Synthesis of High *cis* Polyacetylene with Coordination Catalysts Consisting of Rare Earth Naphthenate

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Abstract

High *cis* polyacetylene films with silvery metallic appearance were prepared by coordination catalysts, comprising of naphthenates of all fifteen rare earth elements, and trialkyl aluminum at room temperature. The resultant polyacetylene (PA) was characterized by infrared spectrophotometry, electron spin resonance, X-ray diffraction, scanning and transmission electron micrography, differential scanning calorimetry and electrical resistivity measurements. The enthalpy and apparent activation energy of thermal *cis–trans* isomerization of 98% *cis* PA were 1.7–1.8 kcal/mol and 19.0 kcal/mol respectively. Rare earth PA shows higher thermal and antioxidization stability than does PA with other catalysts.

Introduction

Polyacetylene is one of the simplest conductive polymers, used to make lightweight high-density plastic for storage batteries, solar energy cells *etc.* Acetylene can be polymerized into high *cis* PA film by $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$ [1], $Co(NO_3)_2$–$NaBH_4$ [2] and rare earth coordination catalysts [3]. The latter is the only catalyst capable of producing tough high-*cis* PA film at room temperature. In this paper are reported further details on the polymerization of acetylene with fifteen lanthanide naphthenates and trialkyl aluminum catalyst systems. We emphasize characteristics of polymerization and characterization of PA so obtained using techniques of infrared spectrophotometry (IR), X-ray diffraction, electron spin resonance, scanning and transmission electron micrography (SEM & TEM), differential scanning calorimetry (DSC) and electrical resistivity measurements. Thermal stability of PA films and activation energy of *cis–trans* isomerization were also studied. Experimental results showed that rare earth PA had far better thermal and antioxidizing stability than did PA prepared by other catalysts.

Experimental

Lanthanide naphthenates were prepared by a direct extraction method [4]. Acetylene purification, polymerization, polymer treatment and characterization were the same as previously described [3]. Thermal isomerization of PA film was carried out under vacuum. The PA film for measuring activation energy of thermal isomerization was first heated at constant temperature (±0.5 °C), then quenched in an ice bath.

Results and Discussion

Those experimental variables known to have strong effects on Ziegler Natta polymerization were investigated, to identify the optimum conditions for acetylene polymerization with $Ln(naph)_3$–$Al(i\text{-}C_4H_9)_3$. The yield of PA film increased slightly with increasing polymerization time within 2.5 h and remained unchanged after 2.5 h (Table I). The *cis* % of PA retained above 92% and did not vary with polymerization time.

TABLE I. Effect of Polymerization Time.[a]

Time (h)	0.5	0.75	1.0	1.5	2.0	2.5	3.0
Yield (g PA/gLn)	15.9	16.6	17.0	19.5	20.6	22.7	22.9
Cis %	92.6	92.2	95.6	93.4	94.6	92.6	92.9

[a] (Nd) = 3×10^{-5} mol/ml; Al/Nd = 5; 30 °C.

Table II lists the results of polymerization at various catalyst concentrations, both the polymer yield and *cis* content were considerable at (Nd) = 3×10^{-5} mol/ml, either with Al/Nd = 3 or 5.

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TABLE II. Effect of Catalyst Concentration.[a]

Al/Nd (molar ratio)	3				5			
$(Nd(naph)_3) \times 10^5$ (mol/ml)	1	3	5	7	1	3	5	7
Yield $\times 10^2$ (gPA/gNd)	8.3	13.8	10.2	7.2	5.4	13.3	11.9	12.4
Cis % of PA	91.9	95.9	94.0	94.0		94.4	92.9	92.8

[a] 30 °C; 1 h.

TABLE III. Effect of Al/Nd Ratio.[a]

Catalyst	$Nd(naph)_3$					$Gd(naph)_3$			
Al/Ln (mol)	2	3	5	7	9	2	3	5	7
Yield $\times 10^2$ (gPA/gNd)	17.8	18.4	31.4	24.6	21.1	5.2	11.5	21.0	12.5
Cis (%)	96.8	96.9	96.0	95.1	93.5	94.3	96.4	95.4	94.0

[a] (Ln) = 3×10^{-5} mol/ml; 30 °C; 1 h.

