; (●) $Sc(OTf)_3$



x	y	Theoretical values
25	0	2011.8
24	1	1997.8
38	0	2949.2
37	1	2935.2
36	2	2921.2

Figure 4. MALDI-ToF MS (Li^+ dopping) of α-hydroxy-ω-vinyl-PTHF

Recyclable system using $Sc(OTf)_3$/PO in ROP of THF in bulk

No. of recycle	Time (min)	Conversion (%)	M_n (KDa)	MWD
0	5	18.6	3.8	1.22
1	9	36.0	6.5	1.33
2	5	12.8	3.0	1.23
3	9	30.0	6.8	1.48
4	11	22.5	5.5	1.40
5	18	29.8	9.0	1.45

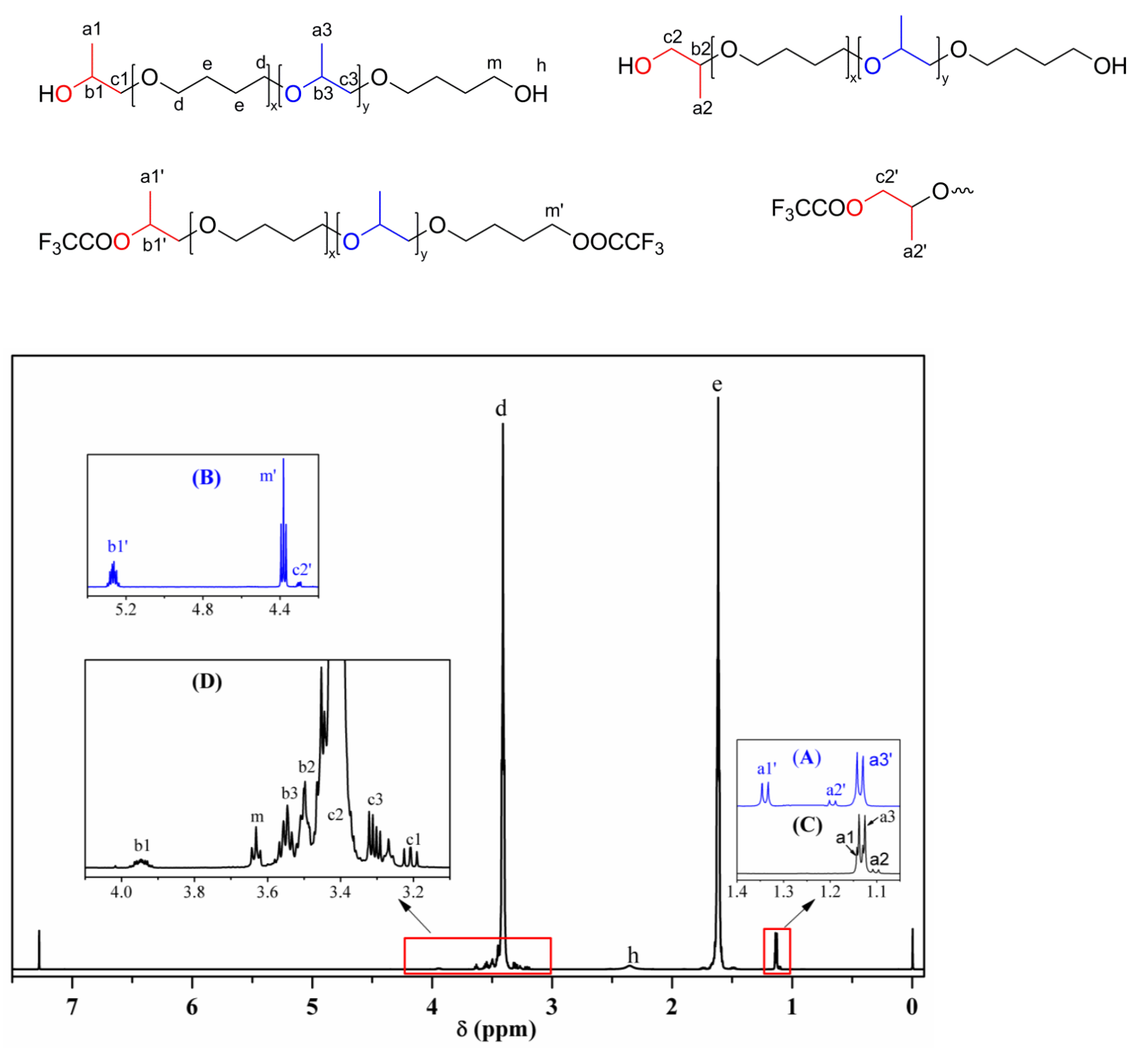


Figure 1. ^1H NMR spectra of PTHF terminated by H_2O including inserts (C) and (D). Spectra (A) and (B) show the corresponding ^1H NMR spectra of the TFA derivatives.

