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Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide

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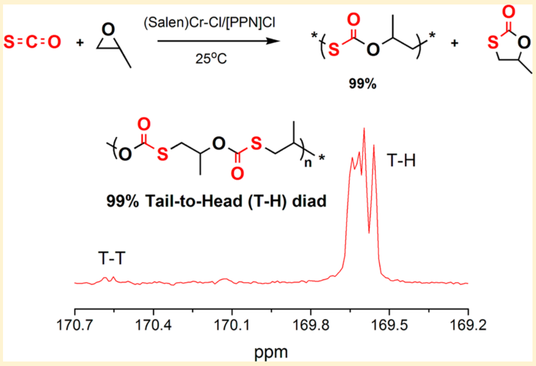
Supporting Information

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 and racemic propylene oxide, using (Salen)CrCl in conjunction with bis(triphenylphosphoranylidene)ammonium chloride. The maximum turnover of frequency of this catalyst system was 332 h^{-1} at 25 °C. The contents of monothiocarbonate and tail-to-head linkages of PPMTC were up to 100% (based on ^1H NMR spectra) and 99.0% (based on ^{13}C NMR spectra), respectively. PPMTC samples have number-average molecular weight (M_n) up to 25.3 kg/mol with polydispersity index of 1.41. The very low decomposition temperature of 137 °C and high refractive index of 1.63 of PPMTC make it a potential scarifying optical adhesive.



■ INTRODUCTION

Carbonyl sulfide (COS) is released from the burning of fossil fuels, coal gas, many chemical processes, volcanic eruption, and plant or protein corruption. Although the COS concentration in the troposphere is currently fairly low (~500 ppt), it causes acid rain and damage of the ozonosphere by a series of photochemical reactions.[1] However, as an asymmetric organosulfur compound with heterocumulene structure, it is an resource of C═O or C═S groups for organic synthetic chemistry.[2] The fixation of COS to chemicals is an intriguing and promising topic in chemistry, but very few publications are reported to date.[3]

Because COS is structurally an analogue of CO_2 (and CS_2), we were strongly motivated to convert COS into polymers, in a way similar with the CO_2−epoxide copolymerization,[4] producing poly(thiocarbonate). This polymeric material has the potential to be applied as photoconductive fiber, heavy metal scavengers, and adhesives because of its high optical properties, excellent chemical resistance, and heavy-metal recognition ability.[5] Although polycondensation,[6] ring-opening polymerization (ROP),[7] and alternating copolymerization[3b,8] (Scheme S1 in the Supporting Information) have been utilized to synthesize poly(thiocarbonate)s, the synthesis of regioregular poly(monothiocarbonate) with asymmetric unit from direct alternating COS-epoxide copolymerization has, up until now, not been reported.

The chemistry involved in COS−epoxide copolymerization process will have all of the issues of CO_2−epoxide copolymerization, including the activity, copolymer selectivity, regioselectivity (for terminated epoxides), enantioselectivity, and control of molecular weight and polydispersity index (PDI).[4c] Moreover, two special problems will be raised when a terminated epoxide (herein propylene oxide, PO) is applied, as shown in Scheme 1.

One is that the oxygen−sulfur exchange reaction (O/S ER) between COS and PO will generate CO_2 and propylene sulfide (PS) in the system.[8b] The crossed copolymerization of the coexistent species (i.e., PO, COS, CO_2, and PS; see Table S1 in the Supporting Information) might occur and produce a copolymer with possible units as **1**−**4** (and cyclic products **1′**−**4′**) in Scheme 1, if assuming preferential coordination of the sulfur atom of COS to the active center (route **A** in Scheme 1).

The other is the stereochemistry control of COS-PO copolymerization involving the two asymmetric monomers. The coordination of the sulfur or oxygen atom of COS to the active center (route **A** or **B** in Scheme 1) will generate −SC(═O)O− and −OC(═S)O− units (**5**) and cyclic byproduct (**5′**), respectively. The occurrence of O/S ER will probably cause the generation of **6** and **6′**. Meanwhile, the attacking manner of propagating species of −OC(═O)S− via route **A** to the carbon of CH_2 or CH of PO will produce four kinds of consecutive monothiocarbonate diads: head-to-tail (H−T), tail-to-head (T−H), tail-to-tail (T−T), and head-to-head (H−H). Note that T−H diad is different from H−T diad due to asymmetric monothiocarbonate structure. All predicted units in the copolymer and cyclic (thio) carbonates are listed in Scheme 1.