TABLE IV. Effect of Polymerization Temperature.[a]

Catalyst	$Nd(naph)_3$						$Y(naph)_3$					
Polymn Temp. (0 °C)	−15	0	15	30	45	60	−15	0	15	30	45	60
Yield $\times 10^2$ (gPA/gLn)	10.2	17.3	24.0	18.6	17.5	11.0	22.6	31.1	39.5	39.0	37.2	25.0
cis % of PA	95.5	95.8	95.1	95.4	93.8	83.4	96.6	97.7	96.4	94.7	92.1	87.3

[a] (Ln) = 3×10^{-5} mol/ml; Al/Ln = 5; 2 h.

The Al/Ln ratio affects the yield of PA, as shown in Table III, taking Nd and Gd naphthenate systems as examples. The maximum yield under the conditions tested was obtained at Al/Ln = 5–7. The *cis* contents of PA film were as high as 95% and remained unchanged with varying Al/Ln in the range of 2–7. This is quite different from the $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$ system. No good film was obtained at Al/Ln ratios greater than 7.

Table IV illustrates the effect of temperature on the polymerization for reaction carried out with (Ln) = 3×10^{-5} mol/ml, Al/Ln = 5 for 2 h. The yield of PA increased as the temperature increased, then decreased at 60 °C, at which point a small amount of black powder was produced. The *cis* content of the PA retained was as high as 95% at polymerization temperatures below 45 °C. *Cis*-rich polyacetylene (more than 80%) can be obtained even at 60 °C.

All naphthenates of fifteen rare earth elements ($Ln(naph)_3$) can be combined with trialkyl aluminum to polymerize acetylene into a silvery high-*cis* content PA film with metallic sheen at Al/Ln = 2–9. Figure 1 illustrates some of the results. Although the chemical properties of lanthanide elements are very similar, their catalytic activity in the *cis* polymerization of acetylene is quite different. The catalytic activity on PA film yield of $Ln(naph)_3$–$Al(i\text{-}C_4H_9)_3$ system at 30 °C decreased in the following order: Y ~ Ce > Nd ~ Tb > Pr > La > Lu ~ Gd > Tm ~ Er > Ho ~ Yb ~ Eu > Sm > Dy.

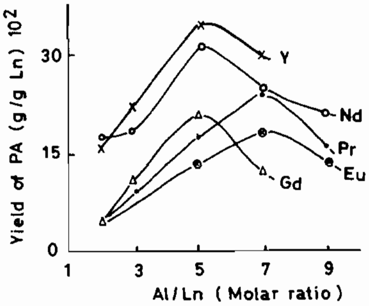

Fig. 1. Variation of PA yield with Al/Ln ratio.

Table V shows that as much as 95% *cis* PA films can be obtained by these systems at 30 °C, except, for the $Eu(naph)_3$ system where 93% *cis* PA film was prepared at 0 °C. These results indicate that lanthanide naphthenate combined with $Al(i\text{-}C_4H_9)_3$ systems are the best catalysts to synthesize easily and conveniently high *cis* PA at room temperature.

The electrical resistivities of PA film so prepared are around 10^9–10^{10} cm ohm, similar to those of $Ln(P_{204})_3$ systems, as shown in Table VI.

TABLE V. *Cis* Content of $Ln(naph)_3$ Systems.[a]

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
cis %	95.0	92.4	96.0	96.9	95.3	88.0	96.4	96.0	95.8	96.6	96.7	96.0	93.6	90.9	96.2

[a] $(Ln) = 3 \times 10^{-5}$ mol/ml; Al/Ln = 2–5; 30 °C; 1 h.

TABLE VI. Electrical Resistivity of PA (20 °C).

Cat.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
$\rho \times 10^{-8}$ (cm ohm)	294	28.4	40.4	181	2.35	78.4	194	490	161
Cat.	Ho	Er	Tm	Yb	Lu	Y			
$\rho \times 10^{-8}$ (cm ohm)	65.9	147	184	68.3	72.1	168			

TABLE VII. Unpaired Electron and G Value of PA.

Electrons	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
(g spins/g) $\times 10^{-16}$	5.6	6.6	5.6	6.5	8.1	7.4	5.9	5.6
G value	2.0044	2.0036	2.0047	2.0049	2.0036	2.0041	2.0038	2.0041
Electrons	Dy	Ho	Er	Tm	Yb	Lu	Y	
(g spins/g) $\times 10^{-16}$	5.3	5.1	4.5	4.9	10.9	9.8	4.5	
G value	2.0038	2.0040	2.0040	2.0041	2.0036	2.0042	2.0039	

TABLE VIII. *Cis–Trans* Isomerization of PA.

