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Atom-Exchange Coordination Polymerization of Carbon Disulfide and Propylene Oxide by a Highly Effective Double-Metal Cyanide Complex

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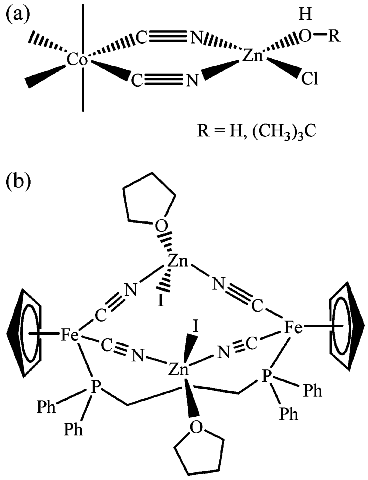
Poly(thiocarbonate), a sulfur-containing polymer that has strong affinity for heavy metal ions as well as superior optical and thermal properties, can be used as a sorbent for wastewater treatment or in the production of optical lenses or fibers. Usually, poly(thiocarbonate) can be synthesized by the reaction of dithiols and phosgene or chloroformates in organic solvents.[1] However, this is not a “green” synthetic route due to the usage of poisonous reactants. Another effective means of synthesizing poly(thiocarbonate) is the ring-opening polymerization of five- or six-membered cyclic dithiocarbonates and trithiocarbonates.[2,3] Poly(thiocarbonate) of well-defined and tunable structure can be obtained by this method. Unfortunately, however, the reactivity of these cyclic compounds is quite low, and they are mainly obtained from selective coupling reactions of carbon disulfide (CS_2) with epoxides, which are difficult to control. On the other hand, CS_2, which can be copolymerized with epoxides, may be considered as an ideal monomer for synthesizing poly(thiocarbonate). A few catalysts have hitherto been reported for promoting the copolymerization of CS_2 and epoxides.[4,5] However, their catalytic activities were found to be low, and so large amounts of these catalysts were required. Long reaction times were required, and even then the molecular weight of the obtained poly(thiocarbonate) was still rather low, e.g., only 560 g/mol.[4]

In our previous work, we found that double-metal cyanide complex (DMCC) catalysts, which have a typical formula of $M^{II}_u[M(CN)_n]_v \cdot xM^{II}X_w \cdot yL \cdot zH_2O$ ($M^{II} = Zn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}$, etc.; $M = Co^{2+}, Co^{3+}, Fe^{2+}, Fe^{3+}$, etc.; L is an electron-donating complexing agent).[6−8] DMCC catalysts based on $Zn_3[Co(CN)_6]_2$ ($Zn-Co^{III}$ DMCC) are considered to be most favorable and effective for the homopolymerization of propylene oxide (PO)[7] and the copolymerization of CO_2/PO.[8] Since CS_2 and CO_2 have similar chemical structures and both sulfur (S) and oxygen (O) are group VIA elements, DMCC catalysts may also be effective for catalyzing the copolymerization of CS_2/PO.

In this Communication, we describe the use of a highly effective $Zn-Co^{III}$ DMCC catalyst to achieve a one-pot polymerization of CS_2/PO. A new sulfur-containing copolymer with a complex structure was produced. The molecular weight of the copolymer was found to be in the range 1.2−5.4 kg/mol, with a relatively low polydispersity (1.24−3.50). Interestingly, an atom-exchange coordination polymerization (AECP) has been discovered.

Scheme 1. (a) Proposed Ground-State Structure of the Active Site of $Zn-Co^{III}$ DMCC Catalyst and (b) Structure of the Well-Defined $Zn-Fe^{II}$ DMCC Catalyst Reported by Darensbourg et al.[11] [a]



[a] In structure (a), two CN^- are shared by the Zn^{2+} and Co^{3+} ions and are calculated as one negative charge in one tetrahedral Zn^{2+} structure, which meets the electroneutrality principle due to the presence of Cl^-. Structure (b) depicts a soluble DMCC in which a tetrahedral Zn^{2+} was chelated with two CN^- (also shared by Fe^{2+} ions), one iodide, and one tetrahydrofuran. Both tetrahedral Zn^{2+} structure are analogous. The Cl^- in structure (a) may serve as a good leaving group (like iodide in structure (b)) and can be easily substituted by the attacking species.

