

Account

## Studies on Ring-Opening Polymerization of Chloromethyl Thiirane with Rare Earth Catalysts and Functional Resins Synthesized therewith

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Studies on ring-opening polymerization of chloromethyl thiirane with rare earth catalysts and functional resins synthesized therewith were reviewed.

**Keywords** ring-opening polymerization, chloromethyl thiirane, rare earth catalysts

### Introduction

Ring-opening polymerization of chloromethyl thiirane (CMT) attracted the first attention in 1952<sup>1</sup> since its resultant polymer contains both sulfur and chlorine which make it a prospective material with anti-solvent, thermostability and flame resistance and an excellent precursor to synthesize functional polymer. It had been reported that cationic initiators, such as  $\text{BF}_3 \cdot \text{OEt}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$ , could convert CMT into tacky solid under  $-78\text{ }^\circ\text{C}$  over several days to weeks, but without definite data of its molecular weight and catalytic efficiency.<sup>2</sup> However, organometallic compounds based on cadmium, zinc and aluminum only afforded the viscous oil Poly(CMT) while anionic initiators were inactive at all.<sup>2</sup> In short, the polymerization of CMT has not been studied thoroughly and had no suitable catalysts before our works.

We recently found<sup>3-5</sup> that the rare earth coordination system composed of rare earth complex and alkyl aluminum had rather higher catalytic activity in the polymerization of CMT as in the polymerizations of alkylene oxide<sup>6,7</sup> and sulfide<sup>8</sup> and white soft solid of Poly(CMT) was obtained, as shown in Tables 1 and 2, although alkyl a-

luminum can convert CMT to liquid Poly(CMT)<sup>2</sup> and rare earth complex is inactive to initiate CMT polymerization. The Lewis acidity of ethyl aluminum sesquichloride is more strong as compared with triisobutyl aluminum, hence, the reaction of aluminum sesquichloride with CMT is rather violent. Therefore, the catalytic system with  $\text{Al}_2\text{Et}_3\text{Cl}_3$  was added into monomer at  $-10\text{ }^\circ\text{C}$ , allowed to slowly heat up to  $30\text{ }^\circ\text{C}$ , finally affording Poly(CMT) with higher molecular weight but lower yields than that with  $\text{Al}(i\text{-Bu})_3$  (Table 1). The various kinds of rare earth phosphonates combined with  $\text{Al}_2\text{Et}_3\text{Cl}_3$  were found to have almost the same activity, as shown in Table 2, whereas the polymer produced by La, Pr or Nd system has higher molecular weight than that by others. GPC and VPO showed that the samples of Poly(CMT) had intrinsic viscosity ( $[\eta]$ ) of 0.080, 0.047, 0.042 and 0.032 dL/g and the average number molecular weight of 10800, 4300, 3700 and 2700, respectively.

In our laboratory, attempt to raise the molecular weight of Poly(CMT) was successful by using rare earth solid superacids prepared from  $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ , superacids modified with lanthanide ions, as shown in Table 3.<sup>9</sup> Prior to our work,  $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ , superacids had been mainly engaged in the acid-catalyzed organic reactions with small molecule since it was discovered in 1978.<sup>10</sup> However, few attention was paid on its application in initiating polymerization. We found that all the three families of  $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ , superacids could convert CMT to opaque white elastic material. Rare earth ions added

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**Table 1** Polymerization of CMT with Nd coordination catalysts

Nd complex <sup>a</sup> cocatalyst	Nd(P <sub>204</sub> ) <sub>3</sub>	Nd(acac) <sub>3</sub>	Nd(P <sub>507</sub> ) <sub>3</sub>	Nd(P <sub>204</sub> ) <sub>3</sub>	Nd(acac) <sub>3</sub>	Nd(P <sub>507</sub> ) <sub>3</sub>	Nd(naph) <sub>3</sub>
	Al( <i>i</i> -Bu) <sub>3</sub> <sup>b</sup>			Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>c</sup>			
Yield (%)	69	72	67	32	34	18	17
[ $\eta$ ] × 10 <sup>2</sup> (dL/g) <sup>d</sup>	3.6	3.5	4.2	9.4	5.8	8.0	10.4