Store time	Cat. (*cis* %)							
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
0 (days)	95.1	90.1	95.8	95.7	94.0	75.7	96.3	95.5
5	91.2	87.2	91.7	93.7	91.4	67.4	91.8	93.6
12	87.3	84.0	86.3	88.6	86.7	61.2	87.2	88.0
19	83.7	80.7	81.8	84.9	84.4	58.0	83.8	82.3
Store time	Cat. (*cis* %)							
	Dy	Ho	Er	Tm	Yb	Lu	Y	
0 (days)	92.6	93.4	96.0	95.4	91.3	90.5	94.0	
5	91.6	87.2	93.2	92.0	84.0	84.3	90.5	
12	86.0	84.0	89.2	86.9	76.9	78.0	85.9	
19	82.0	81.1	82.9	81.6	72.4	75.6	83.6	

The X-ray diffraction pattern of these PA films revealed that the specimens were crystalline polymers characterized by an intense and sharp reflection at a Bragg angle $2\theta = 23.15 \pm 0.05$, except for Eu PA, having a slightly more broad peak.

The electron spin resonance spectra of PA in this study showed that the polymers were paramagnetic and that their unpaired electron concentrations (N) and g values were about 10^{16} spins/g and 2.0042 ± 0.0007, respectively, as shown in Table VII.

Examination of PA films by electron microscopy showed characteristic fibrillar morphology without regard to various catalysts, being the same as PA with $Ti(OC_4H_9)_4$ or $Ln(P_{204})_3$ catalyst.

TABLE IX. Effect of *cis* Content on Enthalpy.

Cis %	95	80	68	56	53	39	24	3.5
H_I (kcal/mol)	1.80	1.60	1.46	1.22	1.11	0.49	0.33	0.12
H_{II} (cal/g)	81.4	81.1	88.0			71.1	78.3	53.8

Polyacetylene prepared with these catalysts is appreciably stable and isomerizes slowly when it is stored in air at room temperature (Table VIII).

The differential scanning calorimetric diagram of PA showed similarly the existence of two exothermic peaks at 200 ℃ (peak I) and 380 ℃ (peak II), and one endothermic peak at 460 ℃. These were attributed to *cis–trans* isomerization, hydrogen migration, crosslinking and decomposition of polyacetylene. These temperatures remained unchanged with variation of different lanthanide elements, Al/Ln ratio or *cis* content of PA.

The enthalpy changes associated with the exothermic phenomena at 200 ℃ and 380 ℃ were found to be 1.8 kcal/mol and 81.4 cal/g respectively, calibrated to 100% *cis* PA; they decreased with increasing *trans* content of PA, as shown in Table IX.

Figure 2 shows kinetic plots of the thermal *cis–trans* isomerization of PA film containing 98% *cis*. By Arrehenius plotting based on isomerization rates over the temperature range of 85–115 ℃, the activation energy of *cis–trans* isomerization was taken to be 19.0 kcal/mol, which was 2 kcal/mol higher than that of PA (88% *cis*) with $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$ catalyst [5].

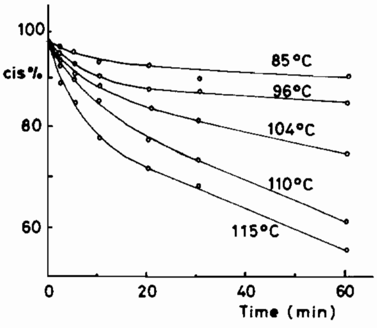

Fig. 2. Variation of *cis* % of PA with time.

Figure 3 shows the IR spectrum of PA films after a thermal treatment *in vacuo* at 325 ℃ for 5 min.

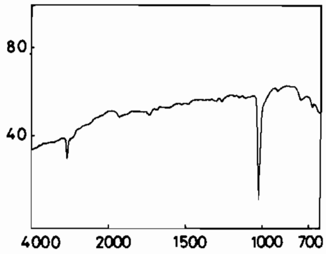

Fig. 3. IR spectrum of PA heated at 325 ℃.

This IR spectrum along with the unchanged X-ray diffraction diagram and scanning electronic microscopy image indicated that rare earth polyacetylene has good thermal and antioxidizing stability.

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