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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The major outcome of the research was the discovery that acetylenes induce metal-derivatives to initiate metatheses of olefins. This discovery provides a simple way to synthesize a variety of polymers from cyclic olefins. Research to demonstrate the mechanism by which acetylenes induce metatheses showed that polyacetylenes appear as a block at the start of polyalkenamer chains. The initiation of the olefin metathesis quenches the acetylene polymerization. The size of the block revealed for the first time how the reactivities toward metal-carbenes differ for acetylenes and alkenes. Continued on the reverse side		

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When molecules are constructed that contain acetylene and alkene functions separated by four atoms—that is, so the alkene function is positioned to interact with a reactive center generated at the position of the acetylene—the acetylene polymerization is quenched after a single cycle of polymerization.

The result is one of two new transformations. If a full equivalent of a metal-carbene is combined with three enynes, the product contains a fragment of the metal-carbene. If only a small amount of a metal-derivative is combined with the enynes, the product is that of a new molecular rearrangement.

The stereochemistries of these transformations revealed for the first time the stereochemistry followed when metal-containing cyclobutenes yield metal-vinyl carbenes.

Other discoveries include these.

Isolable metal-carbenes initiate polymerizations of cyclic alkenes, giving polymers that by conventional procedures could not be prepared at all or could not be prepared as pure.

Metal-carbynes induce acetylenes and alkynes to polymerize.

Functionalized polyacetylenes, materials previously unknown, could be prepared from functionalized acetylenes by using metal-carbenes to initiate the polymerizations.

Metal-carbynes with diynes give phenols. The procedure was demonstrated to give phenols fused to six-, five-, and four-membered rings.

Metal-pentadienyls can be synthesized in a new way, by combining a metal-carbyne with an enyne.

A new NMR technique was used to show that when molybdenum catalysts induce acetylenes to polymerize, the carbons in the polymer that are connected by single-bonds are the ones that in the acetylene were connected by triple bonds. However, when titanium catalysts induce the polymerizations, it is the carbons in the polymers that are connected by double-bonds that derive from these carbons in the acetylene. The experiment distinguishes mechanisms that have confused chemists for years.

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0683

Task No. NR 356-726

FINAL REPORT

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March 18, 1991

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Polymer Syntheses and Mechanisms of Polymerization

(Contract N00014-79-C-0683)

(Project NR356-726)

Final Report

Prepared by

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Accomplishments, with Derivable Conclusions

The major outcome of the research was the discovery that acetylenes induce metal-derivatives to initiate metatheses of olefins. This discovery provides a simple way to synthesize a variety of polymers from cyclic olefins.

Research to demonstrate the mechanism by which acetylenes induce metatheses showed that polyacetylenes appear as a block at the start of polyalkenamer chains. The initiation of the olefin metathesis quenches the acetylene polymerization. The size of the block revealed for the first time how the reactivities toward metal-carbenes differ for acetylenes and alkenes.

When molecules are constructed that contain acetylene and alkene functions separated by four atoms—that is, so the alkene function is positioned to interact with a reactive center generated at the position of the acetylene—the acetylene polymerization is quenched after a single cycle of polymerization.

The result is one of two new transformations. If a full equivalent of a metal-carbene is combined with three enynes, the product contains a fragment of the metal-carbene. If only a small amount of a metal-derivative is combined with the enynes, the product is that of a new molecular rearrangement.

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Technical Reports

- Technical Report No. 1. Preparations of Polymers Using Metal-Carbenes,
- Technical Report No. 2. Induction of Olefin Metathesis by Acetylenes
- Technical Report No. 3. Reactivities of Metal Carbenes toward Alkenes and Alkynes
- Technical Report No. 4. Induction of Olefin Metathesis by Phenylacetylene plus Tungsten Hexachloride
- Technical Report No. 5. Polymerizations of Acetylenes and Cyclic Olefins Induced by Metal Carbynes
- Technical Report No. 6. Polymerization of Functionalized Acetylenes
- Technical Report No. 7. The Mechanism of Ziegler-Natta Polymerization of Acetylene: A Nutation NMR Study
- Technical Report No. 8. Metal-Catalyzed Rearrangement of Alkene-Alkynes and the Stereochemistry of Metallacyclobutene Ring Opening
- Technical Report No. 9. Mechanisms of Phenylacetylene Polymerization by Molybdenum and Titanium Initiators
- Technical Report No. 10. Synthesis of Phenols from Metal-Carbynes and Diynes
- Technical Report No. 11. A Procedure Identifying a Polyacetylene Initiator of Olefin Metathesis. The Reactivities of Metal Carbenes toward Alkenes and Alkynes
- Technical Report No. 12. Reactions of Acetylenes and Alkenes Induced by Catalysts of Olefin Metathesis
- Technical Report No. 13. A Metal Pentadienyl Prepared by Reacting a Metal Carbyne with an Enyne

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