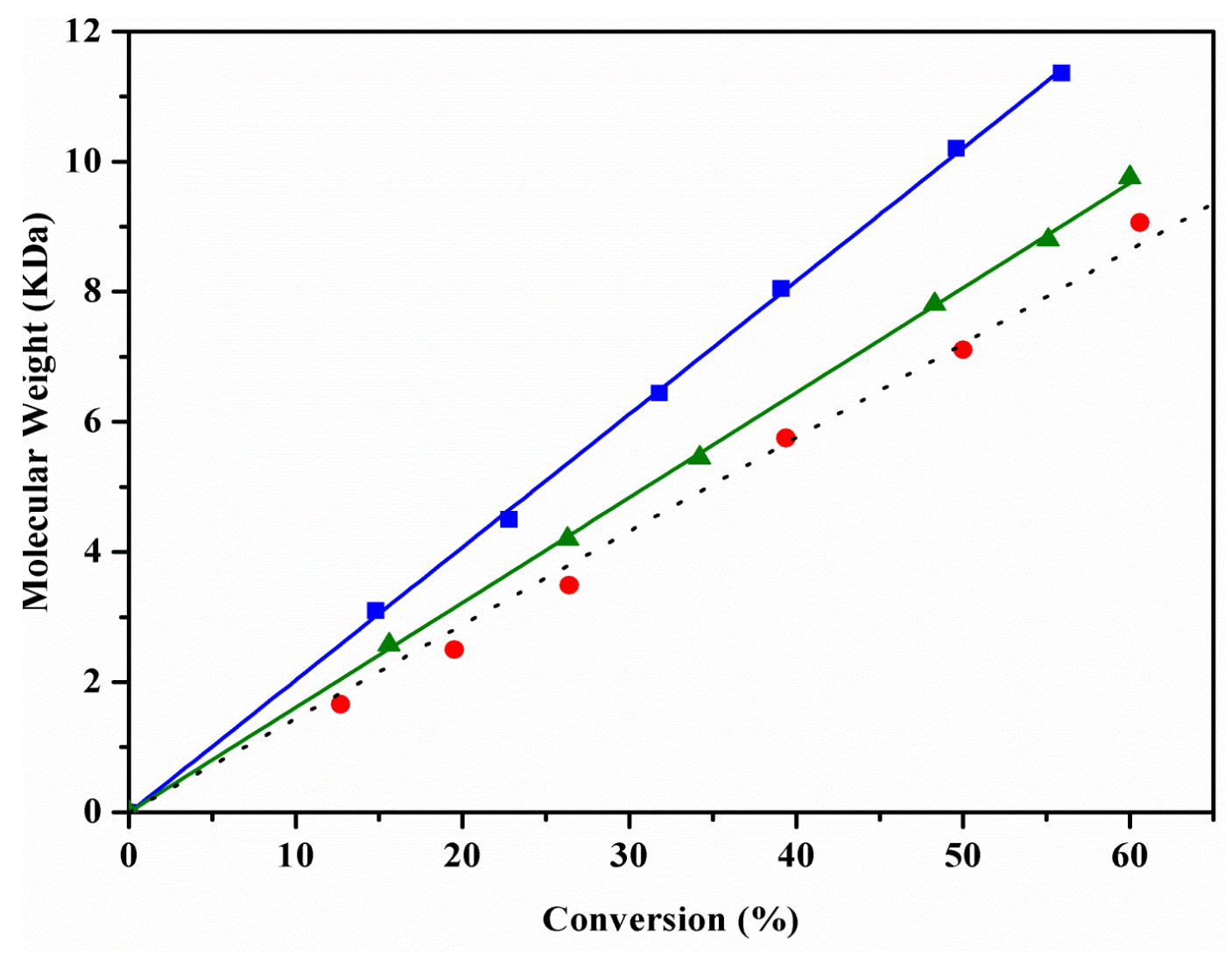


Figure 3. Number-average molecular weight (M_n) as a function of conversion for ROP of THF at 25°C catalyzed by $RE(OTf)_3$ in the presence of PO: (■)$Y(OTf)_3$; (▲)$Lu(OTf)_3$; (●) $Sc(OTf)_3$

