



Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide

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Abstract: We report the first example of a regioregular and fully alternating poly (propylene monothiocarbonate) (PPMTC) from the well-controlled copolymerization of two asymmetric monomers, carbonyl sulfide (COS) and racemic propylene oxide (*rac*-PO), using (Salen)CrCl in conjunction with bis(triphenylphosphoranylidene) ammonium chloride ([PPN]Cl). The maximum turnover of frequency (TOF) of this catalyst system was 332 h⁻¹ at 25°C. The contents of monothiocarbonate and tail-to-head (T-H) linkages of PPMTC were up to 100%(based on ¹H NMR spectra) and 99.0%(based on ¹³C NMR spectra) respectively. PPMTC samples have number-average molecular weight (*M_n*) up to 25.3 kg/mol with polydispersity index (PDI) of 1.41. The very low decomposition temperature of 137°C and high refractive index (*n_D*) of 1.63 of PPMTC make it a potential scarifying optical adhesive.

Results and Discussion:

1) Binary (Salen)CrCl complex/([PPN]Cl) catalyst system

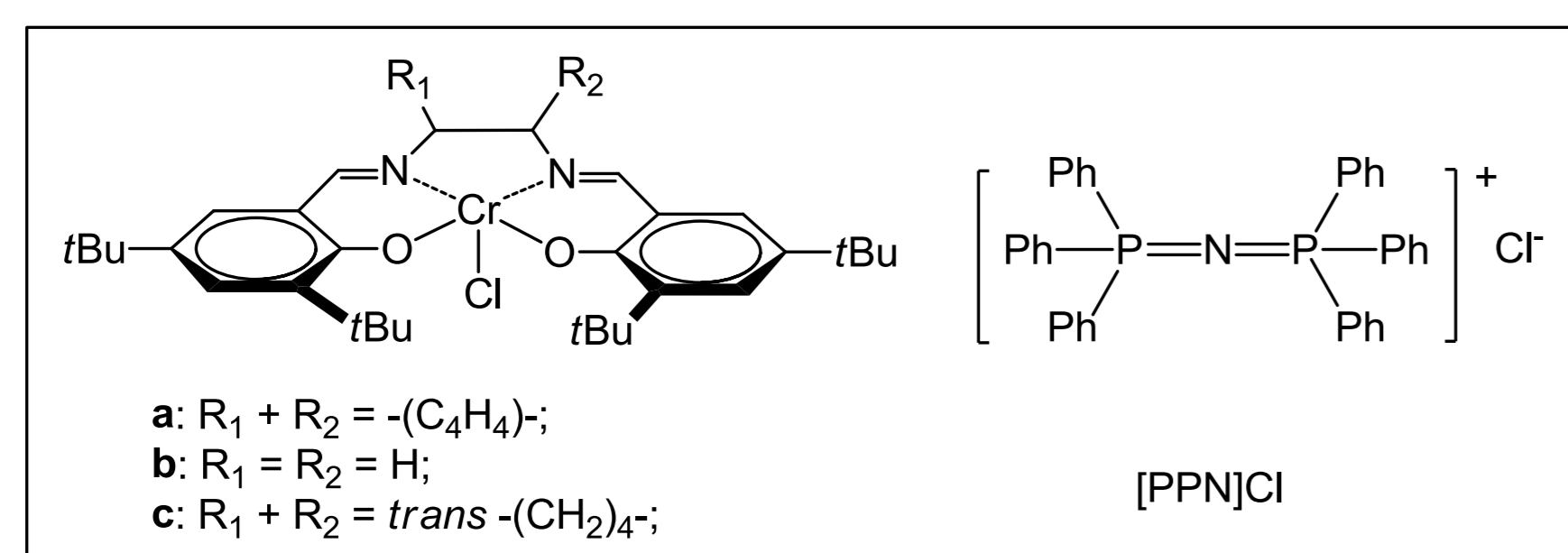


Figure 1. Binary (Salen)CrCl complex/([PPN]Cl) catalyst system

2) the copolymerization of COS/PO yielded PPMTC with contents of monothiocarbonate and tail-to-head linkages up to 100% (based on ¹H NMR spectra) and 99.0%(based on ¹³C NMR spectra) respectively.