Therefore, the selectivity of monothiocarbonate unit **1** depends on the depression extent of O/S ER. We hypothesized

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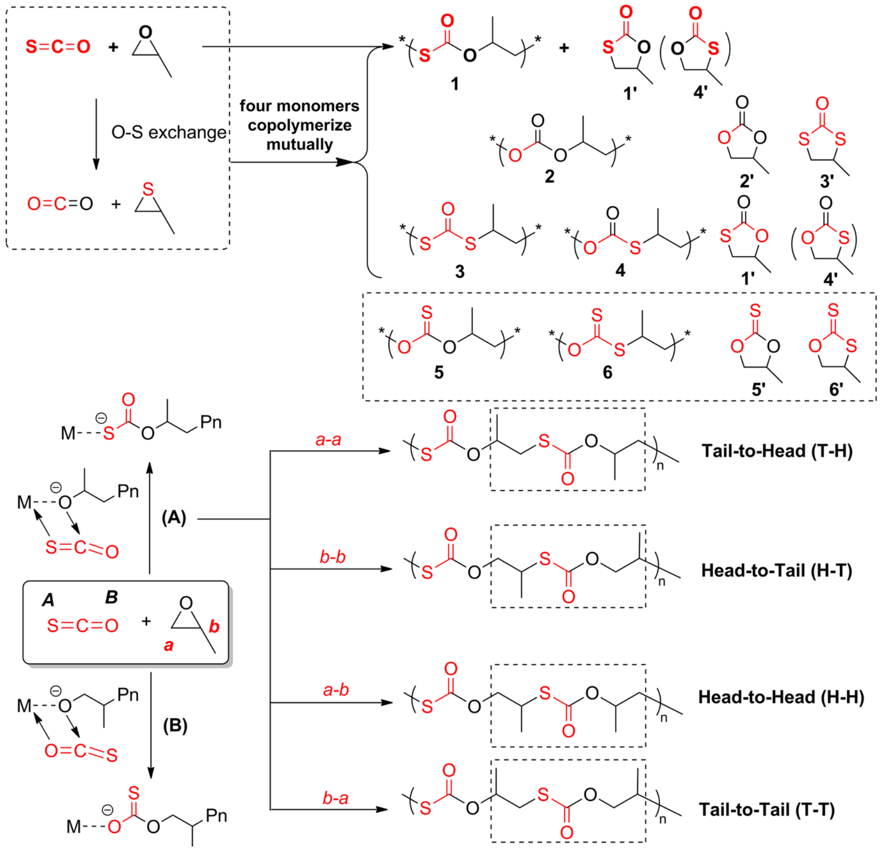
Scheme 1. Prediction of All Possible Products from COS-PO Copolymerization[a]



[a]Upper: If O−S exchange reaction occurs during copolymerization, **1**−**6** and byproducts **1′**-**6′** will be formed by the attack of propagating species to CH_2 of PO. Bottom: Four possible diads of the COS-PO copolymer formed by various regioselective attacks after route **A**.

that metal−OH could result in O/S ER because it was very active to transform CS_2 (or COS) to COS (or CO_2) in the presence of water.[9] Because metal−OH could be generated in our system via chain-transfer reaction of propagating species to trace water,[10] O/S ER could be eliminated by depressing the chain transfer reaction.

