

THE POLYMERIZATION OF ACETYLENE BY COORDINATION CATALYSTS COMPOSED OF NEODYMIUM COMPOUND, ALUMINUM TRIALKYL AND A THIRD COMPONENT*

ZHANG Yifeng (张一峰), CAI Yiping (蔡一平), YANG Mujie (杨慕杰)
and SHEN Zhiquan (沈之荃)

(Department of Chemistry, Zhejiang University, Hangzhou)

ABSTRACT

This paper describes the polymerization of acetylene by coordination catalysts composed of various neodymium compounds, ($\text{Nd}(\text{P}_{204})_3$; $\text{Nd}(\text{P}_{507})_3$; $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$; $\text{Nd}(\text{BA})_3 \cdot 2\text{H}_2\text{O}$; and $\text{Nd}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$), aluminum trialkyl and an electron donor. The catalysts show fairly high catalytic activity and high *cis* stereospecificity on acetylene polymerization at 30°C.

Rare earth coordination catalysts can polymerize acetylene into high *cis* polyacetylene films at room temperature^[1]. In order to gain an insight into the characteristics of acetylene polymerization by these catalyst systems, we highlight the effects of varieties of neodymium compounds, aluminum trialkyls and additional compounds, as well as the preparation conditions of catalyst, on catalytic activities of polymerization and properties of polyacetylene.

EXPERIMENTAL

Neodymium compounds: $\text{Nd}(\text{P}_{204})_3$; $\text{Nd}(\text{P}_{507})_3$; $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$; $\text{Nd}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Nd}(\text{BA})_3 \cdot 2\text{H}_2\text{O}$ were prepared according to the reference [2]. Where $\text{P}_{204} = \begin{matrix} \text{RO} \\ \diagup \\ \text{R} \end{matrix} \text{P} \begin{matrix} \diagdown \\ \text{RO} \end{matrix} \begin{matrix} \text{O} \\ || \\ \text{O} \end{matrix} \text{—OH}$,

$\text{P}_{507} = \begin{matrix} \text{R} \\ \diagup \\ \text{RO} \end{matrix} \text{P} \begin{matrix} \diagdown \\ \text{RO} \end{matrix} \begin{matrix} \text{O} \\ || \\ \text{O} \end{matrix} \text{—OH}$, $\text{R} = \text{CH}_3\text{—}(\text{CH}_2)_3\text{—CH—CH}_2\text{—}$; $\text{P}_{350} = \begin{matrix} \text{RO} \\ \diagup \\ \text{RO} \end{matrix} \text{P} \begin{matrix} \diagdown \\ \text{RO} \end{matrix} \begin{matrix} \text{O} \\ || \\ \text{O} \end{matrix} \text{—CH}_3$, $\text{R} = \text{CH}_3\text{—}$

$(\text{CH}_2)_5\text{—CH—}$; $\text{acac} = (\text{CH}_3\text{CO})_2\text{CH}_2$; $\text{BA} = \text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$. These compounds were

analysed by differential thermal analysis showing no ethanol or H_2O contaminated.

Polymerizations, treatment of polyacetylene and characterization of polyacetylene films were carried out as previously described in the reference [1].

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Other participants include Ling Qing, Feng Wei, Li Liang and Chen Zhi

RESULTS AND DISCUSSION

Effect of ligand on neodymium compound on polymerization

The experimental results showed that silvery polyacetylene (PA) films can be obtained by benzene or toluene solution of coordination catalyst composed of any one of these neodymium compounds and triisobutyl aluminum. But various neodymium systems show the highest catalytic activity at different molar ratio of aluminum alkyl to neodymium compound (Al/Nd molar ratio) and molar ratio of third component to neodymium compound (III/Nd molar ratio). Fig. 1 illustrated the influences of Al/Nd and III/Nd molar ratio on the yield of PA film in Nd (P_{507})₃ system. The favorable polymerization conditions of various neodymium systems are summarized in Table 1.

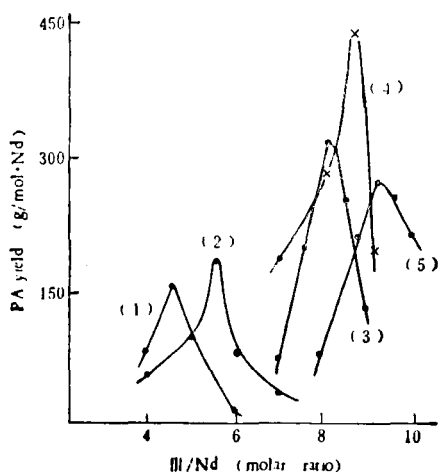


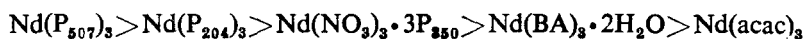
Fig. 1 Effect of Al/Nd, III/Nd on yield of PA film
Al/Nd, molar ratio: (1)7; (2)9; (3)11; (4)13; (5)14.
Conditions: Nd(P_{507})₃-Al(i-Bu)₃- P_{204} system; 30°C; 1 h.