Table 1. *Rac*-PO/COS copolymerization results

entry	catalyst	cocatalyst	TOF(h ⁻¹)	copolymer selectivity	PPMTC linkages(%)	T-H linkages (%)	O/S ER product	<i>M_n</i> (kg/mol)	PDI (<i>M_w</i> / <i>M_n</i>)
1	a	[PPN]Cl	288	99/1	100	98.9	N.F	24.4	1.26
2	a	-	N.D	N.D	N.D	N.D	N.D	N.D	N.D
3	-	[PPN]Cl	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4	b	[PPN]Cl	310	99/1	100	99.0	N.F	21.9	1.35
5	c	[PPN]Cl	332	99/1	100	98.6	N.F	25.3	1.41

Reaction conditions : Neat PO (2.0 ml, 28.6 mmol; catalyst/cocatalyst = 1/1, catalyst/PO = 1/1000, COS/PO = 2/1, all in molar ratio) in a 10 ml autoclave at 25°C for 3.0 h.

3) the O/S exchange reaction (O/S ER) was totally depressed. No O/S ER byproducts or structures were found in ¹³C NMR spectra. The -SC(=O)O- was the unique linkage unit in main polymer chain. High temperature was not beneficial to depress the O/S ER.

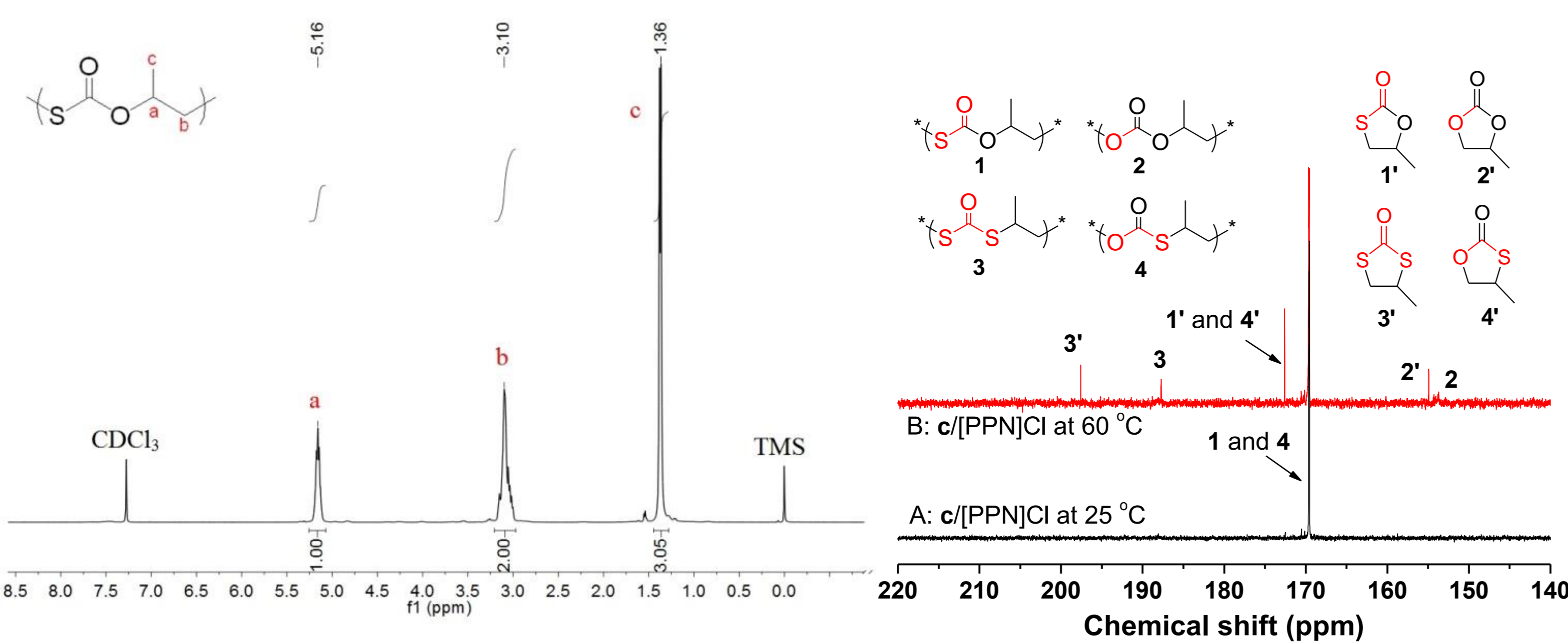


Figure 2. Left: ¹H NMR spectrum of the crude product of entry 1 in Table 1. Right: ¹³C NMR spectra of carbonyl region of the crude products in diverse reaction temperatures.

4) As a result of the effects of the steric hindrance of the methine carbon of PO and the nucleophilic of the sulfur atom of COS, the propagation advanced in a unique way. Thus, the tail-to-head linkages (Figure 3) were in majority of the polymer chain (>98%).