Traditionally, $Zn-Co^{III}$ DMCC has been prepared by the precipitation reaction of excess $ZnCl_2$ and $K_3[Co(CN)_6]$ in water/*tert*-butanol (*t*-BuOH) solution. The use of excess $ZnCl_2$ and an appropriate amount of *t*-BuOH proved indispensable for obtaining $Zn-Co^{III}$ DMCC with high catalytic activity.[7,8] However, the precise structure of the active centers of the catalyst remains unclear due to its heterogeneous nature.[6−10]

To gain some insights into the structure of the $Zn-Co^{III}$ DMCC catalyst used in the present experiments, the catalyst was systematically characterized by infrared spectroscopy (IR), wide-angle X-ray diffraction (WAXD), and X-ray photoelectron spectroscopy (XPS). IR spectra showed that $\upsilon_{C\equiv N}$ and υ_{Co-C} of $Zn-Co^{III}$ DMCC are shifted by 15−20 cm^{-1} to higher wavenumbers as compared with those of pure $Zn_3[Co(CN)_6]_2$ (Figure S1, see the Supporting Information), indicating the change of coordination environment for the zinc atom.[7c] The absorption bands of *t*-BuOH could be detected in the IR spectrum of the $Zn-Co^{III}$ DMCC as well. WAXD results (Figure S2) revealed that the $Zn-Co^{III}$ DMCC was of low crystallinity and that no free $ZnCl_2$ remained in the catalyst. The X-ray photoelectron spectra (Figure S3) confirmed the incorporation of Cl into the $Zn-Co^{III}$ DMCC. Moreover, the binding energy of Zn $2p^3$ for $Zn-Co^{III}$ DMCC (1021.3 eV) is lower than that for $ZnCl_2$ (1023.7 eV[9]), but higher than that for neat $Zn_3[Co(CN)_6]_2$ (1020.8 eV). This may indicate that Zn^{2+} in $Zn-Co^{III}$ DMCC has a different coordination environment from that in neat $Zn_3[Co(CN)_6]_2$. Furthermore, according to the results of elemental analyses, the formula of the $Zn-Co^{III}$ DMCC used in the present work is $Zn_3[Co(CN)_6]_2 \cdot 1.8ZnCl_2 \cdot 2.3t\text{-}BuOH \cdot 3.8H_2O$.

On the basis of the IR, WAXD, and XPS results, it is reasonable to consider that Zn^{2+} in the $Zn-Co^{III}$ DMCC is coordinated by CN^-, *t*-BuOH, and Cl^- or H_2O to form a tetrahedral structure (Scheme 1a). Here, two CN^- are shared by the Zn^{2+} and Co^{3+} ions and thus are calculated as one negative

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Table 1. Results of Copolymerizations of CS_2/PO in the Presence of Zn−Co^{III} DMCC under Different Reaction Conditions[a]

entry	T (°C)	catalyst amount (10^{-4} g/g)[b]	m_{CS_2}/m_{PO}[c]	M_n[d] (kg/mol)	MWD[d]	yield[e]
1	100	3.2	2	4.7	3.50	946
2	80	3.2	2	1.2	1.78	202
3	110	3.2	2	5.4	3.41	1094
4	130	3.2	2	3.9	2.95	996
5	100	1.3	2	1.2	1.24	255
6	100	2.3	2	3.0	1.82	431
7	100	3.2	1	1.9	1.72	310
8	100	3.2	1.5	5.3	3.47	940
9	100	3.2	2.5	4.4	3.50	950

