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# Synthesis of Sulfur-Rich Polymers: Copolymerization of Episulfide with Carbon Disulfide by Using [PPN]Cl/(salph)Cr(III)Cl System

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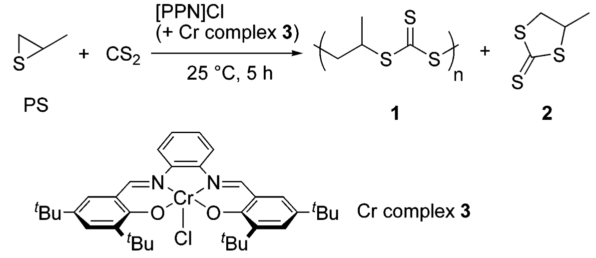
Introduction of sulfur atoms into polymer chain confers attractive features, such as high optical and thermal properties, excellent chemical resistance, and heavy-metal recognition ability on polymers. For example, sulfur-enriched polymers have high refractive index, advantageous for plastic lenses.[1] Some synthetic routes were reported to give polymers with sulfur atoms in the main chain, such as polythioethers,[2] polythiosulfites,[3] poly(di)thiocarbonates,[4] and polythioesters.[5] Polytrithiocarbonates have also been synthesized from $CS_2$ with dihalides and/or dithiols.[4h,6] However, the favorable formation of five-membered cyclic trithiocarbonates resulted in unsuccessful or inefficient synthesis of polytrithiocarbonates with the alternating C2 unit and trithiocarbonate unit $[-C-C-S-C(=S)-S-]_n$, which would be classified into one of the most sulfur-enriched polymers. Synthesis of such poly(ethylene trithiocarbonate)s has also been attempted through the copolymerization of episulfide with $CS_2$. The pioneering work on the copolymerization was reported by Soga et al. in 1970s.[7,8] The copolymerization in the presence of $CdEt_2$, $ZnEt_2$, or $Hg(SBu)_2$ was found to give the copolymer. However, the activity was low and the resulting copolymer contained a large amount of thioether linkages. We herein report the first successful completely alternating copolymerization of episulfide with $CS_2$.

The copolymerization of propylene sulfide (PS) with $CS_2$ (1.0 equiv to PS) was investigated in the presence of anionic initiator (PS/initiator = 500) because (1) episulfides are known to polymerize via anionic or coordination anionic mechanism[2] and (2) $CS_2$ also reacts with anionic species or inserts into metal-thiolate bond,[7a] resulting in the formation of dithiocarboxylate moiety. The use of the combination of thiol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), which is effective initiator system for the living episulfide ring-opening polymerization,[2c] gave only cyclic propylene trithiocarbonate (**2**). In contrast, the copolymerization in the presence of [PPN]Cl (0.20 mol %, $[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$) for 5 h yielded the completely alternating copolymer, poly(propylene trithiocarbonate) (**1**), while the selectivity for the copolymer was low [yield of **1** + **2** = 16%, **1**/**2** = 37/63, $M_n = 11600$ (g·mol$^{-1}$), $M_w/M_n = 1.4$] (Table 1, run 1). The use of tetrabutylammonium chloride also gave the copolymer (Table 1, run 2). However, the use of phosphonium salt $[Ph_3PMe]Cl$ resulted in no polymerization.

Copolymerization rate and the copolymer selectivity were improved by adding a metal complex with salen-type ligand. The screening revealed that (salph)CrCl complex **3** [$(salph)H_2$ = bis-(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene] was the most effective catalyst.[9] Thus, the copolymerization by using a combination of [PPN]Cl and complex **3** at 25 °C for 5 h resulted in higher conversion of PS to give copolymer **1** in higher selectivity [yield of **1** + **2** = 60%, **1**/**2** = 80/20, $M_n = 20300$ (g·mol$^{-1}$), $M_w/M_n = 1.4$] (Table 1, run 3). A blank reaction showed that complex **3** alone does not copolymerize PS with $CS_2$.

***Table 1.*** Copolymerization of Propylene Sulfide with $CS_2$ by Using [PPN]Cl/Complex **3** System[a]



| run | PS/$CS_2$ | initiator/ catalyst | yield of **1** + **2** (%)[b] | **1**/**2**[b] | $M_n$ (g·mol$^{-1}$)[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| 1 | 1/1 | [PPN]Cl | 16 | 37/63 | 11600 | 1.4 |
| 2 | 1/1 | $Bu_4NCl$ | 5 | 42/58 | nd[d] | nd[d] |
| 3 | 1/1 | [PPN]Cl/**3** | 60 | 80/20 | 20300 | 1.4 |
| 4 | 1/0.5 | [PPN]Cl/**3** | 44 | 48/52 | 11000 | 1.6 |
| 5 | 1/0.7 | [PPN]Cl/**3** | 52 | 71/29 | 15400 | 1.6 |
| 6 | 1/2 | [PPN]Cl/**3** | 53 | 88/12 | 18200 | 1.4 |
| 7[e] | 1/2 | [PPN]Cl/**3** | 90 | 92/8 | 42600 | 1.3 |

[a] Reaction conditions: PS (10 mmol), [PPN]Cl or $Bu_4NCl$ (0.20 mol %), [complex **3** (0.20 mol %)], $CS_2$ at 25 °C for 5 h. [b] Determined on the basis of $^1H$ NMR spectroscopy of the crude product by using dodecane as an internal standard. [c] Determined by gel permeation chromatography using a polystyrene standard. [d] nd = not determined. [e] Premixed complex from [PPN]Cl and complex **3** was used.

