

POLYMER-SUPPORTED RARE EARTH CATALYSTS FOR STYRENE POLYMERIZATION

ZHAO Jian (赵健), YANG Mujie (杨慕杰), ZHENG Yi (郑毅)
and SHEN Zhiquan (沈之荃)

(Chemistry Department, Zhejiang University, Hangzhou)

ABSTRACT

The neodymium complex supported on styrene-maleic anhydride copolymer (SMA · Nd) has been prepared for the first time and found to be a highly effective catalyst for the polymerization of styrene. The SMA · Nd polymeric complex is characterized by IR and its catalytic activity, and the polymerization features have been investigated in comparison with that of the conventional Ziegler-Natta catalysts. When $[Nd] = 1 \times 10^{-3} \text{ mol/L}$, $[M] = 5 \text{ mol/L}$, $Al/Nd = 170$ (mol ratio) and $CCl_4/Nd = 50$ (mol ratio), the polymerization conversion of styrene gets to 51.6% in six hours, and the catalytic activity reaches 1852 gPS/gNd, which is much higher than that of conventional rare earth catalysts. The polymerization reaction has an induction period and shows some characteristics of chain polymerization. The polymerization rate is the first order with respect to the concentration of styrene monomer. Addition of $FeCl_3$ does not suppress the polymerization.

INTRODUCTION

Recently interest in the polymer-supported catalysts has prompted extensive research for utilizing in polymerization, which is a valid way to increase catalytic activity and selectivity^[1, 2]. We have reported that ethylene-vinyl alcohol copolymer supported neodymium (EVA · Nd) has showed much higher catalytic activity for styrene polymerization than that of the conventional rare earth catalysts^[3]. This paper deals with the preparation of a styrene-maleic anhydride copolymer (SMA)-neodymium (Nd) polymeric complex and its application to the polymerization of styrene (St) for the first time. The characterization of SMA · Nd polymer complex by IR is described. The features of St polymerization by SMA · Nd-Al(*i*-Bu)₃-CCl₄ catalyst system in terms of Al/Nd mol ratio, CCl₄/Nd mol ratio, the concentrations of catalyst and monomer, and the polymerization time are investigated.

EXPERIMENTAL

1. Materials

Styrene (St) was a chemical reagent and freed of inhibitor by distillation under nitrogen at reduced pressure. Commercial maleic anhydride was purified by recrystallization before use. Triisobutyl aluminium was a commercial product obtained from Roth Chemical Co. Neodymium oxide of 99.99% was from Shanghai Yaolon Chemical Plant. Toluene, benzene, tetrachloromethane, tetrahydrofuran, methanol, and methyl ethyl ketone were all analytical reagents and dried before use.

2. Preparation of styrene-maleic anhydride copolymer (SMA)

SMA was obtained from the copolymerization of St and MA by BPO in a benzene solvent at the reflux temperature. Then the resultant was purified by reflux in benzene in order to remove homopolystyrene. The content of maleic anhydride in the copolymer was measured by acid-base titration after saponification in a NaOH solution. The number molecular weight ($\overline{M}_n$) of SMA was 2.4×10^5 , measured in 0.4% acetone solution at 30 °C, and calculated with the equation: $[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.74} (\text{dl/g})^{[4]}$.

3. Preparation of styrene-maleic anhydride copolymer (SMA) supported neodymium complex (SMA · Nd)

The SMA was dissolved in THF, and mixed with equivalent amount of neodymium chloride in a methanol solution. The SMA · Nd complex was precipitated out by addition of a certain amount of ammonia water while stirring. The complex was washed with pure water until no chloride ion was detected, then dried in vacuum at 50 °C for six hours. The content of Nd in the SMA · Nd complex was determined by complexometric titration after ignition.