[a] Conditions: one-pot polymerization, 0.2 g of polyoxypropylenediol (PPG-400, M_n = 400) was added as an initiator; reaction time: 6.0 h; pressure: 0.4 MPa. [b] The weight percentage of catalyst in the total weight of CS_2 and PO. [c] The molar ratio of CS_2 and PO. [d] M_n and MWD determined by gel-permeation chromatography (GPC) method. [e] Grams of copolymer per gram of Zn−Co^{III} DMCC catalyst.

charge in one tetrahedral Zn^{2+} structure, so this proposed structure meets the electroneutrality principle due to the presence of Cl^- and is analogous to the zinc tetrahedral structure depicted in Scheme 1b,[11] which is a well-defined and soluble DMCC. It was reported that this well-defined DMCC could also initiate the copolymerization of CO_2/epoxide when iodide (a good leaving group) was replaced with phenoxide.[11] Presumably, the Cl^- in the Zn−Co^{III} DMCC catalyst serves as a good leaving group (like iodide in Scheme 1b) and can be easily substituted by the attacking species so that the polymerization is initiated. In several reports[7−11] related to DMCC catalysts, the Zn−O structure has been postulated as the active site for chain propagation.

A series of copolymerizations of CS_2 and PO were then performed for 6 h in a sealed autoclave under a pressure of 0.4 MPa with the Zn−Co^{III} DMCC as the catalyst. The reaction temperature, the amount of catalyst, and the ratio of the monomers were each systematically varied. It should be noted that the copolymerization of CS_2/PO did not occur in the absence of Zn−Co^{III} DMCC and that pure $Zn_3[Co(CN)_6]_2$ did not initiate the reaction. Neat $ZnCl_2$ and $K_3[Co(CN)_6]$ also showed no catalytic activity for the copolymerization of CS_2/PO. Details of the experimental conditions and the outcomes of the reactions are collected in Table 1.

The catalytic activity of the Zn−Co^{III} DMCC increased from 202 to 1094 g polymer/g catalyst when the reaction temperature was raised from 80 to 110 °C. Further increasing the temperature up to 130 °C resulted in a slight decrease in the catalytic activity. The molecular weights of the obtained copolymer showed a similar dependence on the reaction temperature and were in the range 1.2−5.4 kg/mol, much higher than those quoted in previous reports.[4] Increasing the amount of the catalyst enhanced the total catalytic activity and led to a polymer of higher molecular weight and greater polydispersity. The ratio of the monomers was also found to influence the outcome of the reaction. Raising the molar ratio of CS_2/PO from 1.0 to 1.5 resulted in a dramatic increase in the catalytic activity of the catalyst and the molecular weight of the copolymer, and the polydispersity of the copolymer also increased. However, a further increase of the molar ratio of CS_2/PO had a negative influence on the reaction. The optimal conditions for the copolymerization were found to be a temperature of 100 °C with a CS_2/PO molar ratio of 1.5−2.0 and a DMCC loading of 3.2×10^{-4} g catalyst/g reactants.