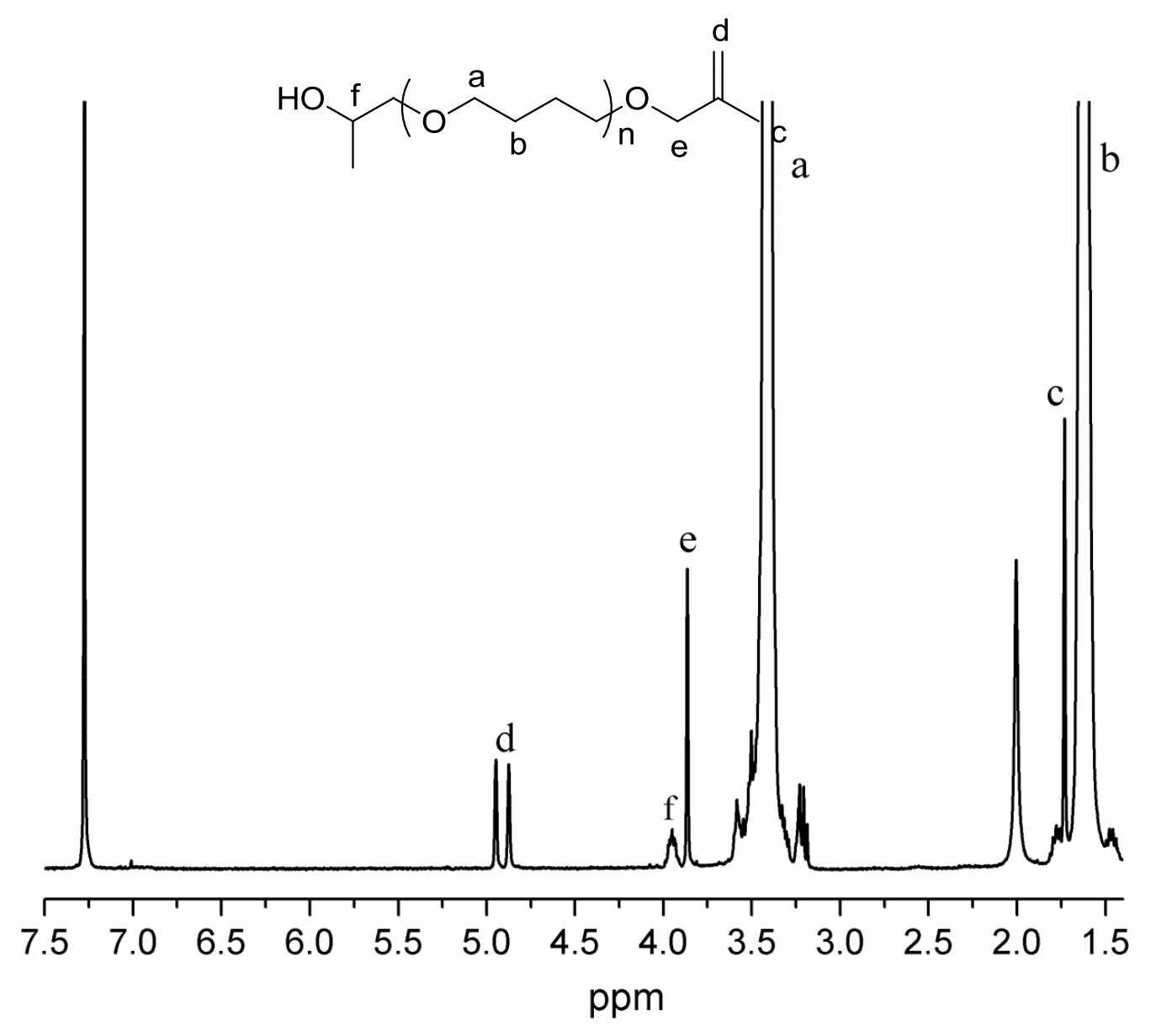


Figure 5. ^1H NMR spectra of the obtained PTHFs functionalized by 2-methylallyl alcohol (MAA)

In conclusion, Rare earth metal triflates [$RE(OTf)_3$, RE=Sc, Y, and Lu] are highly effective catalysts for ROP of THF in the presence of PO .The $Sc(OTf)_3$/PO system catalyzes bulk polymerization in a controlled/living fashion giving predicted MWs and MWDs as low as 1.2. The repeated (up to 6 times) use of a recyclable $Sc(OTf)_3$ catalyst for ROP of THF was demonstrated for the first time.

