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Polymerization of Phenylacetylene by Rare Earth Compound/Trialkylaluminum Catalysts

Zhiquan Shen* and Michael F. Farona

Department of Chemistry, The University of Akron, Akron, OH 44325, USA

Summary

The rare earth naphthenates of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, in combination with triethylaluminum, were investigated as catalysts for the polymerization of phenylacetylene. All were found, at least to a small degree, to be active, and produce atactic polyphenylacetylene showing the presence of both cis and trans double bonds in the chain. These polymers exhibited a low degree ($\sim$ 28%) of crystallinity. However, the neodymium system produced a crystalline (45%) cis-cisoid polymer. An interesting, but as yet unexplained, correlation exists between activity of the catalyst, as indicated by yield of polymer obtained, and the number of f electrons on the metal.

Introduction

Recently, Shen, et al., reported that rare earth compounds, when used with trialkylaluminum, are active catalysts for the stereospecific polymerization of acetylene (1). In that study, polyacetylenes were obtained at room temperature that showed greater than 90% cis content.

Crystalline polyphenylacetylene is known, but relatively uncommon. In the great majority of cases, Ziegler-Natta catalyst systems produce yellow, atactic polymers which show varying amounts of cis and trans content in the chains. Since the rare earth catalysts produced stereospecific polyacetylene, these systems were investigated as polymerization catalysts for phenylacetylene.

Experimental

Materials. Phenylacetylene (Aldrich) was distilled under aspiration vacuum from anhydrous calcium chloride before use. Aromatic solvents were refluxed over, and distilled from, CaH_2 and stored under nitrogen over molecular sieves. Triethylaluminum, trimethylaluminum, and triisobutylaluminum were purchased from Texas Alkyls and made up into 1.5×10^{-3} mol/ml solutions in chlorobenzene or benzene. Rare earth naphthenates and 2-ethyl-hexylphosphonates were prepared by published procedures (1, 2).

Physical methods. Infrared spectra were taken on a Perkin-Elmer 597 spectrophotometer. The compounds were normally sampled as thin films on KBr disks, or as KBr pellets. Nuclear magnetic resonance spectra were recorded on a Varian

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* Visiting Associate Professor from Zhejiang University, Hangzhou, People's Republic of China

EM 360 spectrometer using $CDCl_3$ as the solvent, and TMS as the internal standard. Molecular weights were determined on a Knauer Vapor Pressure Osmometer Type 1100. Softening points of the polymers were taken on a Thomas Hoover Capillary apparatus and are reported uncorrected. X-ray diffraction patterns were recorded on a Phillips X-Ray Diffractometer. Scanning electron microscopy was carried out on a JEOL-3U instrument.

Polymerization reactions. Into a 50-ml, one-neck, round-bottomed flask was placed 0.20 g (2×10^{-4} mol) of the lanthanide naphthenate and a magnetic stir bar. The flask was flushed well with N_2, then a septum was fitted on the neck. Then 5 ml of chlorobenzene or benzene and 3 ml of 2×10^{-4} mol/ml solution of ethanol in chlorobenzene or benzene were injected separately through the septum. The mixture was stirred for 15 min at 30 °C, and 1.5 ml (2.25×10^{-3} mol) of the triethylaluminum solution was added. The mixture was stirred for 45 min at 40 °C, then 2 ml of phenylacetylene was injected. The reaction mixture was stirred for 24 hr at 50-55 °C. After that time, 5 ml of a 10% HCl solution in methanol was added to deactivate the catalyst. The reaction mixture was then poured into 150 ml of methanol, resulting in a precipitation, which was collected by filtration, taken up in a minimum amount of toluene, and reprecipitated by adding cold pentane. The methanol solvent was removed, leaving a viscous oil.

In the case of the neodymium catalyst system, a dark red precipitate formed during the polymerization reaction. This was separated by filtration, and the rest of the reaction was worked up as described above.

Results and Discussion

Polymerization was achieved in all cases, although the yields with certain catalysts were fairly low. Table I shows data on the polymer which is insoluble in methanol but dissolves in aromatic solvents. The other fraction obtained from the methanol solution apparently is a complex mixture of low molecular weight polyphenylacetylene and catalyst, since infrared and nmr spectra show bands and signals arising from polyphenylacetylene and naphthenate anion. This fraction was not examined further.