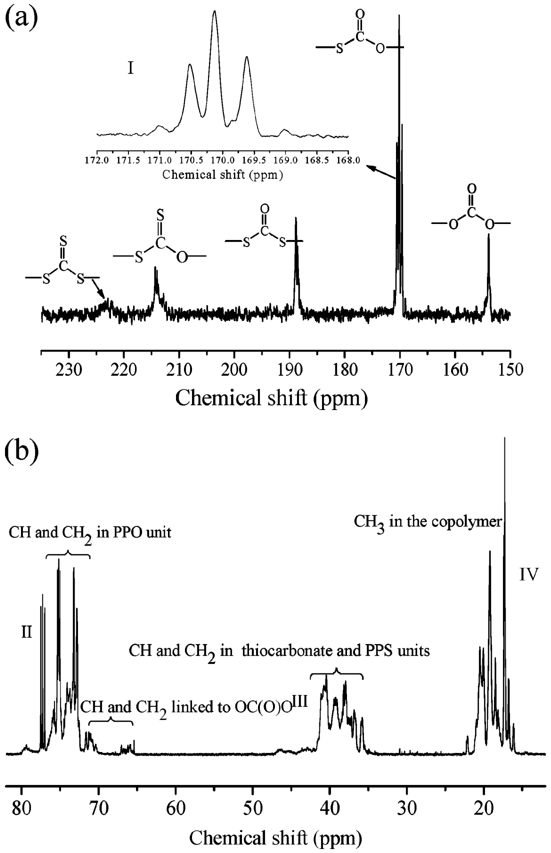


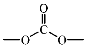
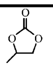
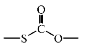
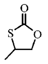
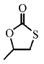
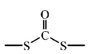
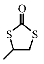
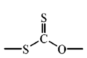
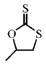
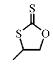
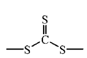
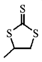
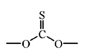
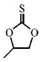
Figure 1. ^{13}C NMR spectrum (Bruker 500 MHz type spectrometer, chloroform-*d*) of the CS_2/PO copolymer produced by catalysis with the Zn−Co^{III} DMCC: (a) five peaks of *C*=O and *C*=S carbons in the copolymer (region I); (b) multiple peaks of *C*H, *C*H_2, and *C*H_3 carbons in the copolymer (regions II−IV).

Figure 1 shows the ^{13}C NMR spectrum of the obtained copolymer. Interestingly, the chemical shifts in Figure 1 can clearly be divided into four regions. The peaks with chemical shifts of δ = 153.44 (s), 170.16 (t), 188.88 (t), 214.42 (m), and 223.23 ppm (m) in region I can be assigned to −O(*O*)*C*O−,[8] −S(*O*)*C*O−,[3a] −S(*O*)*C*S−,[3b,c] −S(*S*)*C*O−, and −S(*S*)*C*S−, respectively. The ratio of the peak areas is 1.0:6.7:2.2:2.0:0.6. These results indicate that the monothiocarbonate unit is one of the main units in the copolymer, which is consistent with the IR spectrum obtained (Figure S4). Region II contains peaks that are mainly attributable to *C*H and *C*H_2 carbons in the −O*C*H(CH_3)*C*H_2− units.[7a] The intensities of the peaks in the range δ = 68−72 ppm are very weak, and these signals can be attributed to *C*H and *C*H_2 linked to the carbonate unit.[8] The peaks in region III are assigned to *C*H and *C*H_2 in the thiocarbonate and −S*C*H(CH_3)*C*H_2− units. The multiple peaks in region IV are due to all of the *C*H_3 groups of the copolymer, which are difficult to assign to any particular unit.

Furthermore, the ^1H NMR spectrum of the copolymer (Figure S5) shows that the molar ratio of the −OCH(*C*H_3)CH_2−, −SCH(*C*H_3)CH_2−, and (thio)carbonate units of the copolymer is about 1.0:1.3:1.3. The O/S molar ratio was thus calculated to be 1.4, which is much larger than that of the ideal alternating copolymer of CS_2 and PO, i.e., 0.5. The NMR results suggest that oxygen atoms are much more easily incorporated into the main chain of the copolymer.

Since the oxygen of the ⟩C=O groups in the copolymer can only come from the PO monomer and no CO_2 was added to the reaction systems, the large O/S molar ratio and the appearance of −O(*O*)*C*O−, −S(*O*)*C*O−, −S(*O*)*C*S−, −S(*S*)*C*O−, and −S*C*H(CH_3)*C*H_2− units indicate the occurrence of an O/S atom-exchange reaction between CS_2 and PO in the course of the polymerization. If this were the case, the intermediate products of carbonyl sulfide (COS) and propylene sulfide (PS) should be detectable during the reactions. Indeed, COS was identified by gas chromatography−mass spectrometry (GC-MS) (Figure S6). However, no PS was detected by GC-MS. A possible

Table 2. Thiocarbonate Units in Copolymer and Cyclic Thiocarbonates from One-Pot Reaction of CS_2/PO in the Presence of Zn−Co^{III} DMCC[a]

