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## *Catalysts*

# Polymerization of Terminal Alkynes by Rare Earth Compound/Trialkylaluminum Catalysts

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## Summary

Rare earth naphthenates and phosphonates with trialkylaluminum compounds were investigated as catalysts for the polymerization of 1-alkynes. The neodymium naphthenate/triisobutylaluminum system was found to promote high conversions to polymers of relatively high molecular weights in the case of alkyl-substituted acetylenes. The polymers obtained showed, by infrared spectroscopy, high cis content in the polyconjugated chains.

## Introduction

Recently we reported the results of the investigation of rare earth(III)/trialkylaluminum (3) systems as catalysts for the polymerization of phenylacetylene and 1-alkynes, respectively. The interest in these studies was prompted by earlier studies on the polymerization of acetylene by rare earth catalyst systems, wherein stereospecific polymerization was promoted (5). This paper reports the results of our investigation of Nd and other rare earth catalyst systems toward the polymerization of alkyl-substituted, terminal alkynes.

## Experimental

Materials. The monomers 1-hexyne, 1-pentyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne, 3-methyl-1-butyne and phenylacetylene were purchased from Farchan. The alkyl-substituted acetylenes were purged with nitrogen before use, and phenylacetylene was distilled under aspirator vacuum from anhydrous calcium chloride. Chlorobenzene and cyclohexane, which were used as solvents, were refluxed over calcium hydride and distilled, then kept under nitrogen over molecular sieves until used.

Triethyl- and triisobutylaluminum were obtained from Texas Alkyls and made up into 1.5 x $10^{-3}$ mol/ml solutions in the above solvents. Rare earth naphthenates and 2-ethylhexylphosphonates were prepared according to published procedures (4, 5).

Physical methods. Infrared spectra were taken on a Perkin-Elmer 597 spectrophotometer. The polymers were normally sampled as thin films on NaCl disks, or as KBr pellets. Proton nuclear magnetic resonance spectra were recorded on a Varian EM360 spectrometer, using $CDCl_3$ as the solvent and TMS as the internal standard. Molecular weights

($\overline{Mn}$) of the polymers were determined on a Mechrolab HP503 membrane osmometer. Ultraviolet spectra were taken on a Beckman Model 25 spectrophotometer using cyclohexane as the solvent.

*Polymerization procedures.* Into a 50-ml, one-necked round-bottomed flask was placed 0.2 g ($2 \times 10^{-4}$ mol) of the rare earth naphthenate ($LnN_3$) or 2-ethylhexylphosphonate ($LnP_3$) and a magnetic stir bar. The flask was flushed with nitrogen and a septum was fitted on the neck. Then 2 ml of the solvent (cyclohexane or chlorobenzene) and 3 ml of $2 \times 10^{-4}$ mol/ml solution of ethanol in the corresponding solvent were injected separately through the septum. The mixture was stirred at 30 °C for 15 min, and 1.0 ml ($1.5 \times 10^{-3}$ mol) of the trialkylaluminum (triisobutyl or triethylaluminum) was added. The catalyst system was aged at 60 °C for 1 hr, allowed to cool to room temperature, and then 0.5 ml of the monomer alkyne was added. The polymerization was allowed to proceed at 20 °C for 20 hr. The reactions were terminated by pouring the reaction mixture into 20 ml of diethyl ether, and adding 5 ml of 6M HCl solution to deactivate the catalyst. The organic layer was treated with $NaHCO_3$ solution and washed with water. The polymer was precipitated from the ether solution by adding methanol, isolated, and dried in a vacuum.

The polymers studied in this work are those that are insoluble in methanol. The portions of polymers that were soluble in methanol were not isolated.

## Results and Discussion

The states, conversion, and molecular weights ($\overline{Mn}$) of the polyalkynes obtained with the $NdN_3/Al(i\text{-}C_4H_9)_3$ catalyst system are shown in Table I. Data on polyalkynes isolated from the $NdN_3/Al(C_2H_5)_3$ and $NdP_3(Al(i\text{-}C_4H_9)_3$ catalyst systems are given in Tables II and III, respectively.