Part II. *Janus Polymerization*: affording multiblock [PCL-*b*-P(THF-*co*-CL)]$_m$ elastomers in one-step.

Table 1. Copolymerization of THF with CL catalyzed by $Lu(OTf)_3$/PO [a]

Run	Time (h)	Conversion (%) THF	Conversion (%) CL	$M_{n(theo)}$ (KDa)	$M_{n(NMR)}$ (KDa)	$M_{n(SEC)}$ (KDa)	MWD
1	3.5h	2.1	1.2	-	-	-	-
2	17h	8.8	4.8	1.9	2.3	5.08	1.34
3	48h	10.4	37.0	5.8	6.3	11.7	1.15
4	59h	10.4	80.1	10.7	11.3	21.5	1.14
5	109h	24.5	100	14.8	-	64.8	1.81
6	11d	36.8	100	17.4	-	181.0	1.81

[a] Polymerization conditions: $[Lu(OTf)_3]_0$:$[PO]_0$:$[THF]_0$:$[CL]_0$ = 1:1.5:200:100 at 25 °C without solvents.

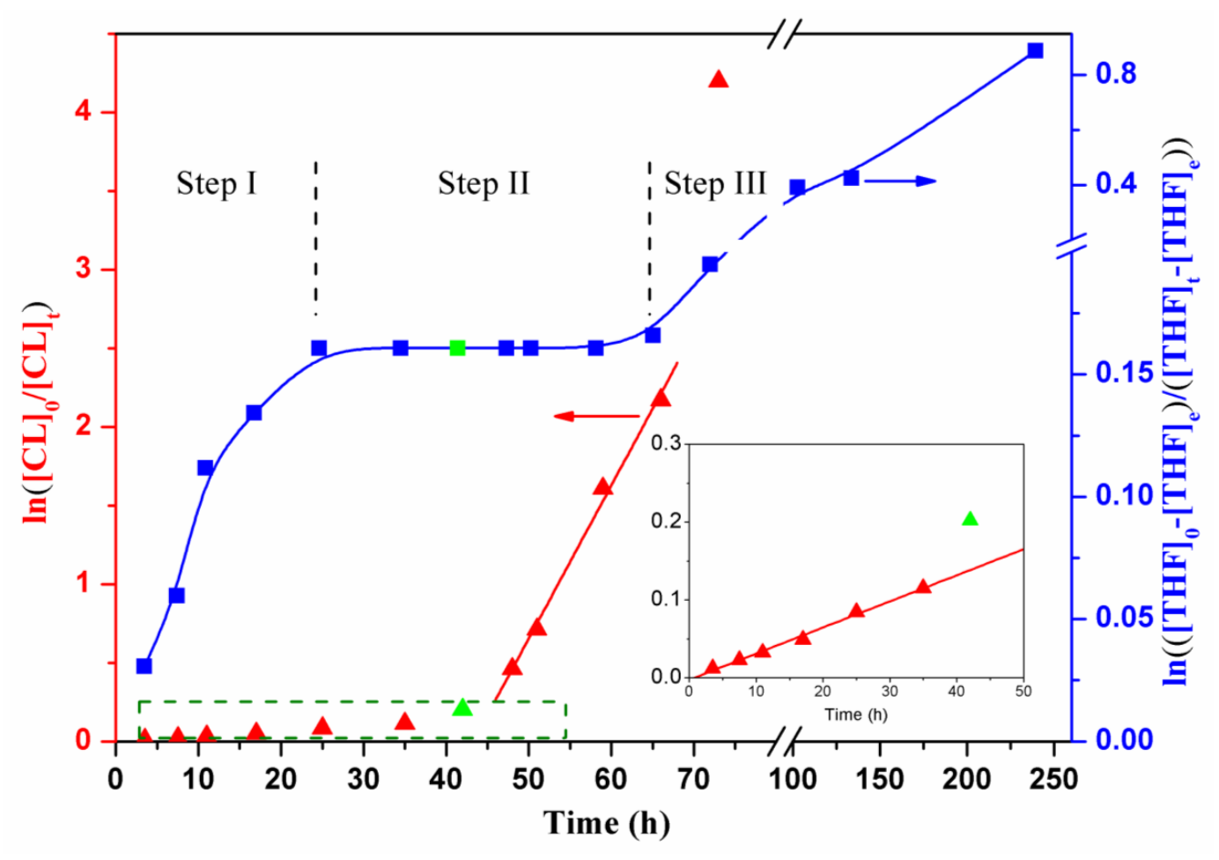


Figure 7. First order kinetic plots of copolymerizatiion of THF and CL (blue line, THF; red line, CL) catalyzed by $Lu(OTf)_3$ in the presence of PO : $[Lu(OTf)_3]_0$:$[PO]_0$:$[THF]_0$:$[CL]_0$ = 1:1.5:200:100.

