New Scandium Coordination Catalysts for the *cis* Polymerization of Acetylene

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Abstract

The catalytic activity of scandium has not been widely studied. This article reports the first study of a new kind of Ziegler-Natta catalyst, the combination of a scandium compound and aluminum trialkyl, for the polymerization of acetylene. Some characteristics and kinetic aspects of acetylene polymerization by scandium catalysts and the results of the characterization of polyacetylene so obtained are described. High *cis* polyacetylene films (95% *cis*) with silvery metallic sheen and high crystallinity (70%) were obtained at ambient temperature (30–0 °C). The electrical conductivity of iodine doped polyacetylene reached hundreds ohm^{-1} cm^{-1}.

Introduction

Scandium is variously considered by specialists of different disciplines as a rare earth element, lanthanide or prelanthanon triad. Its catalytic activity has been little studied. A 1963 patent reported the application of $ScCl_3$ with diethyl zinc to polymerize ethylene and propylene [1] and G. A. Moser recently pointed out that bis(cyclopentadienyl)scandium π-allyl shows a little activity toward ethylene polymerization [2]. In 1983 Shen *et al.* first reported that scandium naphthenate in conjunction with trialkyl aluminum, constituting a new Ziegler-Natta catalyst, was active in promoting the polymerization of terminal alkynes to yield high *cis* content high molecular weight polyalkynes [3]. Polyacetylene is the simplest and most promising conductive polymer. In 1981 we first developed rare earth coordination catalysts, with the exception of scandium, for the stereospecific polymerization of acetylene [4]. It is of interest to us to investigate the catalytic activity of scandium compounds toward acetylene polymerization. Thus a new coordination catalyst consisting of scandium naphthenate or phosphonate in combination with trialkyl aluminum for the *cis* polymerization of acetylene has been developed. In this contribution we highlight some characteristics and kinetic aspects of the polymerization reaction and the results of the characterizations of polyacetylene (PA) so obtained. The study revealed that the scandium coordination catalyst is quite similar to the rare earth coordination catalysts in acetylene polymerization. High *cis*, high crystallinity and paramagnetic PA films with silvery metallic sheen can be prepared by this new scandium catalyst at room temperature also. Considering all the studies on the catalytic activity of the scandium compound toward the polymerization of acetylene and the terminal alkynes, it can be concluded that scandium behaves in the same way as the lanthanides.

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Experimental

Scandium compounds were prepared by the same method as that used to prepare neodymium compounds. Polymerizations were carried out as previously described [4]. PA films were characterized by infrared spectroscopy (Shimadzu IR-408), electron spin resonance (DSG-KI ESR spectrometer), differential scanning calorimetry (CDR-I calorimeter), X-ray diffraction (Geigerflex D/Max-rA diffractometer), scanning and transmission electron micrography and electrical resistivity measurement. Iodine doped PA films were prepared as previously described [5].

Results and Discussion

Features of Polymerization

The experimental results showed that silvery PA films can be obtained either by the $Sc(P_{204})_3$–AlR_3–P_{204} trinary system or by the $Sc(naph)_3$–AlR_3 binary system (where P_{204} is 2-ethyl hexylphosphonate, naph is naphthenate). It had been found that the addition of an appropriate amount of alcohol to the $Sc(naph)_3$ system enhanced the yield of PA film. Thus here we highlight the polymerization characteristics of the trinary system: $Sc(naph)_3$–$Al(i\text{-}C_4H_9)_3$–ROH.

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TABLE I. Effect of Alcohol.[a]

$ROH/Sc(naph)_3$ (molar ratio)	ethanol				butanol			
	R_0[b] $\times 10^5$ (mol/min)	k[c] $\times 10^{-3}$ (l/mol)	Yield $\left(\frac{g\ PA}{g\ Sc}\right) \times 10^2$	*cis* (%) PA	$R_0 \times 10^5$ (mol/min)	$k \times 10^{-3}$ (l/mol)	Yield $\left(\frac{g\ PA}{g\ Sc}\right) \times 10^2$	*cis* (%)
0	10.0	6.7						
2	7.7	4.0	32	90	8.0	3.7	30	88
4	7.1	4.1	70	94	7.4	4.0	82	98
6	5.3	2.9	99	92	6.5	2.8	60	93

[a](Sc) = 3×10^{-2} mol/l; Al/Sc = 9 (molar ratio); toluene; P_A = 520 mm Hg; 30 °C. [b]R_0 = initial rate of polymerization. [c]k = decay constant of polymerization rate.

TABLE II. Effect of Al/Sc Molar Ratio.[a]

Al/Sc (molar ratio)	$R_0 \times 10^5$ (mol/min)	$k \times 10^3$ (l/mol)	yield $\times 10^2$ (g/gSc)	*cis* %
5	4.0	3.6		93
7	6.3	3.4	50	97
9	7.7	4.0	32	90
11	8.0	4.9	black powder	

[a]$ROH/Sc(naph)_3$ = 2; (Sc) = 3×10^{-2} mol/l; P_A = 520 mmHg; 30 °C.

TABLE III. Effect of Polymerization Temperature.[a]

T (°C)	$R_0 \times 10^5$ (mol/min)	$k \times 10^{-3}$ (l/mol)	*cis* % of PA
50	9.1	5.4	88
30	7.1	4.3	93
0	5.4	3.6	100
−18	4.6	1.7	

[a]Polymerization condition same as in Table II.