In this work, we report the synthesis of a regioregular and fully alternating poly(propylene monothiocarbonate) (PPMTC) by using (Salen)CrCl complexes as the catalysts and the confirmation of the above hypothesis. Several (Salen)CrCl complexes with various diamine backbones (**a**−**c**) were employed (Figure 1) for COS−PO copolymerization in the presence of organic bases (Figure 1, Table S2 in the Supporting Information) because they could catalyze CS_2−epoxides[8a] (and PS[8c]) copolymerization and regioselective CO_2−epoxide copolymerization.[10−12]

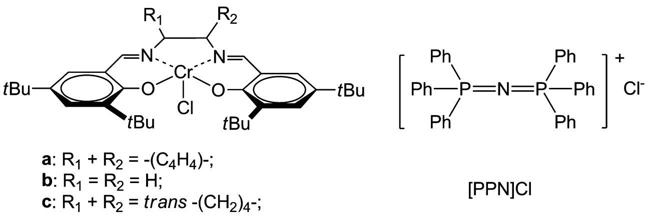
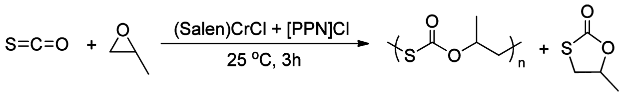


Figure 1. Binary (Salen)CrCl complex/bis(triphenylphosphoranylidene) ammonium chloride ([PPN]Cl) catalyst system used for COS-PO copolymerization.

EXPERIMENTAL SECTION

Method and Materials. All procedures involving air- or moisture-sensitive compounds were carried out in a glovebox under a dry argon atmosphere or with the standard Schlenk technique under dry argon. Propylene oxide (PO) was distilled under a nitrogen atmosphere after drying over CaH_2. COS (99.5%) was purchased from the Mixed Gases Company of Hangzhou New Century and used as received. All of the solvents used were distilled under a nitrogen atmosphere from CaH_2 prior to use. Most of other reagents were used without further purification unless otherwise specified. ^1H and ^{13}C NMR spectra of the resultant copolymers were performed on a Bruker Advance DMX 400 MHz spectrometer. Chemical shift values were referenced to TMS as internal standard at 0.0 ppm for ^1H NMR (400 MHz) and against $CDCl_3$ at 77.0 ppm for ^{13}C NMR (100 MHz, part of samples was characterized by 125 MHz NMR). Molecular weights and molecular weight distributions of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40 °C. The sample concentration was 0.4 wt %, and the injection volume was 100 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular-weight range from 580 to 460 000 Da. Infrared spectra were recorded by using a Bruker Vector 22 FT-IR spectrophotometer. The glass transition temperature (T_g) of the resultant copolymer was determined by using a TA DSC-Q200 differential scanning calorimetry (DSC). The sample was heated in two cycles from room temperature to 80 °C at a rate of 5 °C/min in a nitrogen atmosphere. T_g was determined from the second run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 instrument under a N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 400 °C. Samples for thermal analyses were all purified. The refractive index (*n*D) was measured by Abbe

Table 1. *Rac*-PO/COS Copolymerization Results[a]



entry	catalyst	cocatalyst	TOF (h^{-1})[b]	copolymer selectivity[c]	PPMTC linkages (%)[c]	T-H linkages[d] (%)	O/S ER product[e]	M_n (kg/mol)[f]	PDI (M_w/M_n)[f]
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
6[g]	**c**	[PPN]Cl	266	77/23	100	98.1	F	12.3	1.29
7[h]	**c**	[PPN]Cl	274	97/3	100	94.7	N.F.	6.6	1.06
8[i]	**c**	[PPN]Cl	290	98/2	100	95.2	N.F.	7.3	1.05
9[j]	**c**	[PPN]Cl	282	97/3	100	97.6	N.F.	7.5	1.07

[a] Reaction was performed in 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. [b] (Mol epoxide consumed)/(mol Cr h). [c] Determined by using ^{1}H NMR spectroscopy (Figure S1−5 in the Supporting Information). The polymer selectivity is the molar ratio of polymer **1**/cyclic product. The PPMTC linkages are the molar percentage of monothiocarbonate linkage in polymer chain. [d] Determined by using ^{13}C NMR spectroscopy. [e] Determined by using ^{13}C NMR spectroscopy. O/S ER = oxygen−sulfur exchange reaction. N.F. = not found and F = found. [f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [g] Reaction temperature was 60 °C. [h] (*S*)-PO was used. [i] (*R*)-PO was used. [j] 75%(*S*)-PO/25%(*R*)-PO was used.