The polymers shown in Table I are all yellow or dark yellow powders with low ($\overline{Mn}$ 1000) to moderate ($\overline{Mn}$ 4000) molecular weights. Infrared and nmr spectra of these samples indicated that they are similar to those obtained by Woon and Farona using arenemolybdenum tricarbonyl catalysts (3), and also conform to those reported by Simionescu, et al. (4, 5). A typical nmr spectrum of the benzene-soluble polyphenylacetylene samples is shown in Figure 1.

Whereas the presence of both cis and trans double bonds are suggested from the infrared spectra, the nmr spectra are essentially identical to that reported for a general trans-cisoid structure for polyphenylacetylene. The absence of a discernible signal at δ 5.82 ppm rules out the presence of a cis-transoidal arrangement. Also detected in the nmr spectra of the benzene-soluble polymers is the presence of a very weak, broad signal in the δ 3-4 ppm range, showing that small amounts of cyclic trimers are formed in the polymerization process (4).

TABLE I

Properties of Polyphenylacetylene

Lanthanide[a,b]	Yield (%)	Softening Temp. °C	$\overline{Mn}$
La	11.3	120-130	980
Ce	12.8	115-120	820
Pr	13.6	138-145	1150
Nd	25.2	196-202	3250
Sm	8.2	154-158	1575
Eu	0.5	---	--
Gd	12.1	198-202	4120
Tb	12.8	182-188	2196
Dy	11.5	204-210	4396
Ho	25.8	152-156	1361
Er	12.2	190-194	2330
Tm	25.5	122-128	960
Yb	1.2	---	--
Lu	14.6	140-148	1213

[a] All metals were introduced as M(naphthenate)$_3$, and Al$(C_2H_5)_3$ was used as the cocatalyst in each case. Al:M = 11:1.

[b] Yttrium naphthenate/Al$(C_2H_5)_3$ system yielded 4% polymer with $\overline{Mn}$ 5450.

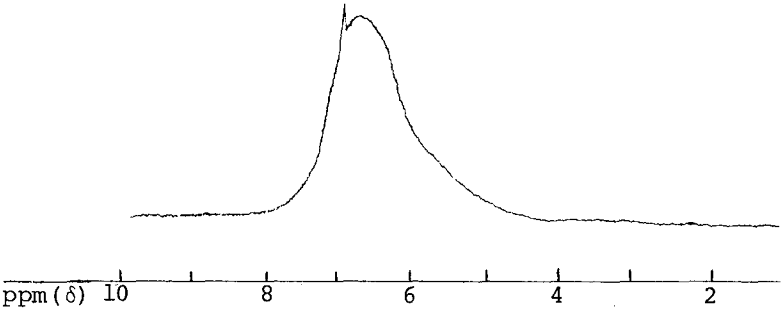

Figure 1. ^{1}H NMR spectrum of polyphenylacetylene.

An interesting but as yet unexplainable correlation exists between activity of the lanthanide element in terms of yield of polymer obtained, and the number of f electrons on the metal. The spherically symmetrical species f^0, f^7, f^{14} (La^{3+}, Gd^{3+}, and Lu^{3+}) show yields in the 11-15% range. The naphthenates of Ce^{3+} and Tb^{3+} (f^1 and f^8, respectively) gave yields of 12.8%. The f^2 and f^9 species Pr^{3+} and Dy^{3+} gave 13.6 and 11.5% yields. The most active species are the f^3 and f^{10} configurations of Nd^{3+} and Ho^{3+}. Yields from these catalyst systems were in the 25-26% range. The f^6 and f^{13} metals were by far the least active; the Er^{3+} catalyst system yielded only 0.5% polymer while that of Yb^{3+} gave 1.2%. The only exception in the correlation is the f^5-f^{12} species, Sm^{3+} and Tm^{3+}, from which yields of polymer of 8 and 25.5%, respectively, were obtained.

The neodymium catalyst systems gave unique results. During the reaction, a dark-red solid precipitated from solution in about 5% yield. The compound is insoluble in common organic solvents at room temperature, but slowly goes into o-dichlorobenzene at 135 °C. These properties are consistent with a cis-cisoidal conformation of polyphenylacetylene, and indeed, the infrared spectrum of this compound is identical with that reported for the polymer (4, 5). The infrared spectrum of the benzene-insoluble polymer is shown in Figure 2.