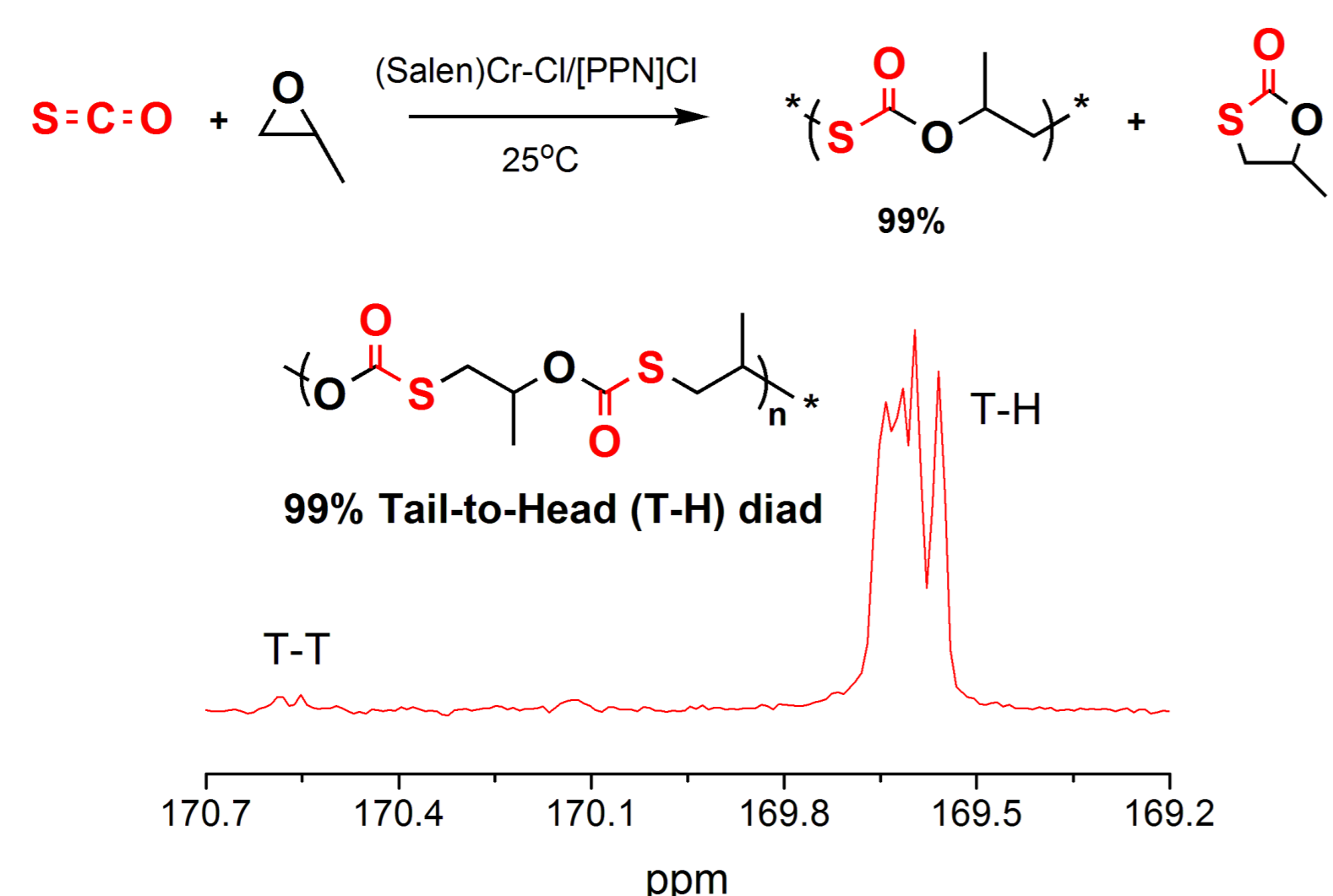


Figure 3. ¹³C NMR spectra of carbonyl region of the purified polymer.

Table 2. *Rac*-PO/COS copolymerization in the presence of various amounts of water

entry	H ₂ O (μL)	H ₂ O:PO (molar ratio)	TOF (h ⁻¹)	copolymer selectivity	PPMTC linkages (mol %)	T-H Linkages (%)	O/S ER Product	<i>M_n</i> (kg/mol)	PDI (<i>M_w</i> / <i>M_n</i>)
1	2.5	1/200	274	99/1	99	97.6	N.F	9.5	1.12
2	5.0	1/100	282	99/1	99	97.1	N.F	8.1	1.08
3	10.0	1/50	288	98/2	99	92.8	F	5.2	1.06
4	15.0	1/33	266	90/10	98	90.9	F	3.9	1.06
5	30.0	1/17	157	86/14	86	76.0	F	1.2	1.15

5) Added water acted as chain transfer agent in the copolymerization. When the molar ratios of H₂O/PO were 1/200~1/33, the TOFs, the selectivity and the alternating degrees of the resultant copolymers kept nearly the same, while *M_n* of the resultant copolymers decreased clearly and PDI kept narrow. And the O/S ER took place when the H₂O/PO molar ratio ≥ 1/50.