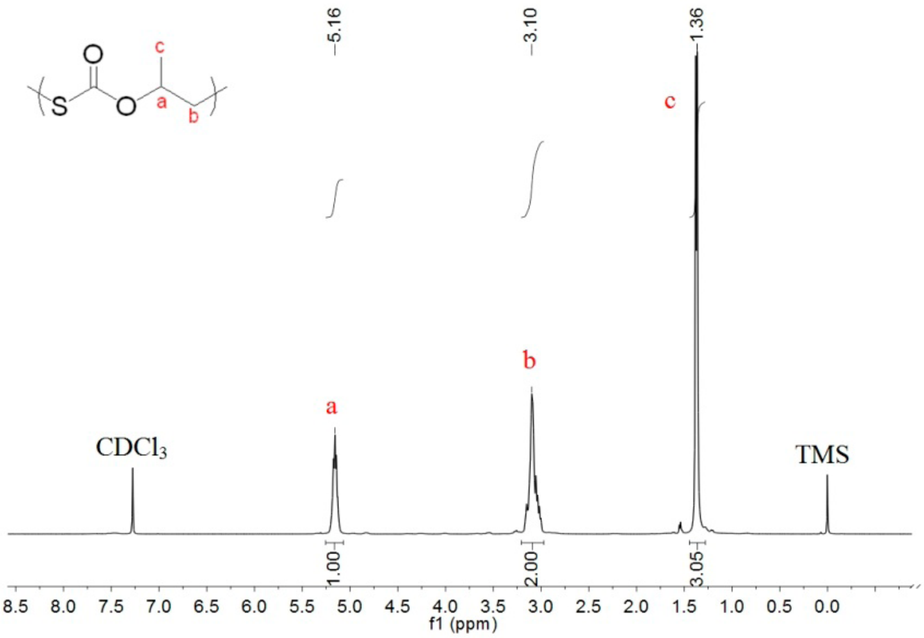


Figure 2. ^{1}H NMR spectrum of the crude product of entry 1 in Table 1.

refractometer. Electrospray ionization-tandem mass spectrometry (ESI−MS) analyses were performed on an Esquire3000 plus mass spectrometer using acetonitrile (CH_3CN) as a solvent for the copolymer. Raman spectra were recorded by using a RM2000 laser Raman spectrometer (powder sample, the measurement range was 100−4000 cm^{-1} resolution of 1 cm^{-1}). The catalysts (Salen)CrCl **a:** *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-benzenediamino chromium(III) chloride, **b:** *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamino chromium(III) chloride, and **c:** (1*R*,2*R*) *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride were synthesized according to the literature method.[11]

Copolymerization of PO with COS. The copolymerization of PO/COS was performed in a 10 mL autoclave equipped with a magnetic stirrer and a barometer. The (Salen)CrCl complex **a** (17.9 mg, 2.86 × 10^{-2} mmol), [PPN]Cl (16.43 mg, 2.86 × 10^{-2} mmol), and PO (2.00 mL, 28.6 mmol) were transferred into the autoclave, which was completely dried in advance. The autoclave was pressurized to the appropriate pressure with COS, and the reaction mixture was stirred at 25 °C for 3.0 h. After copolymerization, the autoclave was cooled and the pressure was slowly vented. The reaction mixture was dried in vacuum at 50 °C for isolating the unreacted reactants and weighed to calculate the TOF of the copolymerization. An aliquot was then taken from the resulting crude product for the determination of the ratio of copolymer **1**/cyclic product **1′** by ^{1}H NMR spectrum. After that, the crude product was dissolved in CH_2Cl_2 (10 mL) and precipitated from methanol (100 mL) three more times. Yellowish precipitate was collected and dried in vacuum at 70 °C to constant weight. The obtained copolymer was analyzed by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, and GPC. ^{1}H NMR ($CDCl_3$) δ 5.19−5.13 (m, 1H), 3.16−3.00 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.58, 73.45, 35.75, 19.01. [propylene monothiocarbonate **1′**: ^{1}H NMR ($CDCl_3$) 4.87−4.79 (m, 1H), 3.57−3.53 (m, 1H), 3.28−3.23 (m, 1H), 1.54 (d, J = 6.2 Hz, 3H)].