Table I illustrates the effect of alcohols on acetylene polymerization. It is seen from the data that there is no difference between ethanol and butanol, and the yield of PA film increases with increasing $ROH/Sc(naph)_3$ molar ratio. However, the initial rate of polymerization decreases slightly. It should be pointed out that a certain amount of oligomer, other than high molecular weight polyacetylene, was formed during the polymerization, but no detailed investigation of the oligomer was made.

The effect of the molar ratio of $Al(iC_4H_9)_3$ to $Sc(naph)_3$ is summarized in Table II. The data showed that the initial rate of polymerization (R_0), decay constant of polymerization rate (k), and *cis*% of PA remained unchanged in the range Al/Sc = 5–9.

It was found that the polymerization reaction catalyzed by the $Sc(naph)_3$ system or the $Sc(P_{204})_3$ system has no induction period and the rate of polymerization is of the first order with respect to both pressure of acetylene (monomer) and catalyst concentration. The polymerization kinetics can be formulated as: $R_P = k'(\text{cat})P$ or $R_P = k_P(C^*)(M)$ where R_P = rate of polymerization, (cat) = the over all concentration of catalyst, P = pressure of acetylene, (C^*) = the concentration of active species and (M) = concentration of monomer acetylene. These kinetic features are in agreement with that of the $Nd(P_{204})_3$–$Al(C_2H_5)_3$–P_{204} system [6]. Under the polymerization conditions tested, the activity of the $Sc(naph)_3$ system is greater than that of the $Sc(P_{204})_3$ system.

Polymerization temperature will not only affect the rate of polymerization but also the *cis* content of polyacetylene, as shown in Table III. The *cis* content of PA decreases with increasing polymerization temperature. It is worth noting that at 0 °C all of the *cis* PA film can be obtained using the $Sc(naph)_3$ catalyst, whereas only 97% *cis* PA film is obtained using the $Sc(P_{204})_3$ system.

From the relationship between the rate of polymerization and polymerization temperature, which is consistent with the Arrhenius equation, we have found that the activation energy difference ($E_P - E_H$) is 1.89 kcal/mol, where E_H refers to the activation energy of the solubility of acetylene in toluene.

Characterization of Polyacetylene

The polyacetylene films prepared by the scandium catalyst have a silvery lustre and are rather flexible and stable. They isomerize only about 1% *cis* per day to *trans* at room temperature in air.

The infrared spectra of the polyacetylenes so obtained are very similar to those of polyacetylenes obtained by other rare earth catalysts showing the strong *cis* C–H out of plane deformation band at

TABLE IV. Relation between Resistivity of PA and its *cis* Content.

cis %	82.5	90	92	94	97
resistivity × 10^{-8} ohm cm	4.2	88	603	1010	2320

TABLE V. Electrical Conductivity of Iodine Doped PA.

PA by $Sc(naph)_3$	
composition	conductivity ohm^{-1} cm^{-1}
cis-$(CHI_{0.005})_x$	4.9×10^{-4}
cis-$(CHI_{0.04})_x$	14.5
cis-$(CHI_{0.09})_x$	3×10^2
PA by $Sc(P_{204})_3$	
composition	conductivity ohm^{-1} cm^{-1}
cis-$(CHI_{0.004})_x$	3.1×10^{-4}
cis-$(CHI_{0.10})_x$	4.2×10^2

740 cm^{-1}. In addition, several very weak absorptions in the 2800 to 2950 cm^{-1} region are found in the spectra, which have been assigned to the deformation vibration of the methyl and methine groups. This suggests that the polymerization reaction of acetylene with the scandium catalyst might take an anionic coordination mechanism [7].

The differential scanning calorimetry of polyacetylene prepared similarly shows the existence of three peaks at 195, 375 and 460 °C, which are related to the *cis–trans* isomerization, crystallization and thermal decomposition respectively.

The electron spin resonance spectra of PA present a singlet without a hyperfine structure and indicate the polymer having a g value of 2.0032 and an unpaired electron concentration of about 3.4 × 10^{16} spins/gPA.

A clear polycrystalline Debye diffraction ring has been observed in the electron diffraction pattern of scandium catalyzed PA. Again no difference in the X-ray diffraction pattern between Sc catalyzed PA and Nd catalyzed PA has been seen. Sc PA is also characterized by an intense and sharp main reflection at a Bragg angle of 2θ = 23.3. Using the method reported in [8], we have found that Sc catalyzed PA has a crystallinity of 70% of the orthorhombic system having the following unit cell parameters: a = 7.58; b = 4.40; c = 4.38.

Observations made using an electron microscope by transmission or a scanning electron microscope showed that the PA film of $Sc(naph)_3$ is composed of fibrils about 200–300 Å in diameter and that the film of $Sc(P_{204})_3$ is composed of fibrils about 300–600 Å in width. It was shown that the morphology of Sc PA is somewhat related to the polymerization condition; for example, the width of fibrils increases with increasing polymerization temperature.

Table IV illustrates the electrical resistivity of Sc PA film. The data show that PA with high *cis* content is an electrical insulator and its electrical resistivity increases as the *cis* content increases. The electrical conductivity of iodine doped PA increased by eleven orders of magnitude, as shown in Table V.

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