<sup>a</sup>Acac: acetylacetonate, naph: naphthenate, P<sub>204</sub>: RO(RO)P(O)O-, P<sub>507</sub>: R(RO)P(O)O-, R: CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>-. <sup>b</sup>Al/Nd = 12, [Nd] = 0.018 mol/L, [CMT] = 4 mol/L, polymerizing at 70 °C for 20 h, toluene as solvent. <sup>c</sup>Al/Nd = 12, [Nd] = 0.012 mol/L, [CMT] = 2.88 mol/L, initiated at 10 °C, polymerizing at 30 °C for 24 h, toluene as solvent. <sup>d</sup> Measured in THF at 25 °C.

**Table 2** Polymerization of CMT with various Ln(P<sub>204</sub>)<sub>3</sub>-Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> systems<sup>a</sup>

Ln	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Er	Y
Yield (%)	32	27	35	32	31	34	34	36	34	42
[ $\eta$ ] × 10 <sup>2</sup> (dL/g) <sup>b</sup>	9.1	5.4	9.1	9.4	3.8	4.4	4.8	4.2	4.0	4.3

<sup>a</sup> Al/Nd = 12, [Ln] = 1.15 × 10<sup>-2</sup> mol/L, [CMT] = 2.88 mol/L, initiated at -10 °C, polymerizing at 30 °C for 24 h, toluene as solvent.

<sup>b</sup> Measured in THF at 25 °C.

**Table 3** Polymerization of CMT with rare earth solid superacid<sup>a</sup>

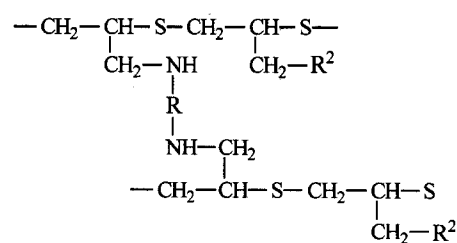
M <sub>x</sub> O <sub>y</sub> Ln	TiO <sub>2</sub>							ZrO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
	/	La	Pr	Nd	Gd	Dy	Y	Nd	Nd
Yield (%)	35	67	62	63	66	57	61	43	41
[ $\eta$ ] <sup>b</sup> (dL/g)	0.17	0.22	0.19	0.19	0.20	0.20	0.21	0.21	0.18
$\overline{M}_n$ <sup>c</sup> × 10 <sup>-4</sup>	3.06	4.14	3.48	3.53	3.79	3.80	4.10	4.07	3.29

<sup>a</sup> 0.1 g SO<sub>4</sub><sup>2-</sup> (1.85)/M<sub>x</sub>O<sub>y</sub>/Ln<sup>3+</sup> (0.052)-600, 1.25 g CMT, 50 °C, 24 h, in bulk. <sup>b</sup> Measured in THF at 30 °C. <sup>c</sup> Calculated by Mark-Houwink equation: [ $\eta$ ] = 0.594 × 10<sup>-4</sup> ·  $\overline{M}_n$ <sup>0.771</sup> (THF, 30 °C).<sup>11</sup>

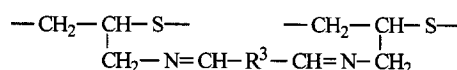
greatly increased their catalytic capabilities, which were not different in the respect of various rare earth elements as shown in Table 3. The molecular weight of obtained Poly(CMT) measured by GPC and viscosity method was found to be 30000 up to 50000 which is rather greater than ever reported.<sup>11</sup> CMT polymerization is proceeding via a cationic mechanism. The catalytic center is a chelating bidentate Brønsted acid.<sup>12</sup>