RESULTS AND DISCUSSION

Catalyst **a**/[PPN]Cl with a molar ratio of 1.0 was successfully applied to COS-PO copolymerization with a TOF of 288 (i.e.: PO conversion: 86.4%, entry 1 in Table 1). Blank reactions showed that **a** or [PPN]Cl did not solely catalyze COS–PO copolymerization (entries 2 to 3, Table 1). The selectivity of copolymer **1**/cyclic thiocarbonte was 99/1 based on the ^{1}H NMR spectrum (Figure 2). The alternating degree of the resultant copolymer **1** was estimated to be >99% because no ether units were observed from the ^{1}H NMR spectrum. No O/S ER had occurred, as confirmed by ^{13}C NMR spectrum (Figure S1c in the Supporting Information). One peak at 169.64 ppm was observed, which was ascribed to the carbon atom of monothiocarbonate linkage (–S(O)CO–, **1**).[7b,8a] Hence, the copolymer **1** was fully alternating and named poly(propylene monothiocarbonate) (PPMTC). The number-average molecular weight (M_n) of copolymer **1** was 24.4 kg/mol with a narrow PDI of 1.26.

Catalysts **b** and **c** could also catalyze COS-PO copolymerization in the presence of [PPN]Cl at 25 °C with high TOFs (entries 4 and 5 with TOFs of 310 and 332, respectively, Table 1). For the copolymer of entry 5, only one peak at 169.64 ppm was observed from ^{13}C NMR spectrum (curve A in Figure 3), which could be ascribed to –SC(=O)O– (**1** and/or **4**).[8a] However, when the COS/PO copolymerization was catalyzed by **c**/[PPN]Cl system at 60 °C (entry 6), considerable amounts of cyclic products (23 wt %) were collected, which were evident by the ^{13}C NMR and ^{1}H NMR spectra (curve B in Figure 3, Figure S4 in the Supporting Information) of the crude product. As seen in curve B in Figure 3, the products mentioned in Scheme 1 such as –SC(=O)S– (188.04 ppm, **3**), –OC(=O)O– (153.48 ppm, **2**), –SC(=O)O– (169.64 ppm, **1** and/or **4**), and cyclic byproducts of **3′** (197.59 ppm), **1′** and **4′** (172.59 ppm), and **2′** (154.92 ppm)[8a] were observed. Moreover, **4′** was confirmed by GC-MS technique (Figure S7 in the Supporting Information). These results indicated that the high reaction temperature will cause the occurrence of O/S ER and weaken the selectivity of the monothoicarbonate units.

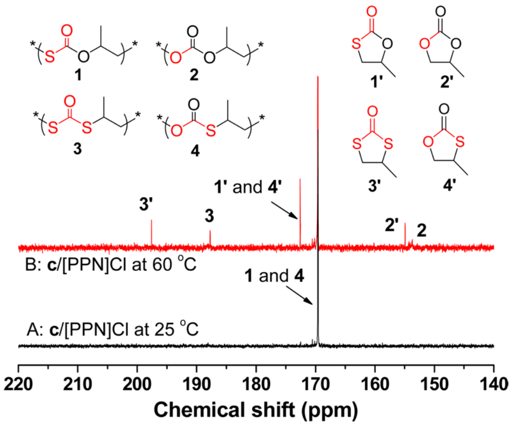
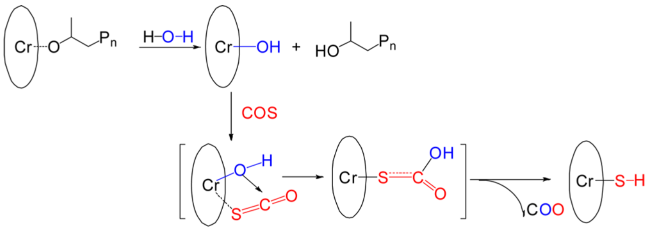


Figure 3. ^{13}C NMR spectra of carbonyl region of the crude products (entries 5 and 6 in Table 1). The formation of **1**–**4** and **1′**-**4′** is shown in Scheme 1 and Table S1 in the Supporting Information.