Run	Possible reactions	Thiocarbonate units		Cyclic thiocarbonates	
		unit structure	molar ratio	structure	molar ratio
1	PO + CO_2	 **a**	1.0	 **1**	1.0
2	PS + CO_2 PO + COS[1]	 **b**[3]	6.7	 **2**  **3**	52.0
3	PS + COS[1]	 **c**	2.2	 **4**	9.3
4	PO + CS_2 PS + COS[2]	 **d**	2.0	 **5**  **6**	6.0
5	PS + CS_2	 **e**	0.6	 **7**	5.6
6	PO + COS[2]	 **f**[4]	0	 **8**[5]	0

[a] Footnotes: [1]Assuming preferential coordination of the sulfur atom of COS to the zinc center on thermodynamic grounds. [2]Assuming preferential coordination of the oxygen atom of COS to the zinc center on thermodynamic grounds. [3]Thiocarbonate unit **b** was mainly generated from the reaction of PO/COS since the amount of CO_2 produced in the reaction system was small. [4]Thiocarbonate unit **f** was not detected in the ^{13}C NMR spectrum of the copolymer. [5]Compound **8** was not detected by GC-MS.

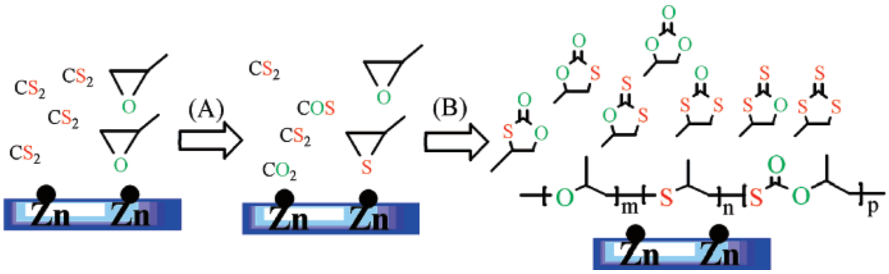
explanation for this is that PS was immediately consumed once it was generated. Further O/S atom exchange between COS and PO took place, as evidenced by the presence of carbonate units in the copolymer and the detection of another product, namely propylene carbonate (Table 2, compound **1**). In fact, seven five-membered cyclic (thio)carbonates (Table 2, compounds **1**−**7**) were identified by GC-MS (Figure S7). The molar ratio **1**:(**2** + **3**):**4**:(**5** + **6**):**7** was about 1.0:52.0:9.3:6.0:5.6. The O/S molar ratio of the cyclic compounds was found to be about 1.3, which is close to that of the copolymer (i.e., 1.4). This suggests that the incorporation of COS and CO_2 into the products is more energetically favorable. Moreover, the accumulation of COS during the reaction indicates that the O/S atom-exchange reaction of CS_2/PO is faster than the reactions between COS and PO or PS, ensuring a high yield of the copolymer.

Because of the O/S atom-exchange reaction, five species, i.e., CS_2, PO, COS, PS, and CO_2, were coexistent (Scheme 2). Their copolymerization in the reaction system then resulted in a copolymer with complex unit sequences. Seven five-membered cyclic compounds were simultaneously generated in the reaction. The total amount of these cyclic species was less than 15 wt % of the total weight of all products, indicating that the reaction had high polymer selectivity. Initiation of the copolymerization is considered to started with PO activation,[7c] based on knowledge of the DMCC catalyst[7,9] and the proposed structure of the Zn−Co^{III} DMCC (Scheme 1a). Herein, Cl^- is presumably a good leaving group and can be easily substituted by the attacking monomers. A proton transfer is regarded as the key step for this PO activation (Scheme 3). Ring cleavage of the activated PO is then believed to be triggered by a nucleophilic attack from the neighboring Zn−OR group, thereby generating complex **A**.