Based on its high reactivity of chloromethyl group in side chain of Poly(CMT), ten families of functional resins containing polythioether in backbone and other special functional groups in side chain, as shown in Fig. 1 and Table 4, were synthesized according to the following ways.<sup>13-16</sup> Poly(CMT) was precrosslinked with a small amount of diamine compound firstly. The residue chloro-groups were converted to amino-groups by Gabriel reaction and CA resins were afforded. CA resins reacted with carbon disulfide to afford CDTC resins and with dialdehyde compounds to afford CSB (Schiff base) resins. The other six families resins were all synthesized from precrosslinked Poly(CMT) and the corresponding agent con-

taining the introduced functional structure via substitution reactions. The structures of prepared resins were confirmed by IR spectra and elemental analysis.



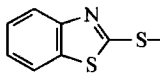
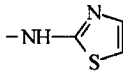
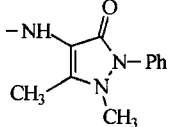
a



b

**Fig. 1** Structures of resins.

Table 4 Structure of resins

Name		Structure		N (%)	S (%)	Functional capacity (mmol/g resin)
Family	<i>n</i>	R <sup>1</sup>	R <sup>2</sup> or R <sup>3</sup>			
	1	-CH <sub>2</sub> CH <sub>2</sub> -		5.90	28.0	7.80
CA <sub>n</sub> (Fig. 1a)	2	-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -		6.64	27.2	5.33
	3	-CH <sub>2</sub> (CH <sub>2</sub> NHCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -	-NH <sub>2</sub>	6.88	26.9	5.39
	4	- <i>p</i> -C <sub>6</sub> H <sub>4</sub> -O- <i>p</i> -C <sub>6</sub> H <sub>4</sub> -		5.91	27.0	7.40
CDTC <sub>n</sub> (Fig. 1a)	1	-CH <sub>2</sub> CH <sub>2</sub> -		4.69	37.0	/
	2	-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -	-NH-C(=S)-S-NH <sub>2</sub>	4.82	34.0	/
	3	-CH <sub>2</sub> (CH <sub>2</sub> NHCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -		5.11	29.4	/
CSB <sub>n</sub> (Fig. 1b)	1		None	5.00	29.4	/
	2	/	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	4.18	22.6	/
	3		- <i>o</i> -C <sub>6</sub> H <sub>4</sub> -	3.54	17.0	/
CMBT <sub>n</sub> (Fig. 1a)	1	-CH <sub>2</sub> CH <sub>2</sub> -		4.86	36.3	3.47
	2	-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -		5.94	38.2	3.33
	3	-CH <sub>2</sub> (CH <sub>2</sub> NHCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -		4.00	33.4	2.50
C2AT (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -		8.15	33.0	3.62
C4AAP (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -		7.79	24.1	2.71
CPTC (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -	-SCN	5.26	40.0	4.45
CST (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -	-S <sub>2</sub> O <sub>3</sub> Na	2.75	33.2	3.15
CSA (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -	-N <sub>3</sub>	10.8	24.3	4.34
CPEA (Fig. 1a)		-CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> -	-S-C(=S)-OC <sub>2</sub> H <sub>5</sub>	4.98	33.0	2.84

As we expected, all the synthesized resins exhibited the excellent sorption properties for noble metal ions, but low ability for non-noble ones, as illustrated in Table 5. It is worthy to be mentioned that CA resins showed outstanding capability in trapping Au(III) (5–7 mmol/g Resin) and Ag<sup>+</sup> (7–9 mmol/g resin), while CDTC resins for Ag<sup>+</sup> (9–11 mmol/g resin). The sorption behaviors of these resins make them possible to be used in separation of noble metals from non-noble ones. The experiments of sorption in the ion mixture solution, containing ten times as the concentration of non-noble metal ions as that of Au(III) or Ag<sup>+</sup>, further confirmed this. Noble

metal ions absorbed can be easily relieved, Ag<sup>+</sup> by 15% aqueous ammonia, others by 2% thiourea aqueous solution, then the resin could be regenerated and reused. It was found that the capacities of CA2, CDTC1, CSB1, C2AT and CPTC for Ag<sup>+</sup> and that of C2AT for Au(III) remained 85%, 96%, 96%, 97%, 97% and 96% of original capacity, respectively, after three times regeneration, which indicated that these resins had excellent reusability.