A series of COS/PO copolymerization were also investigated with various COS/PO molar ratios, solvents, and cocatalysts (Table S2 in the Supporting Information). The polymerization kinetics showed a linear increase in M_n with increasing reaction times (Figure S8 in the Supporting Information). The catalyst **c**/[PPN]Cl was proven to be the best binary catalyst for producing PPMTC with fully alternating degree and the complete depression of O/S ER.

The occurrence of O/S ER at 60 °C intrigued us to probe the structural change of the catalyst during the reaction. As previously mentioned, [Cr]–OH would be generated in our system via the chain transfer reaction. The produced [Cr]–OH could catalyze O/S ER in a proposed way, as shown in Scheme 2 and Scheme S2 in the Supporting Information. Such chain-transfer reaction can be accelerated by either increasing reaction temperature or introducing greater amounts of water (or compounds with active protons) into the system. Herein, the generation of CO_2 was confirmed by the observation of carbonate unit –OC(=O)O– and cyclic carbonate (curve B in Figure 3, Figures S4 and S7 in the Supporting Information), which may support the occurrence of chain-transfer reaction and the production of [Cr]–OH.

Scheme 2. Proposed Mechanism of the O/S ER during COS-PO Copolymerization



For further clarifying the structural change of (Salen)CrCl complex and following O/S ER induced by chain-transfer reaction during copolymerization, a series of control experiments were carried out by adding certain amounts of water to the reaction system, as shown in Table 2 (^{1}H and ^{13}C NMR spectra, see Figures S9–13 in the Supporting Information). When the molar ratios of H_2O/PO were 1/200 to 1/33, the TOFs, the selectivity, and the alternating degrees of the resultant copolymers remained nearly the same, while M_n of the resultant copolymers decreased clearly and PDI remained narrow. These phenomena were typical for the copolymerization with predominant chain-transfer reaction, which was similar to CO_2–PO copolymerization.[10,13] We also observed that O/S ER took place when the H_2O/PO molar ratio ≥1/50 (entries 3–5 in Table 2). The FT-IR (Figure S14 in the Supporting Information) and Raman (Figure S15 in the Supporting Information) spectra of the copolymer from entry 5 of Table 2 showed that it contained end –OH (3540 cm^{-1} in FT-IR) and –SH groups (2665 cm^{-1} in Raman spectrum). ESI-MS spectrum (Figure S16 in the Supporting Information) of this copolymer showed that it had three kinds of m/z species, which represented three copolymers of (i) H-PO-(COS-PO)$_n$-SH + Na$^+$, (ii) H-PO-(COS-PO)$_n$-OH + Na$^+$, and (iii) H-PO-(COS-PO)$_n$-(COS-PS)-SH+ Na$^+$ with relative abundance ratio of 100:18:7. 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.

The observation of copolymer with end –SH group confirmed the generation of [Cr]–SH, which initiated the COS–PO copolymerization. As a result, the transformation of [Cr]–Cl of (Salen)CrCl complex to [Cr]–OH, which could be converted to [Cr]–SH by O/S ER, was resulted from the

Table 2. *Rac*-PO/COS Copolymerization in the Presence of Various Amounts of Water[a]

entry	H_2O (μL)	H_2O:PO (molar ratio)	TOF[b] (h^{-1})	copolymer selectivity[c]	PPMTC linkages[c] (mol %)	T-H linkages[d] (%)	O/S ER product[e]	M_n[f] (kg/mol)	PDI[f] (M_w/M_n)
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

[a] Reaction was performed in neat PO (2.0 mL, 28.6 mmol; **a**/[PPN]Cl = 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. [b] (Mol epoxide consumed)/(mol Cr h). [c] Determined by using ^{1}H NMR spectroscopy (Figures S9−13 in the Supporting Information). The polymer selectivity is the molar ratio of polymer **1**/cyclic product. The PPMTC linkages are the molar percentage of monothiocarbonate linkage in polymer chain. [d] Determined by using ^{13}C NMR spectroscopy (Figure S9−13 in the Supporting Information). [e] Determined by using ^{13}C NMR spectroscopy (Figure S9−13 in the Supporting Information). O/S ER = oxygen−sulfur exchange reaction. N.F. = not found and F = found. [f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

chain-transfer reaction (Scheme S2 in the Supporting Information).