The copolymer/cyclic trithiocarbonate selectivity (**1**/**2**) depends on the molar ratio of PS and $CS_2$. A larger amount of $CS_2$ tends to give higher copolymer selectivity (Table 1, runs 3−6). We conclude that the use of 2 equiv of $CS_2$ to PS is optimal for both high selectivity and good catalytic activity. The organic salt [PPN]Cl has low solubility to the reaction mixture, probably leading to the slow initiation. To meet this problem, the *premixed* complex was prepared by treatment of [PPN]Cl and complex **3** in THF which dissolves both compounds. The resulting *premixed* complex showed higher solubility in a mixture of PS/$CS_2$. In such a condition, the simultaneous initiation should be possible, resulting in higher activity (yield of **1** + **2** = 90%, 5 h, Table 1, run 7). Furthermore, the highest selectivity for the copolymer was also attained (**1**/**2** = 92/8).

The obtained alternating copolymer is highly soluble in $CS_2$, and slightly soluble in $CHCl_3$ and THF, while its solubility to the other common organic solvents is quite low. The main chain sequence was confirmed by $^1H$ and $^{13}C$ NMR spectroscopy (see the Supporting Information). No signal was assignable to the thioether moiety, demonstrating that the sequence was completely alternating. The $^{13}C$ NMR spectrum of the obtained copolymer suggests high head-to-tail regioregularity based on analogous speculation from the $^{13}C$ NMR spectrum of poly(propylene carbonate).[10] The $^{13}C$ NMR signal of each carbon splits into two or three peaks (Figure

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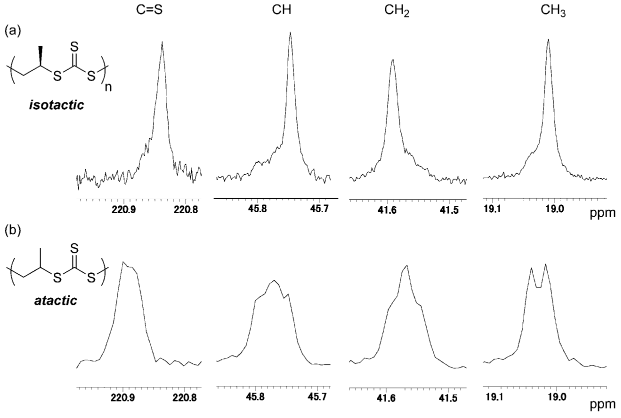

***Figure 1.*** Comparison of $^{13}C$ NMR signals of poly(propylene trithiocarbonate)s from (a) (*R*)-propylene sulfide (90% ee) and (b) *rac*-propylene sulfide (in $CDCl_3 + CS_2$, 125 MHz).

1b). This is likely to reflect the atactic structure of the main chain on the basis of the fact that the copolymer from enantio-enriched PS (90% ee) gives sharp and almost undivided peaks for each of the carbons (Figure 1a). The thermal analyses of the copolymer obtained from *rac*-PS demonstrated that it has glass transition temperature around 25 °C and decomposes rapidly to cyclic trithiocarbonate **2** at around 200 °C.[11] Such thermal behavior is similar to that of poly(propylene carbonate).[12] Refractive index (*n*D) of the obtained copolymer **1** was measured to be 1.78 (22 °C, cast film), which is classified into the largest values among those of the reported sulfur-containing polymers.[1]

Although the reaction mechanism is not clear yet, we speculate that copolymerization takes place via a similar process to the alternating copolymerization of epoxide with $CO_2$ (see the Supporting Information):[13] Chromium complex should work as Lewis-acidic center to activate an episulfide. Both of two axial chloride ligands on the starting chromate complex [(salph)$CrCl_2$][PPN] would be capable to initiate the polymerization.[13d]

Preformation of cyclic trithiocarbonate **2** followed by subsequent ring-opening polymerization is unlikely. Treatment of **2** with a mixture of [PPN]Cl and complex **3** in $CS_2$ did not afford the polymeric materials. Furthermore, the reaction of PS with $CS_2$ under the optimized condition in the presence of cyclic 1,2-butylene trithiocarbonate gave only pure copolymer **1** and the starting cyclic carbonate was quantitatively recovered. Accordingly, it was manifested that the copolymer was produced via the direct alternating copolymerization rather than via cyclic trithiocarbonate formation.

Cyclic trithiocarbonate formation should be via the back-biting from the anionic thiolate-chain end [$-CH_2-CHCH_3-S^-$][11] rather than from the anionic trithiocarbonate-chain end [$-SC(=S)-S^-$]. As mentioned above, the higher concentration of $CS_2$ is effective to suppress the formation of **2** (Table 1, runs 3−6). Under the higher $CS_2$ concentration, $CS_2$ insertion should be accelerated, decreasing the concentration of the thiolate-chain end and increasing the concentration of the trithiocarbonate-chain end. This corresponds to the cyclic trithiocarbonate formation mainly from the thiolate-chain end. We think that the chromium center is also important to suppress the formation of cyclic trithiocarbonate: the chromium center effectively catches the free anionic-chain end which would be more favorable to back-biting than the resulting chromium-bound-chain end. On the other hand, the non-coordinating organic cation is less able to catch the free anionic-chain end, and thus, the copolymerization with [PPN]Cl alone yielded a larger amount of cyclic trithiocarbonate (Table 1, compare run 1 with run 3).

In conclusion, we have reported the alternating copolymerization of episulfide with $CS_2$ by using [PPN]Cl as initiator and chromium complex as activator. The obtained copolymer has a completely alternating sequence and high refractive index. Further studies are directed toward the elucidation of polymerization mechanism and improvement in catalytic performance.

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**Supporting Information Available:** Experimental details, a proposed polymerization mechanism, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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