4. Polymerization procedure and analysis of polystyrene and polymeric complex

All polymerization procedures were carried out under nitrogen atmosphere. The polymerization bottles were sealed, heated, evacuated and filled with nitrogen for several cycles before use for the sake of the exclusion of moisture and air. In a typical experiment, SMA · Nd polymeric complex, monomer, solvent, and $\text{Al}(\text{i-Bu})_3$ were added in this order to a bottle. After shaking for twenty minutes, CCl_4 as a third component was added into this catalyst solution, and shaking was continued for half an hour at room temperature. The polymerization was carried out at 70 °C. At definite reaction time, the polymerization was terminated by adding methanol with 10% HCl. The resulted polymer was precipitated by pouring the reaction mixture into ethanol, then filtered, washed with water and ethanol, and dried at 50 °C in vacuum.

The infrared spectra of the polymer support and its neodymium complex were taken using KBr pellets or films on KBr plate by a FTIR-5DX infrared spectrophotometer. The average molecular weight of polystyrene was determined on a Waters GPC Model 208 at 30 °C, with a standard polystyrene sample as reference.

RESULTS AND DISCUSSION

1. Characterization of the polymer-supported complex (SMA · Nd)

The parameters of the polymer-supported neodymium complex SMA · Nd prepared are listed in Table 1. Figure 1 shows IR spectra of SMA · Nd and its polymer support SMA. In the spectrum of SMA, bands at 1860, 1780 cm^{-1} and 1220, 1070 cm^{-1} show the characteristic absorption peaks of $-\text{C}=\text{O}$ and $-\text{C}-\text{O}-$ groups, respectively. In the spectrum of SMA · Nd, the absorptions of $-\text{C}=\text{O}$ and $-\text{C}-\text{O}-$ groups all become obviously weakened.

And three new broaden peaks appear at 1660, 1550 and 1413 cm^{-1} , which have been demonstrated to be the characteristic absorption peaks of anhydride combined with metal cations^[5]. This indicates that neodymium cations have been bound to complex with the anhydride of the polymer support. In comparison with simple rare-earth complexes, the $\text{SMA} \cdot \text{Nd}$ might have rich covalent bonds.

Table 1 Parameters of polymer-supported complex ($\text{SMA} \cdot \text{Nd}$)

Polymer support	Anhydride groups		Quantity of bound metal	
	wt %	mmol / g	mmol / g	mol / mol of anhydride group
SMA	45	4.44	1.24	0.28

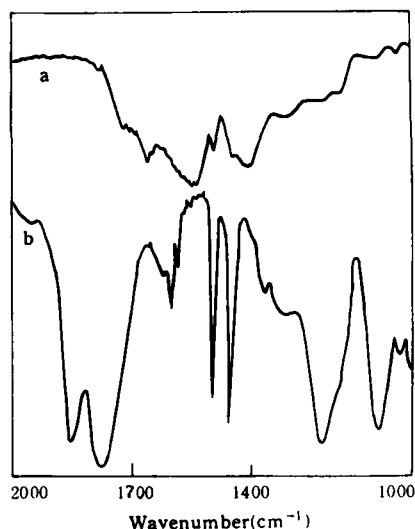


Fig.1 IR absorption spectra of $\text{SMA} \cdot \text{Nd}$ (a) and SMA (b)

2. Features of styrene polymerization by $\text{SMA} \cdot \text{Nd} - \text{Al}(\text{i-Bu})_3 - \text{CCl}_4$ catalyst system

The coordination catalyst composed of $\text{SMA} \cdot \text{Nd}$ and $\text{Al}(\text{i-Bu})_3$ can effectively catalyze the polymerization of styrene in a toluene solution at 70 $^{\circ}\text{C}$. This reveals that the $\text{SMA} \cdot \text{Nd}$ polymer-supported complex has catalytic activity. Similar to $\text{EVA} \cdot \text{Nd}$ catalyst system, the catalytic activity of $\text{SMA} \cdot \text{Nd}$ system will greatly increase by addition of the third component CCl_4 to this system, and so does the molecular weight of the polymer obtained, as shown in Table 2. The conversion and catalytic activity increase with increasing CCl_4 / Nd mol ratio and approach to 51.3% and 1107 gPS / gNd respectively at $\text{CCl}_4 / \text{Nd} = 50$ mol ratio. It indicates that the $\text{SMA} \cdot \text{Nd} - \text{Al}(\text{i-Bu})_3 - \text{CCl}_4$ system is a very active catalyst among other Z-N type catalysts for styrene polymerization^[6].