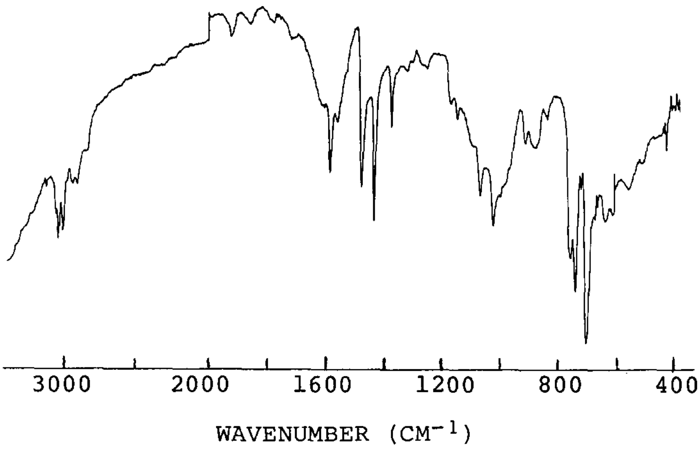

Figure 2. Infrared spectrum of cis-cisoidal polyphenylacetylene.

The degree of crystallinity of the polymers was investigated by x-ray diffraction spectrometry (6). The benzene-soluble polymers showed about 28% crystallinity (Figure 3B) and the cis-cisoidal polyphenylacetylene is about 45% crystalline (Figure 3A).

The neodymium catalyst system was investigated further, changing the alkyl substituent on aluminum. The results are shown in Table II.

Another brief study was carried out comparing the NdN_3/$Al(i\text{-}bu)_3$ (N = napththenate) to NdP_3/$Al(i\text{-}bu)_3$ (P = 2-ethylhexylphosphonate). The yield and molecular weight of polyphenylacetylene obtained using the naphthenate anion are shown in Table II. Those of the phosphonate system were 10.3% and 1500, respectively. For this experiment under the conditions employed, the naphthenate system constitutes the more active catalyst.

Changing solvents between benzene and chlorobenzene showed little, if any, effect on overall yields and molecular weights.

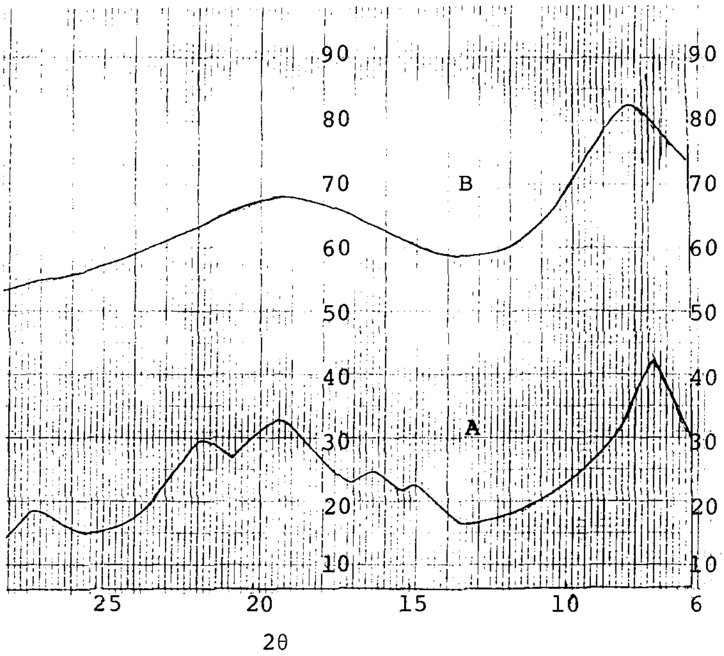

Figure 3. XRD Spectra of (A) cis-cisoidal polyphenylacetylene and (B) benzene-soluble polyphenylacetylene.

TABLE II

Effect of Alkyl Substituent

Catalyst System[a]	Yield (%)	$\overline{Mn}$
$NdN_3 + Al(C_2H_5)_3$	25.2	3250
$NdN_3 + Al(i\text{-}bu)_3$	18.4	4920
$NdN_3 + Al(CH_3)_3$	12.1	920

[a] N = naphthenate

At this stage of the research, we are not prepared to comment on the mechanism of polymerization. However, we have found that the neodymium catalyst system polymerizes internal acetylenic monomers, such as 2-hexyne. This would appear to rule out a mechanism requiring an initiating process of insertion of a metal into the terminal CH bond to create a metalacetylide species, such as that exhibited by group VII and VIII transition metal catalysts.

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