NOTES

Ring-Opening Polymerization of Chloromethyl Thiirane with AlCl_3 and $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$ Coordination Catalyst

Weishi LI, Zhiquan SHEN,[†] Fuyao ZHANG, Yifeng ZHANG, Lianfang SHEN,*
and Hanzhen YUAN*

Department of Polymer Science and Engineering, Zhejiang University,
Hangzhou 310027, People's Republic of China

* State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics,
Wuhan Institute of Physics, Academia Sinica, Wuhan 430071,
People's Republic of China

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Since poly(chloromethyl thiirane) (PCMT) contains sulfur and chlorine, it could be developed into a new material with anti-solvent, thermostability, and flame resistance. It is an excellent precursor agent for synthesis of functional polymers. The polymerization of CMT was first reported in 1952.¹ In 1980s' Zussman *et al.* found only $\text{BF}_3 \cdot \text{OEt}_2$, $\text{CF}_3\text{SO}_3\text{H}$ and H_2SO_4 etc. cationic catalysts could convert CMT to PCMT with low molecular weight.² The $\text{Nd}(\text{P}_{204}^{*1})_3 - \text{Al}(\text{tBu})_3$ rare earth coordination catalyst was used here for this polymerization to obtain the PCMT of $\bar{M}_n$ 4000.³ This paper report the synthesis of PCMT with higher molecular weight using AlCl_3 and $\text{Nd}(\text{acac}^{*2})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$ coordination system as catalysts.

EXPERIMENTAL

Chloromethyl thiirane was prepared by reaction of epichlorohydrin and thiourea after Tabushi method⁴ and distilled (bp 54–56°C/97 mmHg) from CaH_2 . $\text{Al}_2\text{Et}_3\text{Cl}_3$ was purified by distillation. $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ was prepared from Nd_2O_3 (>99.99%). $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$ catalyst was prepared by adding $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$, toluene, and $\text{Al}_2\text{Et}_3\text{Cl}_3$ into a dehydrated bottle and aging at 60°C for 1 h. All polymerizations were carried out in purified nitrogen and terminated by ethanol with 10% HCl. After drying in air and in vacuum at 40°C, a white elastic solid poly(chloromethyl thiirane) (PCMT) was obtained.

The intrinsic viscosity of PCMT was measured by a Ubbelohde viscometer in tetrahydrofuran (THF) (0.1 g/25 ml) at 30°C (AlCl_3) or 25°C ($\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$). $^1\text{H} - ^{13}\text{C}$ two dimensional chemical shift correlation NMR and DEPT (distortionless enhancement by polarization transfer) ^{13}C spectra were obtained on a Bruker AR500 NMR spectrometer, using CDCl_3 and tetramethylsilane (TMS) as the solvent and internal reference, respectively. PCMT molecular weight and distribution were determined by a WATERS-150 gel

permeation chromatograph employing THF as eluent at 30°C, and calculated using the Mark-Houwink equation⁶:

$$[\eta] = 0.594 \times 10^{-4} \times \bar{M}_v^{0.771} \quad (30^\circ\text{C}, \text{THF})$$

The differential scanning calorimetric diagram of the polymer was obtained using a Perkin Elmer DSC7.

RESULTS AND DISCUSSION

AlCl_3 was an effective catalyst for CMT polymerization for the first time. The effects of Al/CMT molar ratio and temperature on this polymerization are shown in Table I. The favorable polymerization conditions are the following: $\text{Al/CMT} = 2 \times 10^{-2}$, 30°C. PCMT prepared has a maximum $[\eta]$ value of 0.170 dl g^{-1} in THF at 30°C. GPC analysis showed its molecular weight ($\bar{M}_v$) to be 31000 and $\bar{M}_w/\bar{M}_n$ to be 2.06.

Like other rare earth coordination catalysts that have high activity in the polymerization of alkylene oxides and sulfides, $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$ exhibits good capability to convert CMT to PCMT. The polymerization in *n*-hexane with CMT concentration of 3 mol L^{-1} is more suitable than others. Although $\text{Al}_2\text{Et}_3\text{Cl}_3$ can

Table I. Polymerization of CMT with AlCl_3 ^a

Temperature/°C	0 ^b	30	30	30	30	50
Al/CMT $\times 10^2$	2	0.667	1	2	4	2
Yield/%	42	33	54	81	91	93
$[\eta] \times 10^2/\text{dl g}^{-1}$	17.9	9.9	15.2	17.0	8.7	4.1

^a Al/CMT = 2%, 24 h, in bulk. ^b Polymerizing for two weeks.

