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Polymerization of Phenylacetylene by an Olefin Metathesis Catalyst

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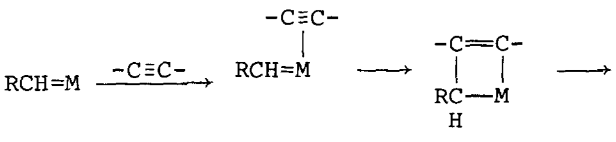
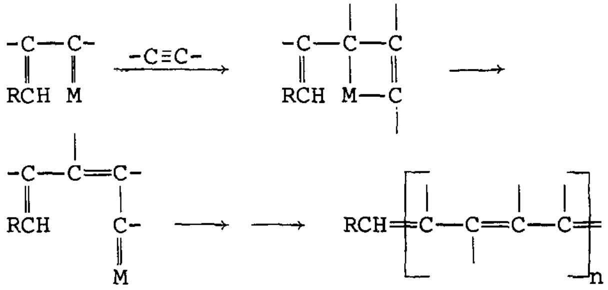
Summary

A test of the proposed mechanism of polymerization of acetylenes by metal carbene compounds was carried out. Using the Re(CO)$_5$Cl/C$_2$H$_5$AlCl$_2$ olefin metathesis catalyst, the metathesis of 1,7-octadiene was interrupted by the addition of phenylacetylene. The polymer isolated contained the required C$_7$ fragment of the 1,7-octadiene as the end group on polyphenylacetylene.

Introduction

At present, three mechanisms have been suggested for the propagation steps in transition-metal-catalyzed polymerizations of alkynes. The first of these, demonstrated primarily by catalysts of the group VII metals (BROWN, et al. 1971; FURLANI, et al. 1969; KERN 1969, MERIWETHER, et al. 1961; MERIWETHER, et al. 1962; SINGER and WILKINSON 1968) and Re(CO)$_5$Cl (TSONIS and FARONA 1979), involves successive insertion reactions of coordinated alkyne into the metal-carbon bond of the growing chain. The second of these involves cycloadditions of the alkynes on some arene group VIB tricarbonyl complexes to form ladder intermediates, followed by a catalyzed transformation of the ladder to the final, polyconjugated structure (WOON and FARONA 1974). The third method, suggested by MASUDA, et al. (1975) and demonstrated by KATZ and LEE (1980), involves a process analogous to that of olefin metathesis, whereby propagation proceeds by successive addition of coordinated alkyne to a metal-carbene compound forming a metallacyclobutene intermediate. This procedure is shown below.





The polymerization of alkynes was initiated with the metal-carbene species diphenylcarbenepentacarbonyltungsten, showing that initiation and propagation steps analogous to those of olefin metathesis are feasible (KATZ and LEE 1980).

A test of the proposed mechanism can be devised if a metal carbene species of known composition can be used to polymerize an alkyne, and the final structure of the polymer is such that it does not interfere with spectroscopic studies of the initiator. For example, in the metathesis of 1,7-octadiene, the species of propagation are $M{=}CH_2$ and $M{=}CH(CH_2)_4CH{=}CH_2$. If the latter species could be used to initiate polymerization of phenylacetylene, then the final polyphenylacetylene polymer would contain an end group which is specifically $P{=}CH(CH_2)_4CH{=}CH_2$. Furthermore, there should be only one of these C_7 fragments per polymer chain. It is possible to study the end group since polyphenylacetylene shows nmr signals only in the δ 6.8-7.2 region, whereas the end group will show aliphatic and olefinic hydrogens. A comparison of molecular weight of the polymer with the relative intensities of the phenyl and aliphatic proton signals can show the number of groups derived from 1,7-octadiene per polymer chain.

Results and Discussion

In this study, an olefin metathesis reaction was carried out on 1,7-octadiene using the catalyst system $Re(CO)_5Cl/C_2H_5AlCl_2$ (GREENLEE and FARONA 1976). After the metathesis reaction was established, phenylacetylene was injected into the reaction mixture. It was expected that metathesis would be interrupted and the carbene species $Re{=}CH(CH_2)_4CH{=}CH_2$ would react with the alkyne in a polymerization reaction. Like the reactions reported by KATZ and LEE (1980) the polymerizations promoted by the Re system are slow.