PO was in the middle rather than chain end

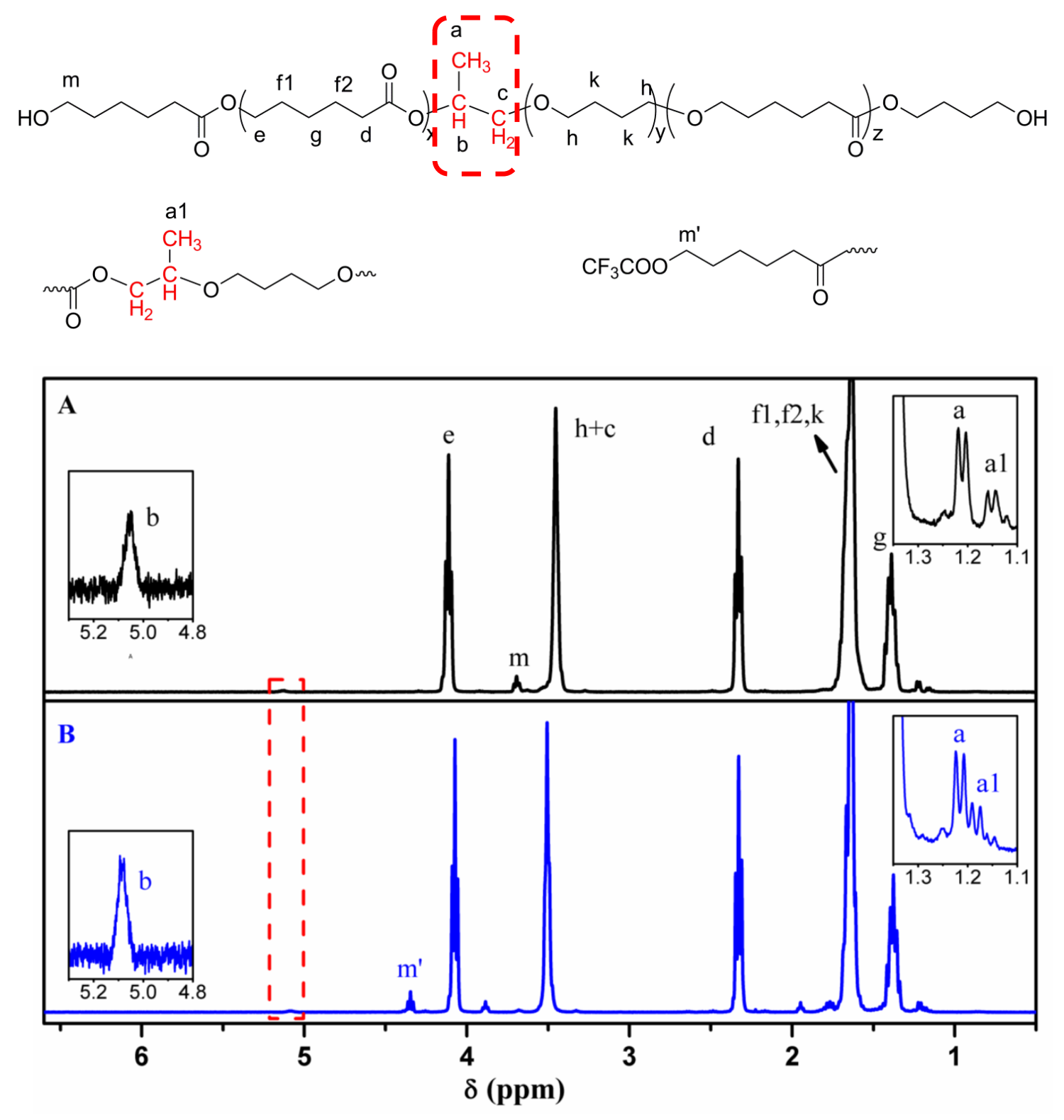
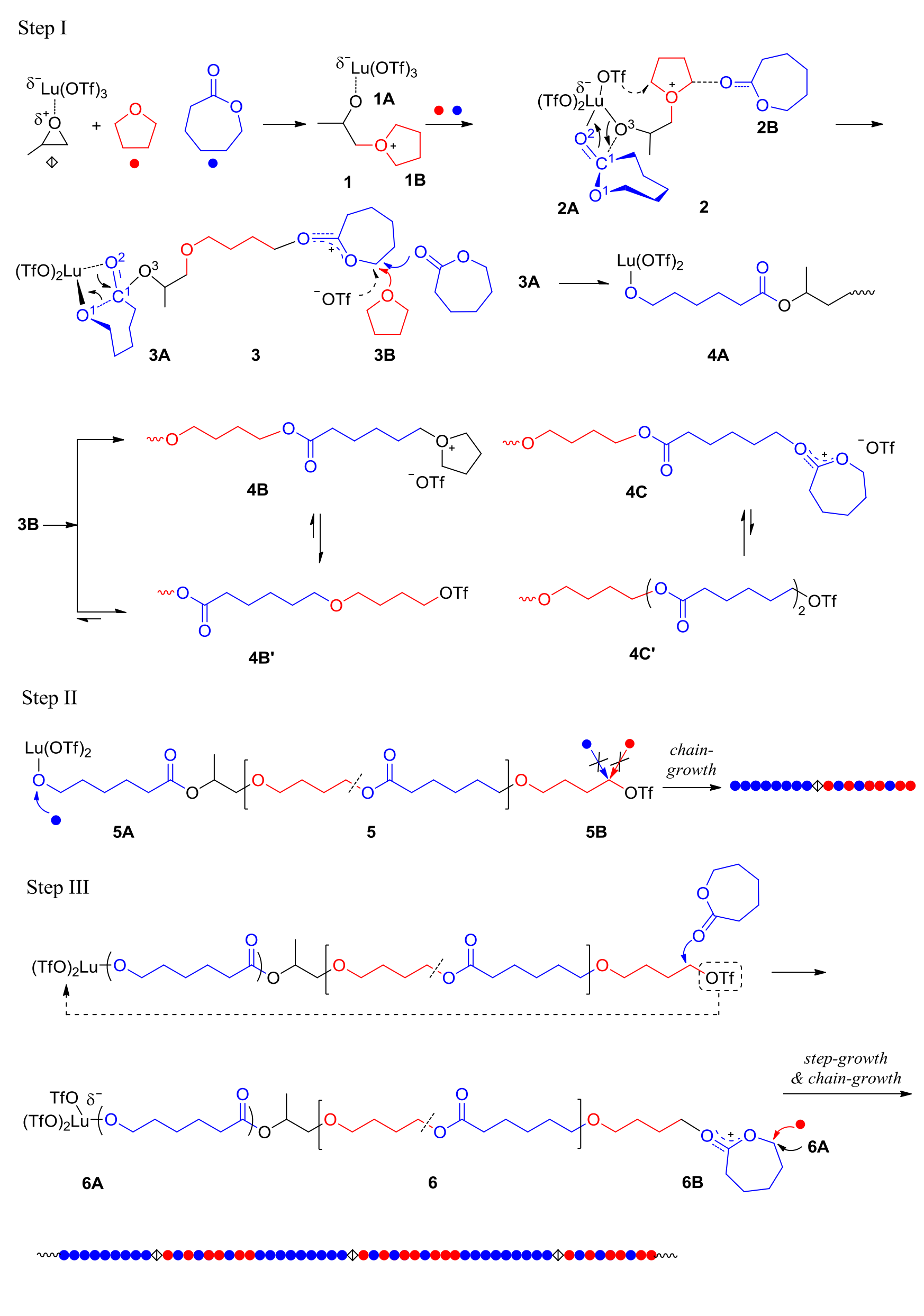