Table II. Effect of Al/Nd Molar ratio on CMT polymerization with $\text{Na}(\text{acac})_3 \cdot 3\text{H}_2\text{O} - \text{Al}_2\text{Et}_3\text{Cl}_3$ ^a

Al/Nd	0	4	8	10	12	14	18	22	∞ ^b
Yield/%	0	3	30	35	47	52	61	50	54
$[\eta] \times 10^2/\text{dl g}^{-1}$	/	/	7.6	7.6	7.9	8.0	5.7	4.7	3.9

^a Nd/CMT = 0.4%; [CMT] = 2.88 mol L^{-1} ; initiated at -10°C ; polymerizing at 30°C for 24 h; *n*-hexane as solvent. ^b [Nd] = 0; [Al] = 0.115 mol L^{-1} .

[†] To whom correspondence should be addressed.

*¹ P_{204} , $\text{RO}(\text{RO})\text{P}(\text{O})\text{O}-$; R, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2-$.

*² acac, acetylacetonate.

afford a liquid PCMT and $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ is ineffective to initiate CMT polymerization, as shown in Table II, the two compounds together at an Al/Nd molar ratio of 12–14 exhibit high activity and give PCMT of high molecular weight with high yield. Figure 1 and Table III show that the increase of Nd/CMT molar ratio or temperature leads to increase yield but decrease in the molecular weight of PCMT. Compared with AlCl_3 , polymers produced with this catalyst have lower molecular weight and wider polydispersity. The sample with $[\eta]$ of 0.080 dl g^{-1} (in THF, 25°C) was found to have 10800 molecular weight ($\bar{M}_v$) and 5.6 polydispersity index.

Due to anchimeric assistance by backbone sulfur atoms, PCMT units (A) can be slowly rearranged and form poly(3-chlorothietane) units (B)²:

There are eight different combinations of A and B in a triad sequence, as shown in Table IV. ^{13}C shifts of the middle units of these sequences were estimated according to empirical additive rules by ^{13}C NMR software. Table IV assigns the signals in ^1H - ^{13}C two dimensional chemical shift correlation NMR spectrum in Figure 2. These assignments were confirmed by the DEPT ^{13}C NMR spectrum of PCMT. A ^{13}C peak at 36.6 ppm appeared in the given NMR spectrum of paper² but had not been referred. This signal, attributed to sequences of ABB, ABA, BAA, and AAB, presents strong evidence for the existence of linkages between A and B.

The differential scanning calorimetric diagram of PCMT shows two thermal transitions at -65°C and -32°C .

AlCl_3 and $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ - $\text{Al}_2\text{Et}_3\text{Cl}_3$ are effective catalysts for CMT polymerization under mild conditions, producing PCMT with molecular weights ($\bar{M}_v$) of 31000

Table III. Effect of temperature on CMT polymerization with $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ - $\text{Al}_2\text{Et}_3\text{Cl}_3$ ^a

Temperature/ $^\circ\text{C}$	-10	0	20	30	40	50	60	70
Yield/%	12	15	37	45	49	50	52	68
$[\eta] \times 10^2/\text{dl g}^{-1}$	11.9	9.5	8.4	8.0	6.7	5.7	4.1	2.9

^a Al/Nd = 12; *n*-hexane as solvent; other conditions are the same as in Table II.

Table IV. ^{13}C shifts of middle units of PCMT triad sequences

Sequence	Calculated			Observed			Ref 2			^1H Shift		
	C-1	C-2	C-3	C-1	C-2	C-3	C-1	C-2	C-3	H-1	H-2	H-3
AAA	33.2	46.7	50.6	35.0								
AAB	33.2	46.6	50.6		48.6	46.0	34.96	49.28	46.88	3.06	3.06	3.90
BAA	36.4	46.4	50.6	36.6								
BAB	36.4	46.3	50.6									
BBB	39.0	57.9	39.0	38.4								
BBA	39.0	58.2	39.1		59.0	38.4	39.93	60.92	39.93	3.06	4.2	3.06
ABB	35.8	58.2	39.0	36.6								
ABA	35.8	58.2	39.1									

and 10800, respectively, in fairly good yield. The polymer chain structure containing CMT and 3-chlorothietane units was identified by ^1H - ^{13}C two dimensional shift correlation NMR and ^{13}C DEPT NMR spectra.

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Figure 1. Polymerization of CMT with $\text{Nd}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ - $\text{Al}_2\text{Et}_3\text{Cl}_3$ dependence on molar ratio of Nd/CMT. Conditions: Al/Nd = 12; *n*-hexane as solvent; others are the same as in Table II.

Figure 2. The ^1H - ^{13}C two dimensional chemical shift correlation NMR spectrum of PCMT.

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