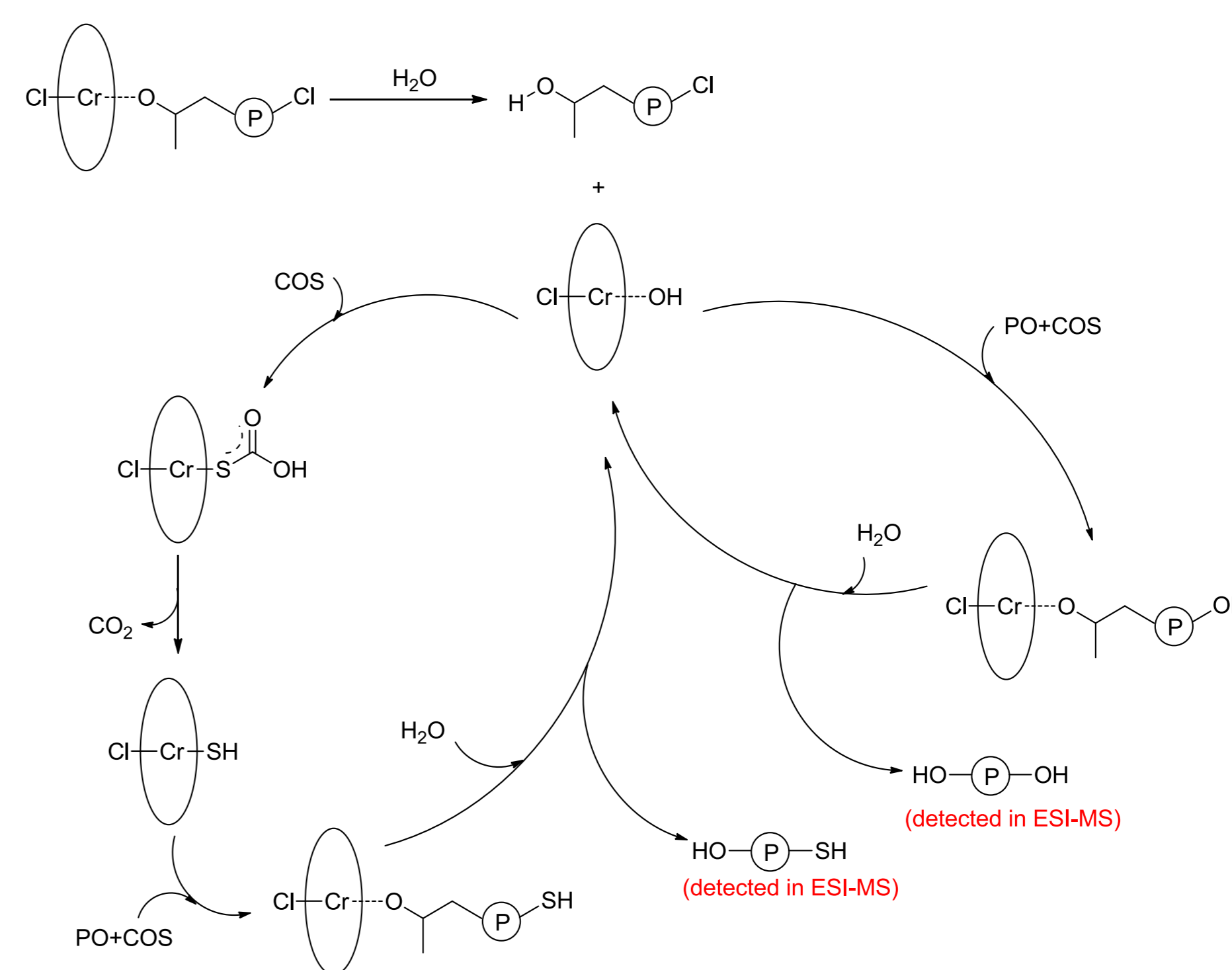


Figure 4. The mechanism of the H₂O as a chain transfer agent.