The relationship among $\text{SMA} \cdot \text{Nd}$, $\text{Al}(\text{i-Bu})_3$, CCl_4 played an important role in catalytic activity which influenced the molecular weight of PS, as shown in Table 3. It can be seen that only when $\text{Al} / \text{Nd} > 18$ mol ratio, the polymerization reaction can take place. The catalytic activity increases continuously and appears to be optimum at $\text{Al} / \text{Nd} = 170$ mol ratio with increasing

Table 2 Effect of additional quantity of CCl_4 on the catalytic activity and molecular weight of PS

CCl_4 / Nd (mol ratio)	Conversion (%)	Catalytic activity (gPS / gNd)	GPC		
			$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	MWD
0	16.3	353	0.45	0.71	1.6
5	23.1	498	0.44	0.74	1.7
10	34.6	747	0.59	1.05	1.8
20	40.4	872	0.69	1.42	2.1
35	44.9	969	0.61	1.23	2.0
50	51.3	1107	0.49	1.01	2.1
70	51.9	1120	0.43	0.90	2.1

Polymerization conditions :

$[\text{Nd}] = 1 \times 10^{-3} \text{ mol / L}$, $[\text{M}] = 3 \text{ mol / L}$, $\text{Al / Nd} = 120 (\text{mol ratio})$, 70°C , 6hr.

Table 3 Effect of Al/Nd mol ratio on the catalytic activity and molecular weight of PS

Al / Nd (mol ratio)	Conversion (%)	Catalytic activity (gPS / gNd)	GPC		
			$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	MWD
18	trace	/	/	/	/
35	13.8	298	1.60	7.07	4.41
70	36.5	789	1.04	2.24	2.16
100	38.8	837	0.77	1.58	2.07
120	44.9	969	0.57	1.07	1.87
135	54.2	1170	0.52	0.96	1.84
170	58.0	1253	0.42	0.76	1.82
200	58.5	1264	/	/	/

Polymerization conditions :

$\text{Al} / \text{CCl}_4 = 3.4 \text{ mol ratio}$, (for the others see Table 2).

Al / Nd mol ratio, while the MW and MWD of PS decrease gradually. It reveals that only under high Al / Nd mol ratio, the $\text{SMA} \cdot \text{Nd}$ polymeric complex can effectively interact with $\text{Al}(\text{i-Bu})_3$ to form active centers and show high catalytic activity. It may also be associated with that $\text{Al}(\text{i-Bu})_3$ has to eliminate impurity in the polymerization system including the excess functional groups on the SMA polymer support. Since $\text{Al}(\text{i-Bu})_3$ is almost exhausted by impurity but CCl_4 is excess under lower Al / Nd mol ratios, the concentration of active centers formed is low and the excess CCl_4 takes part in transfer reactions such that the molecular weight and MWD of PS become high. Under higher Al / Nd mol ratios, the MWD of PS keeps constant because $\text{Al}(\text{i-Bu})_3$ almost does not join in transfer reaction during this polymerization. This is different from that in $\text{EVA} \cdot \text{Nd} \cdot \text{Al}(\text{i-Bu})_3 \cdot \text{CCl}_4$ system^[3]. Furthermore the Al / CCl_4 mol ratio is a key factor to obtain high catalytic activity in this system, which is consistent with the results from Tables 2 and 3. From the above discussion, one can see that the preferable conditions for this polymerization system are $\text{CCl}_4 / \text{Nd} = 50$, $\text{Al} / \text{Nd} = 170$, and $\text{Al} / \text{CCl}_4 = 3.4 \text{ mol ratio}$.

Table 4 shows the effect of the concentration of polymer-supported catalyst ($\text{SMA} \cdot \text{Nd}$) and monomer on the polymerization activity. Under the following

conditions : $[\text{SMA} \cdot \text{Nd}] = 1 \times 10^{-3} \text{ mol/L}$, $[\text{M}] = 5 \text{ mol/L}$, $\text{Al} / \text{CCl}_4 = 3.4 \text{ mol ratio}$, $\text{Al} / \text{Nd} = 120 \text{ mol ratio}$, after 6 hours polymerization, the polymerization conversion and catalytic activity reached 51.6% and 1852 gPS/gNd respectively. The catalytic activity was about forty times higher than that with conventional rare earth catalyst systems^[7].