Table 1 The favorable conditions of various Nd systems

Nd compd.	Cat. conc. (mole/ml) $\times 10^5$	Al/Nd (molar ratio)	III/Nd (molar ratio)	PA yield (g/mole Nd)
Nd(P_{204}) ₃	2.3	10	7	284.2
Nd(P_{507}) ₃	2.4	13	8.5	434.2
Nd(NO ₃) ₃ ·3 P_{350}	4.0	15	5	131.3
Nd(acac) ₃ ·2H ₂ O	6.0	13	8	85.1
Nd(BA) ₃ ·2H ₂ O	8.0	14	9	104.0

30°C; 1 hour; benzene or toluene; Al(i-Bu)₃.

The catalytic activity of various Nd systems under their best conditions is in the following order:



This sequence shows that the electron donating ability of the ligand increases, the catalytic activity will be promoted. Table 2 listed the *cis* content and properties of PA obtained by various Nd systems. More than 86% *cis* content of PA films are obtained by all these systems at 30°C except $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$. The lower electrical resistivity and higher concentration of unpaired electron of PA system with $\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$ are obviously due to its higher *trans* content.

Table 2 *Cis* content and properties of polyacetylene

Nd compd.	<i>cis</i> (%)	ΔH^{*1} (gauss)	$N^{*2} \times 10^{-16}$ (spins/g)	$\rho^{*3} \times 10^{-10}$ (ohm·cm)	d^{*4} (Å)	density (g/cm ³)
$\text{Nd}(\text{P}_{204})_3$	93.1	9.80	2.16	41.4	3.81	1.1670
$\text{Nd}(\text{P}_{507})_3$	92.0	—	1.86	36.1	3.83	1.1709
$\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$	75.2	11.5	19.4	1.16	3.84	1.1644
$\text{Nd}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$	86.6	10.65	4.41	8.4	3.83	1.1644
$\text{Nd}(\text{BA})_3 \cdot 2\text{H}_2\text{O}$	86.0	11.17	4.38	8.0	4.00	1.1640

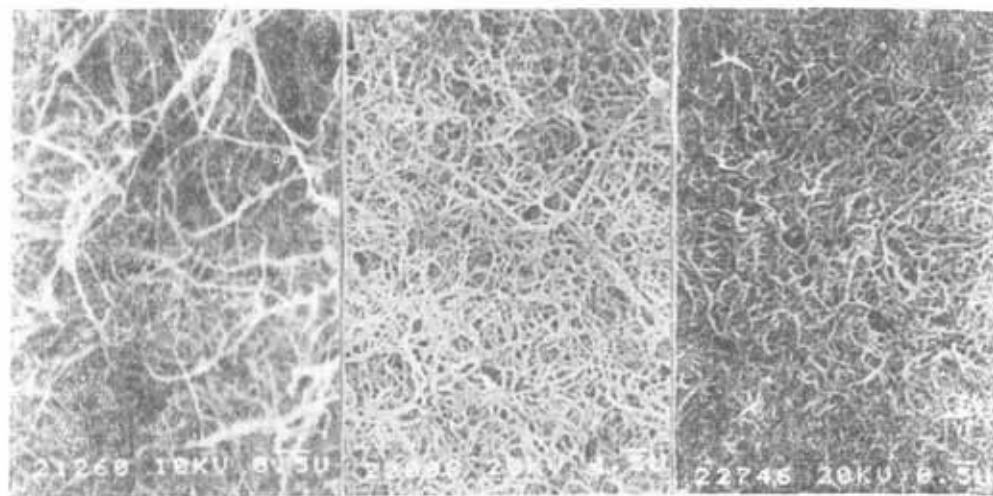
* 1 ESR line width;

* 2 Concentration of unpaired electron;

* 3 Electrical resistivity;

* 4 Distance of crystal face.

Observations from a transmission microscope and scanning electron microscope showed that the PA films were composed of aggregation of disordered fibrils about 200–650 Å in width, irrespective of ligands used, as shown in Fig. 2 and Fig. 3.