6) The ESI-MS spectrum of the product of the water-added sample certificated the correctness of the proposed mechanism. The copolymer had three kinds of *m/z* species. No observation of copolymer with -Cl end group indicated that the chain transfer reaction was very fast in the presence of considerable amounts of water.

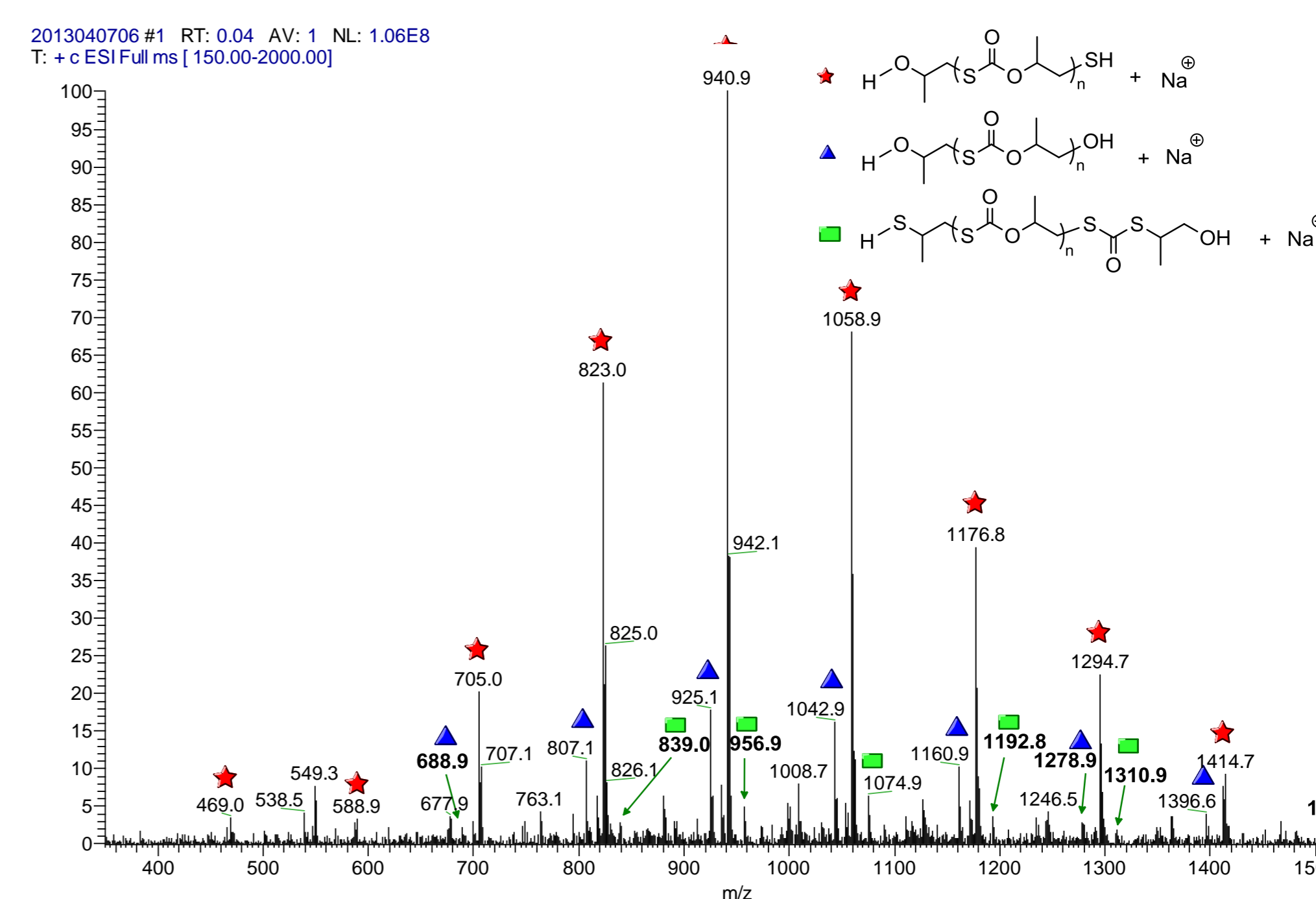


Figure 5. ESI-MS analysis for the products of COS-PO copolymerization.

Conclusion

The regioselective and alternating copolymerization of COS and PO are reported for the first time using the binary (Salen)CrCl/[PPN]Cl catalyst system. The O/S ER could be completely inhibited at 25°C. The resultant copolymers had 98.1–99.0% T–H linkages and full alternating asymmetric monothiocarbonate units. Importantly, it also presented a new copolymerization model involved two asymmetric monomers.

Acknowledgement

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