Table 4 Dependence of the polymerization conversion and activity on the concentrations of $\text{SMA} \cdot \text{Nd}$ and St

$[\text{Cat}] \times 10^3 (\text{mol/L})$	0.5	1	2	3	4	5
Conversion (%)	31.6	45.3	68.3	71.5	73.4	77.8
Catalytic activity (gPS/gNd)	1364	974	737	516	397	337

$[\text{M}] (\text{mol/L})$	1	2	3	4	5	6
Conversion (%)	38.5	41.4	51.3	46.9	51.6	37.4
Catalytic activity (gPS/gNd)	276	593	1103	1345	1852	1607

Polymerization conditions :

a) $[\text{M}] = 3 \text{ mol/L}$, b) $[\text{Cat}] = 1 \times 10^{-3} \text{ mol/L}$; $\text{Al} / \text{Nd} = 120$, $\text{Al} / \text{CCl}_4 = 3.4 (\text{mol ratio})$,
(for the others see Table 2).

Table 5 and Figure 2 present the kinetic behavior of St polymerization by $\text{SMA} \cdot \text{Nd-Al}(\text{i-Bu})_3\text{-CCl}_4$ catalyst. It can be seen that the polymerization reaction had an induction period of 18 minutes and showed first order with respect to the monomer concentration at the initial stage. It may be considered that styrene monomer was slowly diffused into the radicals of the polymer-supported catalyst. From Table 5 it also can be seen that the MW of PS almost kept constant during the polymerization, which was different from that in $\text{EVA} \cdot \text{Nd-Al}(\text{i-Bu})_3\text{-CCl}_4$ catalyst system^[3].

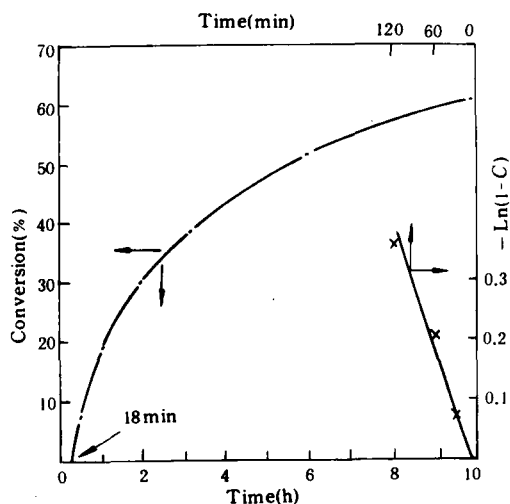


Fig. 2 The curves of the conversion vs. polymerization time (Conditions see Table 2).

Table 5 The dependence of polymerization conversion and MW of PS on polymerization time

Time	Conversion	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	MWD
(hr)	(%)	GPC		
0.5	7.7	0.56	0.96	1.70
1	19.6	0.44	0.75	1.70
2	30.1	0.54	0.92	1.70
4	38.8	0.63	1.10	1.75
6	51.3	0.57	1.07	1.87
10	61.5	0.59	1.15	1.94

Conditions : see Table 2 .

By addition of FeCl_3 in an amount of 0.5% monomer weight , the polymerization was not suppressed but activated , the conversion of which increased from 51.6% to 71% . It indicates that FeCl_3 can take part in catalyzing the polymerization of St . This feature was similar to that in $\text{EVA} \cdot \text{Nd-Al}(\text{i-Bu})_3 \cdot \text{CCl}_4$ system^[3] . The polystyrene obtained with $\text{SMA} \cdot \text{Nd-Al}(\text{i-Bu})_3 \cdot \text{CCl}_4$ system showed completely atactic structure . This was examined by IR spectrum and methylethylketone extraction method^[6] .

Keywords :

Polymer-Supported Rare-Earth Catalyst ; $\text{SMA} \cdot \text{Nd}$; Polymerization of Styrene

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