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Polymerization of Acetylene and 1-Alkynes by Rare-earth Coordination Catalysts

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Polyacetylene has been shown to be an electrical conductor in the metallic range when doped with various agents; hence, considerable attention has been focused on this macromolecule in both industrial and academic laboratories. A natural extension of these studies is the investigation of the polymerization of substituted alkynes. Only a few transition metal catalysts are known to produce high molecular weight polyacetylenes: *e.g.*, $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ for acetylene, $Fe(acac)_3/Al(i\text{-}C_4H_9)_3$ for alkylacetylenes, and WCl_6 and $MoCl_5$ for phenylacetylene and other 1-alkynes. This study reports the first example of a systematic investigation of rare earth compounds as catalysts for the polymerization of acetylene and 1-alkynes.

The polymerization of acetylene, which was carried out at –16 to –100 °C at an optimum AlR_3/Ln (Ln = rare earth compound) mol ratio in the 3 – 9/1 range, yielded crystalline, high *cis*, metallic lustrous films. The polymers were characterized by infrared spectrophotometry, differential scanning and transmission electron micrography, and electrical resistivity measurements.

The nature, yield, and other properties of the polyacetylene obtained in the reactions depends somewhat on the nature of the counterion of the lanthanide ion, the alkyl group on aluminum, the solvent, and donor additives to the solvent, the results of which will be presented.

The polymerization of phenylacetylene was catalyzed by rare-earth naphthenates in combination with triethylaluminum in chlorobenzene at 50 °C. Moderate molecular weight, atactic polyphenylacetylene was obtained in all cases in relatively low yield, and all polymers showed the presence of both *cis* and *trans* double bonds in the chain. The polymers exhibited a low degree (~28%) of crystallinity, although 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 the yield of the polymer obtained, and the number of f electrons on the metal. The polymers were characterized by vapor-osmometry, infrared and nuclear magnetic resonance spectrometry, and X-ray diffraction, the results of which will be presented.

The polymerization of alkyl-substituted, terminal acetylenes, as well as phenylacetylene, was carried out at 20 °C, using rare earth naphthenates with triisobutylaluminum or triethylaluminum as the catalyst. The monomers 1-hexyne, 1-pentyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne, and isopropylacetylene gave light yellow, occasionally elastomeric polymers in very high yields in some cases. Membrane osmometric measurements revealed that the molecular weights of the polymers obtained are in the 80,000–170,000 range, which is extremely high for polymers of substituted acetylenes. These polymers were studied by ultraviolet, infrared and NMR spectrometry.

The ultraviolet spectra show absorptions at much lower wavelengths than those expected for a polyconjugated structure. However, NMR data show aliphatic to olefinic intensity ratios very close to those calculated for the linear polyacetylene (*e.g.*, for poly-1-hexyne, the calculated and observed integrated intensity ratios are 9:1, aliphatic:olefinic). The UV spectra are very similar to those found previously for poly-1-hexyne and poly-4-methyl-1-hexyne, and the presence of low wavelength absorption is explained by the presence of large pendant groups on the main chain. These groups, through steric interaction, apparently cause the chain to be twisted somewhat from planarity, thus effectively negating the molecular orbital overlap that should result from polyconjugation. The net effect is that the polymer appears to be made up of blocks of conjugation of two or three units.

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Surface Properties of Uranium Antimony Mixed Oxide Catalysts: Xps and Adsorbed Phase NMR Studies

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The mixed oxides of uranium and antimony are quite interesting compounds on the fundamental side, because of their electronic structure aspects, and pratically, since they are promising as hydro-

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