(1) $\text{Nd}(\text{P}_{204})_3$

(b) $\text{Nd}(\text{P}_{507})_3$

(c) $\text{Nd}(\text{BA})_3 \cdot 2\text{H}_2\text{O}$

Fig. 2 SEM images of PA films

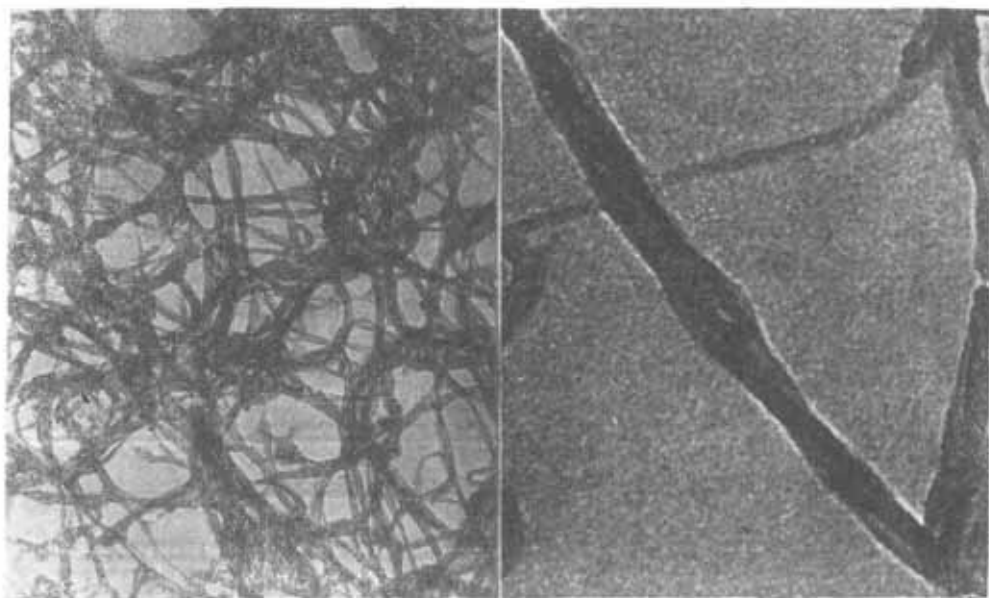
(a) $\text{Nd}(\text{P}_{204})_3$ Magnification=40,000(b) $\text{Nd}(\text{P}_{507})_3$ Magnification=400,000

Fig. 3 TEM images of PA films

Polymerization temperature affects the catalytic activity and *cis* content of PA differently in various systems, as shown in Table 3. $\text{Nd}(\text{P}_{204})_3$ and $\text{Nd}(\text{P}_{507})_3$ systems display fairly high catalytic activity and *cis* stereospecificity at 30°C. Lowering polymerization temperature down to 0°C or even lower, the *cis* content of PA increases and the catalytic activity decreases somewhat. Yet with β -diketone chelate system, it is preferable to polymerize acetylene at 0°C or below 0°C in order to get higher catalytic activity and *cis* content of PA. The yield of PA film increased while lengthening the polymerization period in $\text{Nd}(\text{P}_{204})_3$ and $\text{Nd}(\text{P}_{507})_3$ systems. Nevertheless the PA yield of other Nd systems reached the maximum after polymerization for one hour.

Table 3 Effect of Polymerization Temperature

Nd compd.	-13°C		0°C		30°C		50°C	
	PA yield (g/mol Nd)	<i>cis</i> (%)	PA (g/mol Nd)	<i>cis</i> (%)	PA (g/mol Nd)	<i>cis</i> (%)	PA (g/mol Nd)	<i>cis</i> (%)
$\text{Nd}(\text{P}_{507})_3$	—	—	226.5	95.1	434	92.0	264	81.0
$\text{Nd}(\text{P}_{204})_3$	—	—	92.3	95.4	284	93.1	92.3	83.1
$\text{Nd}(\text{NO}_3)_3 \cdot 3\text{P}_{350}$	—	—	85.1	92.0	137	75.2	black powder	—
$\text{Nd}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$	163	98.3	82.2	97.6	85	86.6	black powder	—
$\text{Nd}(\text{BA})_3 \cdot 2\text{H}_2\text{O}$	87	97.0	100	95.6	104	86.0	black powder	—

$\text{Al}(\text{i-Bu})_3$; toluene; 1 hour; other conditions as Table 1.

Effect of additives

Table 4 showed that Nd (P_{204})₃-Al (C_2H_5)₃ binary system only produce PA at very low Al/Nd=2. As well known the polymerization reaction at such low Al/Nd is usually easy to be affected by environmental condition. Although Nd(P_{204})₃-Al (i-Bu)₃ binary system gave PA film at Al/Nd molar ratio in the range of 3—7, the yield and *cis* content of PA were not high enough. We found that a certain amount of electron donor (additive) added to the catalyst could facilitate the formation of silvery PA film and raise the *cis* content of PA from 86% to above 92%. The effectiveness upon the addition of 11 kinds of donors used is in the following order:

P_{204} > dioxane > pyridine > tributyl phosphate > n-octanol > triethyl amine > aniline > triphenyl phosphine > butanol > butanone > anisole.

