Polymerization of Phenylacetylene Catalysed by Arene–Group VIB Tricarbonyls

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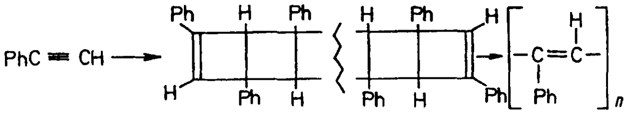
Summary $ArM(CO)_3$ (Ar = arene; M = Cr, Mo, W) catalyses the polymerization of alkynes to relatively high molecular weights, which proceeds through an intermediate which has been isolated and identified as a ladder compound composed of fused cyclobutane rings; the final product is the linear, polyconjugated poly(acetylene).

In catalysed polymerizations of alkynes, generally only low-molecular weight materials are obtained, probably since acetylenes show a strong tendency to trimerize, thus providing a ready termination step. We have found that $ArM(CO)_3$ (Ar = arene; M = Cr, Mo, W) catalyses the polymerization of several terminal and internal acetylenes to linear polyconjugated compounds. In the case of phenylacetylene using $(tol)Mo(CO)_3$ (tol = toluene) as the catalyst, we have obtained the highest molecular weight of poly(phenylacetylene) reported so far. Whereas thermal[1] polymerizations of phenylacetylene have resulted in products with molecular weights in the 1000—1200 range, and catalysis by $VO(salicylaldehyde)_2–Et_3Al$ gives poly(phenylacetylene) with molecular weight of 7700,[2] we have observed a number-average molecular weight of 12,000 in our reaction (determined by gel permeation chromatography).



Scheme

In the case of the molybdenum catalyst, the reaction is very fast in heated aromatic solvents or neat at ambient temperatures, and only the final polymer is obtained in quantitative yield, although an intermediate compound (see below) has been detected during the course of the reaction. When $(mes)M(CO)_3$ (mes = mesitylene; M = Cr, W) is used as the catalyst the reaction is much slower and, during the initial stages of the reaction, small amounts of an intermediate compound can be isolated. This intermediate has been identified by i.r. and n.m.r. spectral studies as a ladder compound composed of fused cyclobutane rings. Molecular weight measurements indicate that the intermediate is approximately an icosomer.

The ladder compound is stable in refluxing heptane; however, upon addition of catalytic amounts of $(tol)Mo(CO)_3$, it is converted rapidly and quantitatively into the final product, poly(phenylacetylene) (see Scheme).

Based on the above information, it is clear that polymerization does not proceed by a concerted mechanism. The mechanism of formation of the ladder polymers appears to be a series of successive 2+2 cycloadditions producing substituted cyclobutadiene, Dewar benzene, *etc.* Support for this proposed mechanism was obtained in the polymerization of but-2-yne with (tol)Mo$(CO)_3$, wherein the presence of hexamethyl Dewar benzene was detected.

The ladder compound is then converted into the higher molecular weight poly(phenylacetylene) possibly by a series of olefin metathesis reactions to join the chains[3] followed by an isomerization of the electronic structure to the final product.

The fact that no aromatic trimers are produced from these reactions supports previous contentions made in experiments on hydrogenation of olefins[4] and Friedel–Crafts reactions,[5] both types catalysed by ArM$(CO)_3$, that the arene ring stays on the metal during the course of the reaction.

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