Under the premise of the complete depression of O/S ER, the stereochemistry of COS-PO copolymerization can be clarified. The units of −OC(=S)O− (**5**), −SC(=S)O− (**6**), and corresponding cyclic products of **5′** and **6′** were not observed in ^{13}C NMR spectra of all copolymers listed in Tables 1 and 2. It indicated that the insertion path **B** in Scheme 1 was totally prohibited. That is, the coordination of the sulfur atom of COS to the active center was completely selective. As a result, only one propagating species (−OC(=O)S^-, via route **A**) existed before PO insertion. The nucleophilic attack of −OC(=O)S^- to CH_2 or CH of PO determines the regioregularity of the resultant copolymer (Scheme 1 and Scheme S3 in the Supporting Information).

It seems hard to accurately assign the multiple peaks of −SC(=O)O− unit [curve (A), Figure 4] to the various microstructures (i.e., H−T, T−H, T−T, and H−H diads) of the copolymer **6** (entry 6, Table 1). If the cyclic monothiocarbonate could be predominantly generated via the backbiting from the anionic alkoxy−chain end,[10] as shown in Scheme 3, then the molar ratio of cyclic monothiocarbonates **1′** to **4′** could represent the molar ratio of the units −OC(=O)$SCH_2CH(CH_3)O$− to −OC(=O)$SCH(CH_3)CH_2O$− in the copolymer. GC-MS measurements were then carried out to clearly differentiate **1′** and **4′**, and the diads of the copolymer could be deduced. The GC-MS results showed that the molar ratio of cyclic monothiocarbonates **1′** to **4′** was 40 for the system of entry 6 in Table 1, as shown in Figure S7 in the Supporting Information, indicating that the −OC(=O)S CH_2CH $(CH_3)O$− unit was the main structure of the copolymer even if O/S ER had occurred. Furthermore, the content of T−H diad of copolymer **6** was estimated to be 97.6% from the molar ratio of **1′**/(**1′** + **4′**), which was consistent with that of 98.1% calculated from ^{13}C NMR spectrum (entry 6 in Table 1). The multiple peaks at 169.64 ppm could be then assigned to the T-H diad. The content of T-H diad in all copolymers in Table 1 was calculated as 98.1 to 99.0%, indicating that the copolymerization was highly regioselective.