TABLE I

Polymerization of Terminal Alkynes by $NdN_3/Al(i\text{-}C_4H_9)_3$

| Monomer | State of Polymer | Cyclohexane | | Chlorobenzene | |
|---|---|---|---|---|---|
| | | Conversion % | $\overline{Mn} \times 10^{-4}$ | Conversion % | $\overline{Mn} \times 10^{-4}$ |
| 1-Hexyne | Yellow rubbery solid | 100 | 3.5 | 99 | 2.0 |
| 1-Pentyne | Yellow rubbery solid | 100 | 3.7 | 99 | 2.4 |
| 3-Methyl-1-pentyne | Light yellow solid | 38 | 3.0 | -- | --- |
| 4-Methyl-1-pentyne | Yellow solid | 63 | 2.6 | 69 | 2.3 |
| 3-Methyl-1-butyne | Light yellow solid | 29 | 0.8 | 30 | 0.9 |

TABLE II

Polymerization of Terminal Alkynes by $NdN_3/Al(C_2H_5)_3$*

| Monomer | Conversion, % | $\overline{Mn} \times 10^{-4}$ |
|---|---|---|
| 1-Hexyne | 60 | 11.7 |
| 1-Pentyne | 50 | 16.8 |
| 3-Methyl-1-pentyne | 26 | 4.1 |
| 4-Methyl-1-pentyne | 41 | 2.8 |
| 3-Methyl-1-butyne | 19 | 1.2 |

*In cyclohexane solvent. Reactions were carried out for 24 hr.

TABLE III

Polymerization of Terminal Alkynes by $NdP_3/Al(i\text{-}C_4H_9)_3$*

| Monomer | Conversion, % | $\overline{Mn} \times 10^{-4}$ |
|---|---|---|
| 1-Hexyne | 30 | 0.6 |
| 1-Pentyne | 31 | 0.7 |
| 4-Methyl-1-pentyne | 24 | 4.0 |
| 3-Methyl-1-butyne | 21 | 3.8 |

*In cyclohexane solvent. Reactions were carried out for 48 hr.

It is clear that the highest conversions are achieved with the $NdN_3/Al(i\text{-}C_4H_9)_3$ catalyst system, but higher molecular weight polymers are obtained from $NdN_3/Al(C_2H_5)_3$. The solvent, cyclohexane or chlorobenzene, is of little consequence in either conversions or molecular weights. Phosphonate counter ions afford less effective catalyst systems than naphthenates.

Conversions and molecular weights are dependent on the degree of steric hindrance. The position of the methyl group with respect to the triple bond is a major factor in the rate of polymerization of the monomers. Whereas quantitative conversions are obtained from the straight-chain alkynes, the lowest conversions are obtained in the cases where the methyl group is in the 3-position. Significantly higher yields are obtained from 4-methyl-1-pentyne.

Like the polymers produced from the $ScN_3/AlR_3$ system (3), the polyalkynes obtained in this work are rubbery materials or solids of high molecular weight. The infrared and nmr spectra are identical with those obtained from the $ScN_3/AlR_3$ system, and are, therefore, of high cis content. For example, there is a lack of absorption in the 950-1000 $cm^{-1}$ region, and a medium intensity band is present at 720 $cm^{-1}$. This shows a lack of trans double bonds in these polymers, whereas relatively strong cis absorption is observed in all cases (6). A polyene of high cis content, particularly a cis-cisoid conformation, would be helical and twisted from planarity.

To provide further evidence for the indication of a cis-cisoid conformation, the polymerization of phenylacetylene was investigated under the present polymerization conditions. The polymer obtained was identical to that obtained from the $ScN_3/AlR_3$ catalyst system, which was shown to be crystalline and of cis-cisoid stereochemistry (2).