The chain structure of the copolymer is fundamentally determined by the mode of insertion of COS into the complex **A** (i.e., the propagating chain) and the ring-opening positions of PO and PS (α- or β-cleavage). COS might coordinate to the zinc center in two different ways, i.e., through nucleophilic attack of the oxygen atom or the sulfur atom (Scheme 3, **B** and **C**). For CS_2 and CO_2, however, there is only one insertion path. Given that all possible insertion reactions and both cleavages of PO and PS occurred during the polymerizations, six (thio)carbonate units and eight five-membered cyclic compounds could have been produced (Table 2, units **a**−**f**, compounds **1**−**8**). However, only five (thio)carbonate units were detected by NMR and only seven five-membered cyclic products were detected by GC-MS. The −O(*S*)CO− unit (unit **f** in Table 2) and 4-methyl-1,3-dioxalane-2-thione (compound **8** in Table 2) were not found, which meant that the insertion path **b** in Scheme 3 was possibly prohibited. That is to say, the sulfur atom of COS preferentially coordinated to the zinc center, both kinetically and thermodynamically.[12] As a result, the insertion of COS proceeded via nucleophilic attack of the thiocarbonyl sulfur at the zinc center (path **a** in Scheme 3). An encounter complex **C**, which possessed the lowest energy of all possible products of nucleophilic attack,[12a] was generated. Complex **D** was then generated from complex **C** by a proton-transfer process, the zinc−sulfur bond being more stable than the zinc−oxygen bond.[12] Subsequently, PO could be inserted into the zinc−sulfur bond to generate complex **E**. The five-membered cyclic compound **3** (monothiocarbonate) could then be generated from complex **E** by an intramolecular nucleophilic attack (i.e., a “backbiting” process). The similar O/S molar ratios in the cyclic compounds (1.3) and the copolymer (1.4) may support this proposed “backbiting” process. The insertion reactions of CS_2 or CO_2 at the zinc center were presumably similar to that of COS at the zinc center. However, the stabilities of the encounter complexes formed by the coordination of CS_2, COS, and CO_2 at the zinc center are different, and this may be responsible for the various contents of the different (thio)carbonate units in the copolymer and the various types of cyclic compounds.

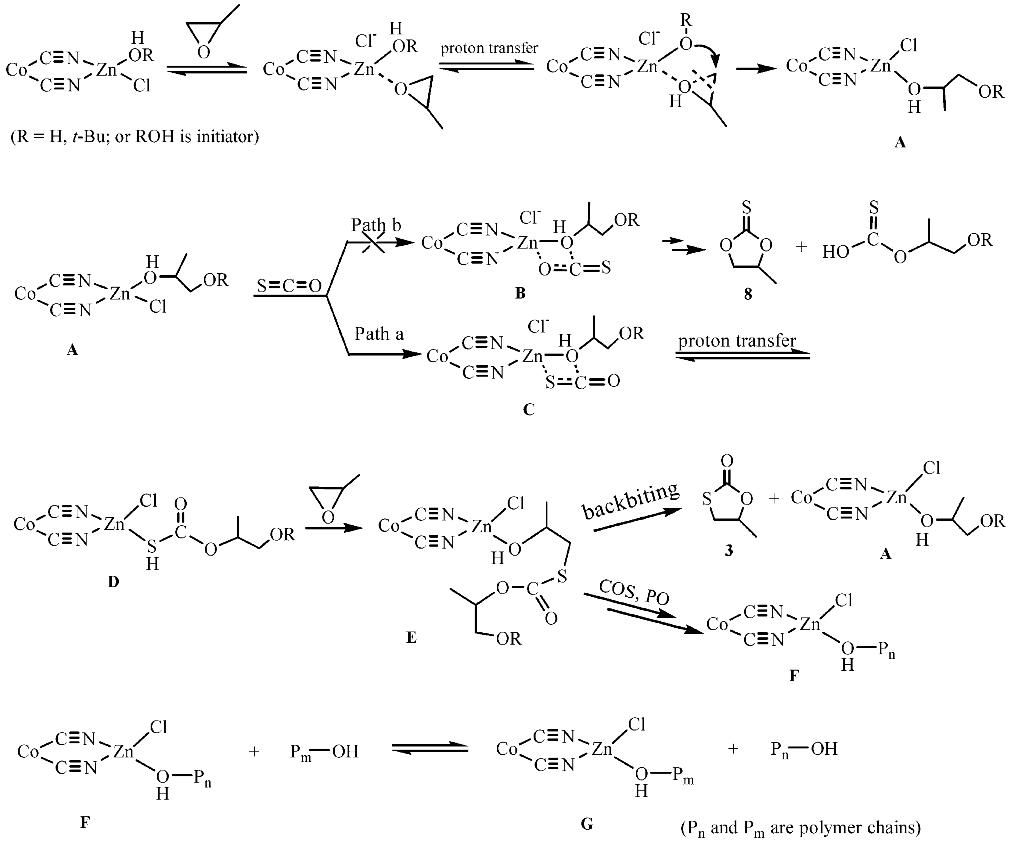
Although the mechanisms of the reaction are very complicated, the copolymer shows only a single elution peak with a relatively narrow polydispersity in GPC measurements (Figure 2, Table 2). The copolymer may result from a random copolymerization of the above five species, such that it has a random sequence of the complex units. The mechanisms proposed for Zn−Co^{III} DMCC-catalyzed PO homopolymerization[7a] and CO_2/PO copolymerization[8] suggest rapid chain-exchange reactions between the propagating chains and “dead” chains (**F** to **G** in Scheme 3), thereby maintaining the number of growing polymer chains. Such chain-exchange reactions may also be responsible for the random structure of the copolymer.