Table 4 The polymerization of acetylene by Nd(P_{204})₃-AlR₃ binary system

Al/Nd molar ratio	2	3	4	5	6	7	8
PA yield (g/mol Nd)	32.1	—	—	—	—	—	—
Al(C_2H_5) ₃ <i>cis</i> (%)	86.6	—	—	—	—	—	—
PA yield (g/mol Nd)	red gel	24.5	36.1	49.6	57.7	42.0	black powder
Al(i-Bu) ₃ <i>cis</i> (%)	—	87.0	89.0	89.0	89.0	75.1	—

35°C; 1 hour; concentration of catalyst = 3.5×10^{-5} mol/ml.

Fig. 4 illustrated the comparison of additional effectiveness of P_{204} , P_{507} and P_{350} . It might conclude that the more acidic the additive the greater the effectiveness, since the P_{ka} of P_{204} is 3.32, P_{ka} of P_{507} is 4.10, and P_{350} is neutral.

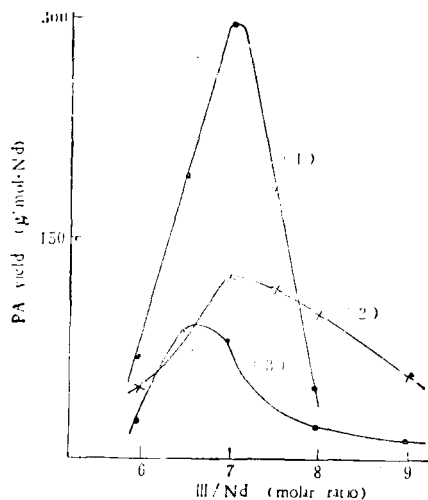


Fig. 4 Comparison of additional effectiveness of phosphonates Nd(P_{204})₃-Al(i-Bu)₃-III system; (1) P_{204} ; (2) P_{507} ; (3) P_{350} .

The catalytic activity difference between ternary systems combined with $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{i-Bu})_3$ was negligible, as shown in Table 5.

Table 5 Effect of variety of AlR_3 in ternary system

AlR_3	Al/Nd (molar ratio)	III/Nd (molar ratio)	Hour of polym.	PA yield (g/mol Nd)	cis(%)
$\text{Al}(\text{C}_2\text{H}_5)_3$	6	3.5	1.5	155.8	95.2
$\text{Al}(\text{i-Bu})_3$	7	5	2.0	147.1	95.8

Concentration of catalyst = 3.5×10^{-5} mol/ml.

Effect of preparation condition of catalyst

The preparation condition of ternary catalyst system $\text{Nd}(\text{P}_{204})_3\text{-AlR}_3\text{-P}_{204}$ affected significantly the formation of PA film. Table 6 and Table 7 illustrated the influences of catalyst aging mode and aging time on acetylene polymerization. It can be concluded that Nd compound and Al compound, or three components aged together no more than 2 hours gives silvery metallic sheen and tough PA films with fairly high yield.

Table 6 Effect of catalyst aging mode

Mode	Aging under acetylene	Aging under III component	Nd-Al aging
PA yield (g/mol Nd)	135.3	104.3	98.1
cis (%)	—	93.8	91.3
Phase condition of catalyst	Have precipitate	Homogeneous	Homogeneous
Film looking	No metallic sheen, brittle	Silvery metallic sheen, tough	Silvery metallic sheen, tough

$\text{Nd}(\text{P}_{204})_3\text{-Al}(\text{C}_2\text{H}_5)_3\text{-P}_{204}$ system; Al/Nd = 6; III/Nd = 3; 35°C; 1 hour.

Table 7 Effect of catalyst aging time

Aging time (minute)	15	30	60	90	120	150	840
PA yield (g/mol Nd)	76.5	91.0	100.3	100.0	95.2	75.2	Red powder
cis (%) of PA	92.1	92.5	93.0	93.0	93.2	92.0	—

$\text{Nd}(\text{P}_{204})_3\text{-Al}(\text{C}_2\text{H}_5)_3\text{-P}_{204}$ system; Al/Nd = 5; III/Nd = 1.5; 35°C; 1 hour.

The appropriate aging concentration of catalyst at which PA films were formed with good yield was in the range of $1.2\text{--}1.8 \times 10^{-4}$ mole Nd compound/ml.

REFERENCES

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- [2] The 4th Laboratory, Changchun Institute of Applied Chemistry, Collected Papers on Synthetic Rubbers by Rare Earth Catalysts, Science Press, Beijing, **1981**, p. 113.