Figure 6. ^1H NMR spectra of P(THF-*co*-CL)-*b*-PCL terminated by H_2O (Table 1, run 3) without (A) and with trifluoroacetic anhydride (B).

Proposed Mechanism



Scheme 2. Mechanismof copolymerization of THF and CL catalyzed by $Lu(OTf)_3$/PO in bulk.

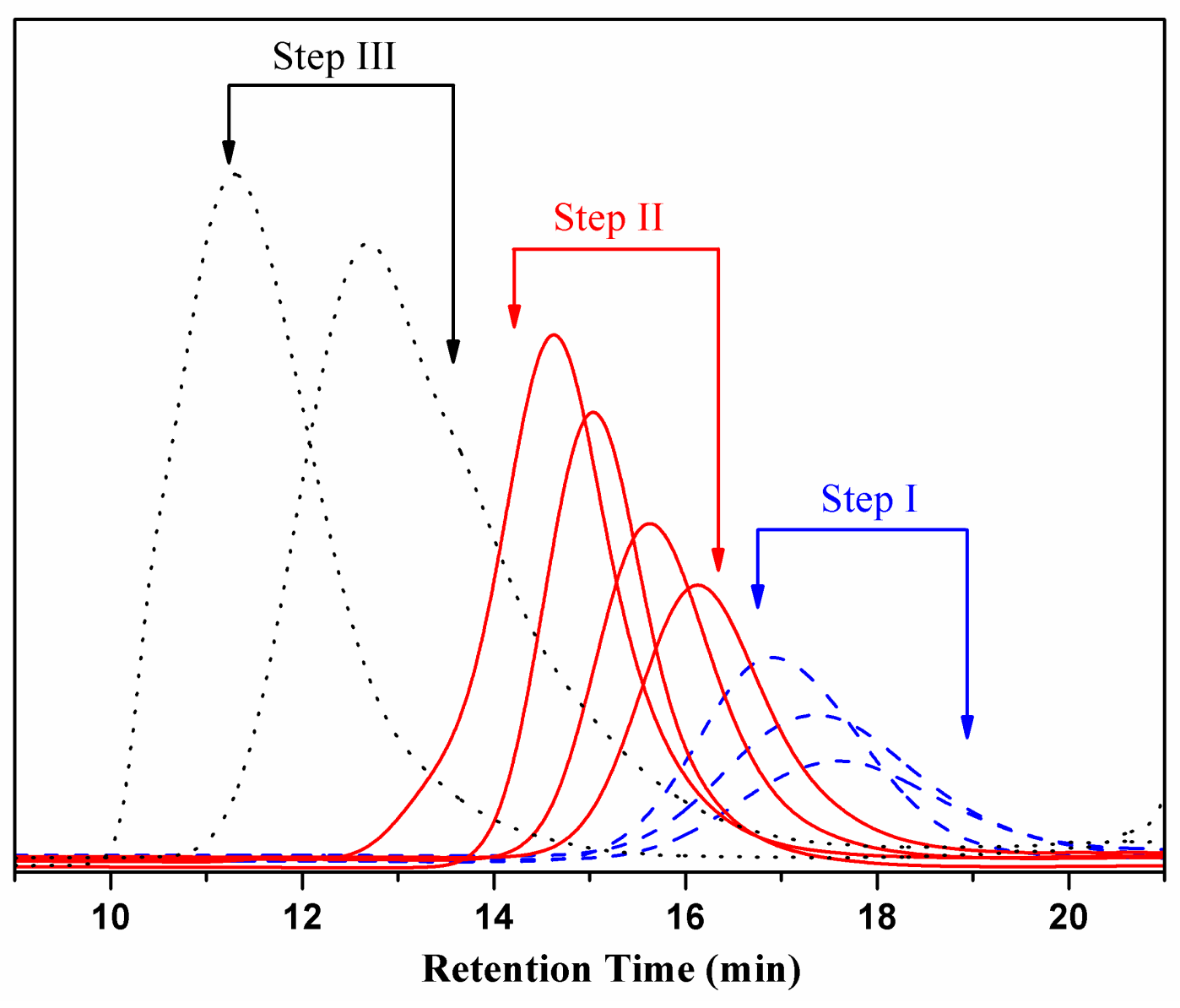


Figure 8. SEC traces of P(THF-co-CL) (Step I, dashed blue line), PCL-b-P(THF-co-CL) (Step II, solid red line) and multiblock [PCL-b-P(THF-co-CL)]m (Step III, dotted black line) copolymers.