Infrared and UV spectra provide further evidence of the cis-cisoid arrangement. Fully conjugated, planar, polyenes exhibit $\nu(C=C)$ absorptions around 1600 $cm^{-1}$ and isolated double bonds absorb near 1680 $cm^{-1}$. All polymers obtained in this work show the major $\nu(C=C)$ band at 1675 $cm^{-1}$, and a weak band is observed at 1620 $cm^{-1}$. Therefore, the double bonds in these polymers behave more like isolated, rather than polyconjugated, systems. This can result from a helical, cis-cisoid arrangement, where the chain would be twisted from planarity such that the molecular orbital overlap in the conjugated chain is decreased.

The UV spectra are in support of the infrared spectral indications. Fully conjugated, planar, polyene should absorb in or near the visible region (7). Yet, electronic transition absorptions in these polymers are observed in the 200-325 nm region, showing that the effects of polyconjugation are not present. The same results were observed previously by Ciardelli and coworkers on polyalkylacetylenes obtained using the tris(acetylacetonato)iron(III)/$Al(i\text{-}C_4H_9)_3$ catalyst system (8, 9). Table 4 gives the UV spectra of the polymers in this study.

TABLE 4

Ultraviolet Spectra of Polyalkylacetylenes

| Polymer | Catalyst* | λ max (nm) | ε |
|---|---|---|---|
| poly-1-hexyne | $NdN_3$ | 204 | 2170 |
| poly-1-pentyne | $NdN_3$ | 204 | 2270 |
| poly-3-methyl-1-pentyne | $NdN_3$ | 300<br>203 | 3620<br>3340 |
| poly-4-methyl-1-pentyle | $NdN_3$ | 320<br>225 | 3260<br>3690 |
| poly-3-methyl-1-butyne | $NdN_3$ | 206 | 3270 |
| poly-1-hexyne | $YN_3$ | 204 | 2740 |
| poly-1-pentyne | $YN_3$ | 204 | 2720 |
| poly-1-hexyne | $LaN_3$ | 204 | 3450 |
| poly-1-pentyne | $LaN_3$ | 204 | 1380 |
| poly-1-hexyne | $PrN_3$ | 204 | 2270 |
| poly-1-pentyne | $PrN_3$ | 204 | 1570 |

*Cocatalyst in all cases was $Al(i\text{-}C_4H_9)_3$.

Typical infrared and nmr spectra of selected polyalkynes can be seen in our previous publications (2, 3).

The results obtained from these polymers with respect to stereochemistry are not necessarily typical of polyalkynes yielded by other Ziegler-Natta systems. The polymers of methylpentynes synthesized by Masuda, et al. (10), show infrared and UV spectral properties more in accord with those expected for planar polyenes.

Finally, we carried out the polymerization of three alkynes by other rare earth catalyst systems in chlorobenzene. The conversions (%) of the monomers with the $LnN_3/Al(i\text{-}C_4H_9)_3$ catalyst systems are given in Table 5.

The scandium and neodymium catalyst systems show the highest activities. Clearly, these Ziegler-Natta catalysts are capable of promoting high molecular weight, cis-cisoid polymers in high yields.

TABLE V

Conversion (%) Data on the Polymerization of Terminal Alkynes by $LnN_3/Al(i\text{-}C_4H_9)_3$ Catalysts*

| Monomer | Sc | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Hexyne | 95 | 23 | 12 | 9 | 11 | 100 | 6 | 3 | 6 | 19 | 11 | 32 | 12 | 17 | 10 | 17 |
| 1-Pentyne | 96 | 26 | 12 | 8 | 10 | 100 | 5 | 2 | 5 | 18 | 10 | 30 | 11 | 17 | 9 | 15 |
| Phenyl-acetylene | 46 | 2 | 3 | 2 | 2 | 40 | 5 | 1 | 2 | 4 | 3 | 5 | 4 | 7 | 5 | 4 |

*Reaction conditions. Monomer/$LnN_3$ = 25 (molar ratio); $CrH_5OH/LnN_3$ = 3 (molar ratio); $Al(i\text{-}C_4H_9)_3/LnN_3$ - 7.5 (molar ratio); [M] = 1.0 mol/l; 20 °C, 24 hr.

## References and Notes

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