In conclusion, rare earth coordination systems and rare earth solid superacids can catalyze the ring-opening polymerization of CMT with rather higher efficiency and

**Table 5** Sorption capacities for metal ions (mmol/g resin)<sup>a</sup>

Resin	Au(III)	Pt(IV)	Ag <sup>+</sup> <sup>b</sup>	Ag <sup>+</sup> <sup>c</sup>	Hg <sup>2+</sup>	Pb <sup>2+</sup>	Ni <sup>2+</sup>	Fe <sup>3+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>
CA1	5.19	1.98	7.55	6.94	1.67	0.469	0.220	0.992	0.274	1.150
CA2	5.52	1.28	7.69	7.42	1.65	0.040	0.190	0.340	0.046	0.170
CA3	6.76	0.90	8.79	8.45	1.98	0.115	0.192	0.948	0.124	1.013
CA4	7.24	0.20	7.29	6.22	1.29	0.385	0.227	0.808	0.077	0.736
CDTC1	1.24	0.75	10.64	9.63	1.46	0.719	0.050	0.498	0.295	0.660
CDTC2	0.43	0.76	9.94	9.57	1.57	0.249	0.018	0.375	0	0.213
CDTC3	0.70	1.76	9.88	9.50	1.42	0.976	0.032	0.377	0.134	0.725
CSB1	0.02	0.623	6.21	5.20	0.29	0.070	0.025	0.098	0.021	0.093
CSB2	2.15	0.597	6.43	5.41	1.58	0.094	0.141	0.333	0.084	0
CSB3	0.14	0.338	4.23	2.36	0.11	0.017	0.080	0.176	0.016	0.200
CMBT1	3.06	0.729	1.424	0.721	0.18	0.090	0.131	0.056	0.047	0.052
CMBT2	2.46	0	7.23	4.80	2.91	0.110	0	0.165	0.162	0.132
CMBT3	1.22	1.01	2.079	1.24	0.41	0.094	0.094	0.143	0.171	0.100
C2AT	2.62	1.27	6.52	5.81	2.73	0.285	/	/	0.88	0.74
C4AAP	4.44	0.17	6.44	6.76	7.83	0.294	/	/	0.63	0.19
CPTC	1.98	0.84	8.02	5.75	4.64	0.598	/	/	0.38	0.17
CST	3.35	2.05	5.53	8.70	6.96	3.75	/	/	0.34	0
CSA	1.69	0.99	6.77	5.45	3.96	0	/	/	0.38	0
CPEA	0.83	0.71	8.00	4.27	1.87	/	/	/	0.18	0

<sup>a</sup>Sorption conditions for Au(III): 12.5 mg of resin, 25 mL of Au(III) solution (1.0 mg/mL), in HCl (2 N); for Pt(IV): 12.5 mg of resin, 25 mL of Pt(IV) (1.0 mg/mL) solution in HCl (2 N); for Ag<sup>+</sup>: 100 mg of resin, 25 mL of Ag<sup>+</sup> solution (0.1 mol/L). <sup>b</sup> in HNO<sub>3</sub> (1 N). <sup>c</sup> in pH = 7; for Hg<sup>2+</sup>: 60 mg of resin, 25 mL of Hg<sup>2+</sup> solution (0.025 mol/L), in HNO<sub>3</sub> (1 N); for other ions: 60 mg of resin, 25 mL of ion solution (0.025 mol/L), pH = 5.6; at room temperature for 24 h.

yield solid Poly(CMT) with rather higher molecular weight. From resultant Poly(CMT), ten families of chelating resins having novel sorption properties for noble metal ions were synthesized.

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