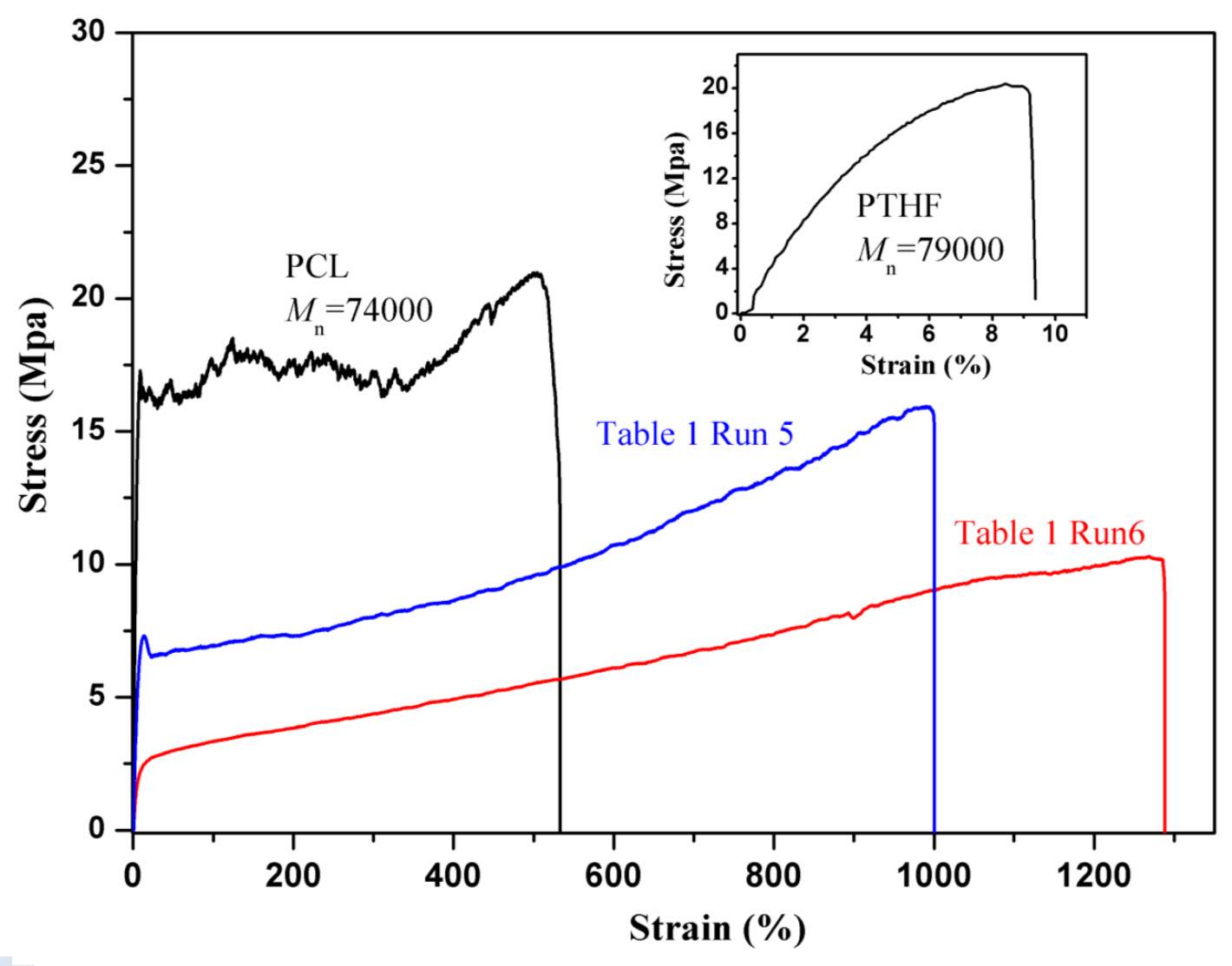


Figure 9. Stress-strain curves for PTHF, PCL and multiblock [PCL-b-P(THF-co-CL)]m copolymers.

CONCLUSION

A Janus polymerization is defined to include a cationic and an anionic polymerizations (CROP and AROP) on both ends of a single living polymer chain. Herein we demonstrate an example to implement such a concept, where $Lu(OTf)_3$/PO is used as the catalytic system for THF and CL polymerizations. It involves three separate steps. In step I the *in situ* generated zwitterionic species **1** initiated simultaneous AROP of CL at **1A** side and CROP of THF with CL at **1B** side, producing PCL and P(THF-*co*-CL) segments, respectively. THF polymerization is suspended in step II due to the deactivation of cationic side, and a living chain-growth AROP of CL is achieved toward high conversion of 90%. After the depletion of CL in step III, the activated cationic propagation sites perform continuous coupling reactions with coordinated anionic ones, which builds up a step-growth polymerization.

A Janus polymerization shall essentially comprise a controlled chain-growth polymerization and the subsequently step-growth polymerization, which, as a consequence, is a feasible way to afford well-defined multiblock copolymers directly from two monomers in a one-step process without any tedious intermediate functionalization reactions or postpolymerizations.

Acknowledgement

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Reference:

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