In reactions carried out for less than 48 hours, polyphenylacetylene containing the C_7 headgroup could be isolated; however, the yields were quite low and numerous other compounds could also be separated from the reaction mixture. These compounds all contained metal carbonyl as determined by infrared spectroscopy after isolation from column chromatography.

In order to increase the yield of polyphenylacetylene, the reaction was allowed to continue for 30 days, whereupon polyphenylacetylene was the only solid compound recovered.

The infrared spectrum of the dark yellow polymer shows all the bands attributable to polyphenylacetylene: 1375, 1260, 970, 770 and 740 cm^{-1} which indicate a mixed cis and trans stereochemistry about the double bonds (TSONIS and FARONA 1979; SIMIONESCU, et al. 1977). Also observed in the infrared spectrum are the olefinic and aromatic ν(CH) bands in the 3025-3050 cm^{-1} region, and aliphatic C-H stretching bands in the 2850-2925 cm^{-1} region, indicating the presence of the $=CH(CH_2)_4CH=CH_2$ head group, as required by the proposed mechanism.

The nmr spectrum of the polymer exhibits signals as follows: δ 5.8-7.5, broad, aromatic and conjugated olefinic; δ 4.85, terminal olefinic; δ 2.2, aliphatic and δ 0.9-1.2, broad, aliphatic. The number average molecular weight of the polymer was found to be 2135 by vapor pressure osmometry. If only one C_7 end group is incorporated in the polymer as required by the mechanism, then the minimum integration of aromatic to aliphatic hydrogens would be 15:1, since there would be 20 phenylacetylene units per C_7 end group. The relative intensities of aromatic to aliphatic hydrogens found in the polymer was about 19 to one, showing that only one C_7 fragment is incorporated per polymer chain, and, most likely, that polymers initiated by the $Re=CH_2$ group are also present. These polymers would contribute intensity only to the aromatic-conjugated olefinic signals.

The polymer obtained in this work conforms exactly to that required by the proposed mechanism for polymerization of an alkyne by a metal-carbene complex, and demonstrates that a process analogous to that of olefin metathesis is feasible.

Experimental

Starting materials and solvents. Phenylacetylene (98.5%), 1,7-octadiene (98.5%) and 1-pentene (99%) were purchased from Aldrich and used as received. Dirhenium decacarbonyl was obtained from Strem Chemical Co. Rhenium pentacarbonyl chloride was prepared by the method described by KRAUS (1972). Ethylaluminum dichloride was purchased as a 25.5% solution in heptane from Texas Alkyls, and used as received. Chlorobenzene was distilled and stored over molecular sieves under nitrogen.

Physical methods. Infrared spectra were recorded on a Perkin-Elmer 597 Infrared Spectrophotometer as thin films. Nuclear magnetic resonance spectra were taken on a Varian Anaspect EM-360 NMR spectrometer using deuterochloroform or carbon tetrachloride as the solvent. Tetramethylsilane was used as the internal standard for all samples. Molecular weights were determined by Galbraith Laboratories.

Polymerization of phenylacetylene. The reaction was carried out in a 50-ml, four-necked, round-bottomed flask equipped with a gas adaptor connected to a nitrogen source, a reflux condenser, a thermometer, and a rubber septum. The condenser had attached at the top a glass adaptor connected to a trap in series with an oil bubbler. This arrangement allowed for the release of gases from the reaction flask, but prevented air and/or oil from backing up into the flask.

Into the flask were placed 10 ml (7.5 g, 0.07 mol) of 1,7-octadiene, 0.18 g (0.5 mmol) of $Re(CO)_5Cl$ and 10 ml of chlorobenzene. The reaction mixture was stirred magnetically and heated to 95°C by means of an oil bath. At that point, 0.6 ml (1 mmol) of ethylaluminum dichloride was injected through the septum. The metathesis of 1,7-octadiene was allowed to proceed for 15 min (90% conversion) whereupon 100 ml (92.7 g, 0.91 mol) of phenylacetylene was added. The mixture was allowed to react at 98°C for 30 days, after which the reddish-brown, viscous mixture was quenched by pouring it into 500 ml of methanol. This resulted in a yellow-orange precipitate which was recovered by filtration. The yield of the dried precipitate was 84.1 g (90%) and showed a melting point of 81°C. Spectral analysis (ir and nmr) revealed it to be polyphenylacetylene containing the C_7 fragment. The M_n was found to be 2135 g/mole by vapor pressure osmometry.

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