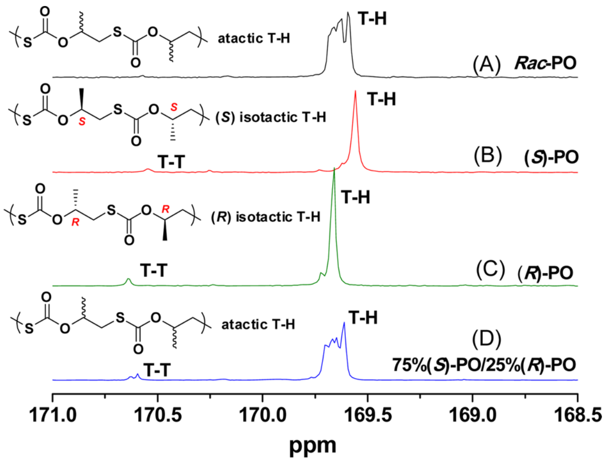


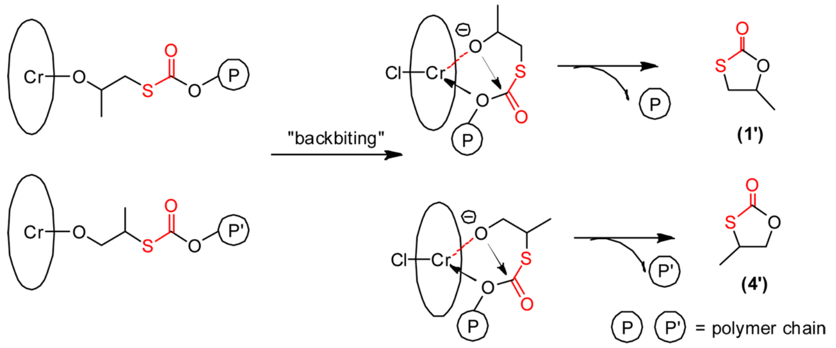
Figure 4. Carbonyl region of the ^{13}C NMR spectra of PPMTC resulted from (A) *rac*-PO/COS (entry 6, Table 1) and (B) (*S*)-PO/COS (entry 7, Table 1); (C) (*R*)-PO/COS (entry 8, Table 1) and (D) 75%(S)-PO/25%(*R*)-PO/COS (entry 9, Table 1). Note that (*S*)-PO, (*R*)-PO, and 75%(S)-PO/25%(*R*)-PO were used without further purification.

For further demonstrating the unique regioregularity of PPMTC, (*S*)-PO, (*R*)-PO, and 75%(S)-PO/25%(*R*)-PO were copolymerized with COS by using the catalyst **c**/[PPN]Cl (entries 7−9, Table 1). Note that (*S*)-PO, (*R*)-PO, and 75%(S)-PO/25%(*R*)-PO were used without further purification. The (*S*) [or (*R*)]-configuration of methine carbon of (*S*) [or (*R*)]-PO was expected to be retained after copolymerization if just **a**−**a** propagating manner took place. Hence, the isotactic T−H diad would be the only configuration of the resultant copolymer and will cause one single peak in its ^{13}C NMR spectrum. This expectation was proved by the ^{13}C NMR spectrum of COS/(*S*)-PO copolymer and COS/(*R*)-PO copolymer, as shown in curves (B) and (C) in Figure 4. Moreover, the copolymer from COS with 75% (S)-PO/25% (*R*)-PO presented similar multiple peaks as those observed for *rac*-PO/COS copolymer [curve (A), Figure 4], and the sharp peak at right-hand [(S) isotactic T-H diad, curve (D)] became relative stronger because of greater amounts of (*S*)-PO in the system.

The obtained PPMTC is highly soluble in common solvents, such as, CH_2Cl_2, $CHCl_3$, and THF. The glass-transition temperature (T_g) of PPMTC of entry 7 in Table 1 was 22.4 °C (Figure S17 in the Supporting Information). Interestingly, the initial decomposition temperature of this copolymer was 137 °C and rather low (Figure 5). Refractive index (*n*D) of this copolymer was measured to be 1.63(22 °C, cast film), which can be classified into polymers with large refractive index. Such low decomposition temperature and high refractive index of PPMTC make it a potential scarifying optical adhesive.

In 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

Scheme 3. Proposed Production of Cyclic Monothiocaarbonate 1′ and 4′ by "Backbiting" Mechanism



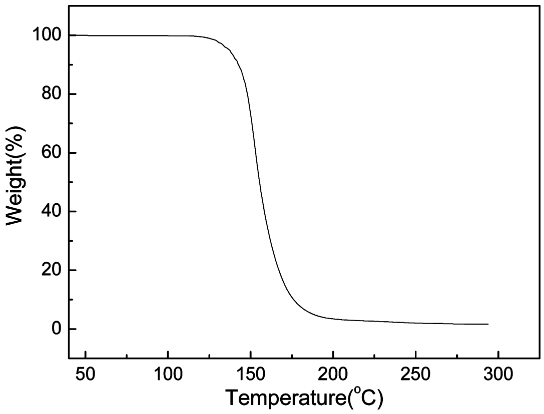


Figure 5. TGA curve of the COS-PO copolymer (entry 1, Table 1).

could be completely inhibited at 25 °C. The resultant copolymers had 98.1 to 99.0% T−H linkages and full alternating asymmetric monothiocarbonate units. Importantly, it also presented a new copolymerization model involved two asymmetric monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving general experimental procedures and characterization data for PO−COS copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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