Progress Report for the Period 11/30/89-12/1/90 (DE-FG02-86ER13564)**Controlled Synthesis of Polyenes by Catalytic Methods****Richard R. Schrock**

The controlled synthesis of polyenes, a project started by Konrad Knoll, a NATO Postdoctoral Fellow, has developed in several directions.

Lee Park has completed a large study of the synthesis of polyenes by ring opening metathesis using tricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes (TCDT's) and a molybdenum catalyst ($\text{Mo}(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$; $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-i-Pr}_2$) that is analogous to the tungsten catalyst employed by Knoll. She found that the molybdenum catalyst is better behaved than the tungsten catalyst, and in particular that *living polyenes* can be generated and are relatively stable in coordinating solvents. Preparation of discrete polyenes via the ring-opening of the bis CO_2Me derivative or the parent hydrocarbon are relatively unsuccessful, presumably because of secondary intermolecular metathesis. Optimum yields were obtained using $\text{TCDT}-(\text{CF}_3)_2$. Vinyl alkylidene species formed from living poly-TCDT- $(\text{CF}_3)_2$ have been explored in detail, in particular the isomerization of *cis* to *trans* forms. Capping of these living polyenes with conjugated dialdehydes provides a relatively mild route to relatively long polyenes that will form the basis of further research. The incorporation of acetylene itself into block copolymers containing polynorbornene also has been explored extensively. A significant problem is that acetylene is polymerized primarily to an all *trans* form, the least soluble and most prone to crosslinking. A full paper describing this work has been submitted to *Macromolecules*.

Collaborations have continued with three groups, and other collaborations are developing. A group at Exxon headed by Dr. Ron Chance has studied the linear optical properties of an homologous series of t-butyl-capped polyenes by Raman spectroscopy. Some of these results have been reported as proceedings of a conference (see publication list) and a paper has been submitted. Dr. Thomas Bally of the University of Fribourg has generated the radical cation of a variety of polyenes by γ irradiation in an inert matrix at low temperature and studied them by visible spectroscopy. Because a series of homologs could be studied he was able to show that

previous studies of radical cations of β carotenes were in error. He is also in a position to address the question concerning the fundamental nature of the transitions in these unsubstituted polyene radical cations. Related studies involving synthesis of radical cations of these polyenes in zeolites has begun at duPont. A collaboration between Lee Park and David Ofer in M. S. Wrighton's group has taken the form of exploring the conductivity of well-characterized polyenes and polyene mixtures prepared using TCDT-(CF₃)₂ versus applied potential using microelectrode techniques. We can say with certainty that chain length alone is insufficient for facile conductivity of doped polyenes. These results should be very interesting to compare with analogous studies involving polyanilines and polythiophenes. A publication on this work is in preparation.

It should be advantageous to prepare specific polyenes by Wittig-like methods rather than mixtures containing a distribution of polyenes by a catalytic method. A stoichiometric method also would allow introduction of various functionalities at the ends or within the polyene chain in a specific manner. Fortunately catalyst synthesis is now simple enough to consider using such complexes as stoichiometric reagents. We have employed **1** and **2** in reactions such as that shown in equation 1. We are in the process of perfecting the "reverse," the reaction between

difunctionalized reagents linked by an unsaturated chain and aldehydes synthesized from polymeric living alkylidenes to give triblock copolymers (equation 2; P = polymer). We know such species to be significantly more soluble, we believe soluble enough to carry out NLO (EFISH)

spectroscopic and electrochemical studies on them for the first time. Possible collaborations with Prasad at SUNY Albany are in the preliminary stages. The difunctionalized reagent shown in equation 2 has been prepared from octatetraene, an analog has now been prepared from hexatriene, and we have shown that a monoaldehyde can be synthesized by adding a dialdehyde to an alkylidene complex.

A recent report (Masuda, T.; Hamano, T.; Tsuchihara, K.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374) suggested that sterically-encumbered phenylacetylenes (specifically *ortho*-trimethylsilylphenylacetylene) could be polymerized to a soluble purple-red material ($\lambda_{\text{max}} \approx 520 \text{ nm}$) which we believed could be a polyene encased in TMS-substituted phenyl rings, a kind of "molecular wire." Such materials could be stable to air and to cross-linking, and therefore have potentially useful NLO properties. We have shown that we can prepare this polymer using $\text{Mo}(\text{CH-t-Bu})(\text{NAr})[\text{OC}(\text{CF}_3)_2(\text{CF}_2\text{CF}_2\text{CF}_3)]_2$ as the catalyst and have isolated and identified oligomers. Molecular mechanics calculations in our lab have shown that the preferred conformation of the chain backbone is *trans-s-cis*, and that this conformation most likely is enforced by the TMS-substituted phenyl groups and the double bonds therefore conjugated to a significant degree. Such molecules should be relatively rigid. We are in the process of studying this polymerization in detail and studying other *ortho*-substituted derivatives of phenyl acetylene. A significant problem in polymerizations of this type will prove to be control of the regio chemistry as shown in equation 3 ($P = \text{polymer}$). If the monosubstituted acetylene adds the wrong way then a relatively unreactive disubstituted alkylidene is formed. Our results suggest that the acetylene is adding the "right" way $\sim 90\%$ of the time, but this percentage must be improved in order to synthesize long polyenes. Block copolymers should be preparable after substituting the OR_F groups for *t*-butoxides.

Research in the next year will focus on the synthesis of specific polyenes (alone, in polymers, or containing various functionalities) by Wittig-like reactions using Mo or W alkylidene complexes as stoichiometric reagents. Polymerization of ortho-substituted phenylacetylenes will continue, as will collaborations that produce physical studies of the unique molecules that we prepare.

Publications that have appeared during the report period.

"Preparation of *tert*-Butyl-Capped Polyenes Containing up to 15 Double Bonds"

Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

"Direct Polymerization of Acetylene to Give Living Polyenes"

Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.

"Linear Optical Properties of a Series of Oligomers of Polyacetylene"

Schaffer, H. E.; Chance, R. R.; Knoll, K.; Schrock, R. R.; Silbey, R. J. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, J. Bredas and R. Chance, Ed., Kluwer, 1990, p. 365.

Papers Submitted.

"The Preparation of Discrete Polyenes and Norbornene-Polyene Block Copolymers Using

$\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ "

L. Y. Park, L. Y.; Stieglitz, S. G.; Crowe, W. M.; Schrock, R. R. *Macromolecules*

"Conjugation Length Dependence of Raman Scattering in a Series of Linear Polyenes: Implications for Polyacetylene"

Schaffer, H. E.; Chance, R. R.; Silbey, R. J.; Knoll, K.; Schrock, R. R. *J. Chem. Phys.*

Papers in Preparation.

"Synthesis and Study of Radical Cations Prepared from a Homologous Series of Di-*t*-Butyl-Capped Polyenes"

Bally, T.; Park, L.; Schrock, R. R.

"Finite Windows of Conductivity Measured for a Series of Polyenes of Known Chain Length"

Ofer, D.; Park, L.; Wrighton, M. S.; Schrock, R. R.

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