Scheme 2. Atom-Exchange Coordination Polymerization of Carbon Disulfide and Propylene Oxide in the Presence of Zn−Co^{III} DMCC[a]



[a] (A) O/S atom-exchange reaction of PO and CS_2. (B) Copolymerization and coupling reaction among CS_2, PO, COS, PS, and CO_2.

Scheme 3. Proposed Mechanism for Initiation, Propagation, and Chain Exchange for CS_2/PO Copolymerization in the Presence of Zn−Co^{III} DMCC (PO and COS as Examples for Illustration)



In summary, the Zn−Co^{III} DMCC catalyst has exhibited high efficiency in catalyzing the copolymerization of CS_2 and PO and may also be applied for the copolymerization of CS_2 with other epoxides, e.g., the copolymerization of CS_2 with cyclohexene oxide (CHO). A novel sulfur-containing copolymer with a complex structure sequence has been synthesized by a convenient one-pot polymerization with Zn−Co^{III} DMCC as the catalyst. An atom-exchange coordination polymerization (AECP) has been observed. Further efforts and experiments are ongoing in order to further explore the mechanism of the atom-exchange copolymerization and with a view to synthesizing a sulfur-containing polymer with controllable stereochemical structures.

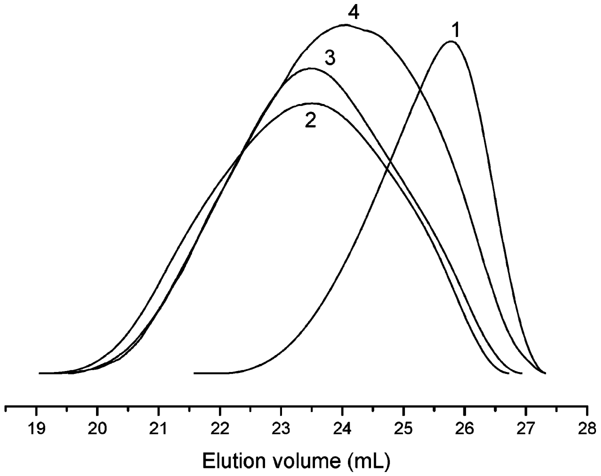


Figure 2. GPC profiles of the obtained CS_2/PO copolymer: (1) CS_2/PO = 1, (2) CS_2/PO = 1.5, (3) CS_2/PO = 2, and (4) CS_2/PO = 2.5.

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Supporting Information Available: Details of the experiments; IR, WAXD, and XPS data of the catalyst (Figures S1, S2, and S3); IR and ^1H NMR spectra of the copolymer (Figures S4 and S5); and GC-MS analyses (Figures S6 and S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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