

Controlled Synthesis of Polyenes by Catalytic Methods

Progress Report for the period 12/01/92 - 11/30/93

Richard R. Schrock

Five papers have appeared in the last year (see list at end), numbers 225, 229, 233, 236, and 240.

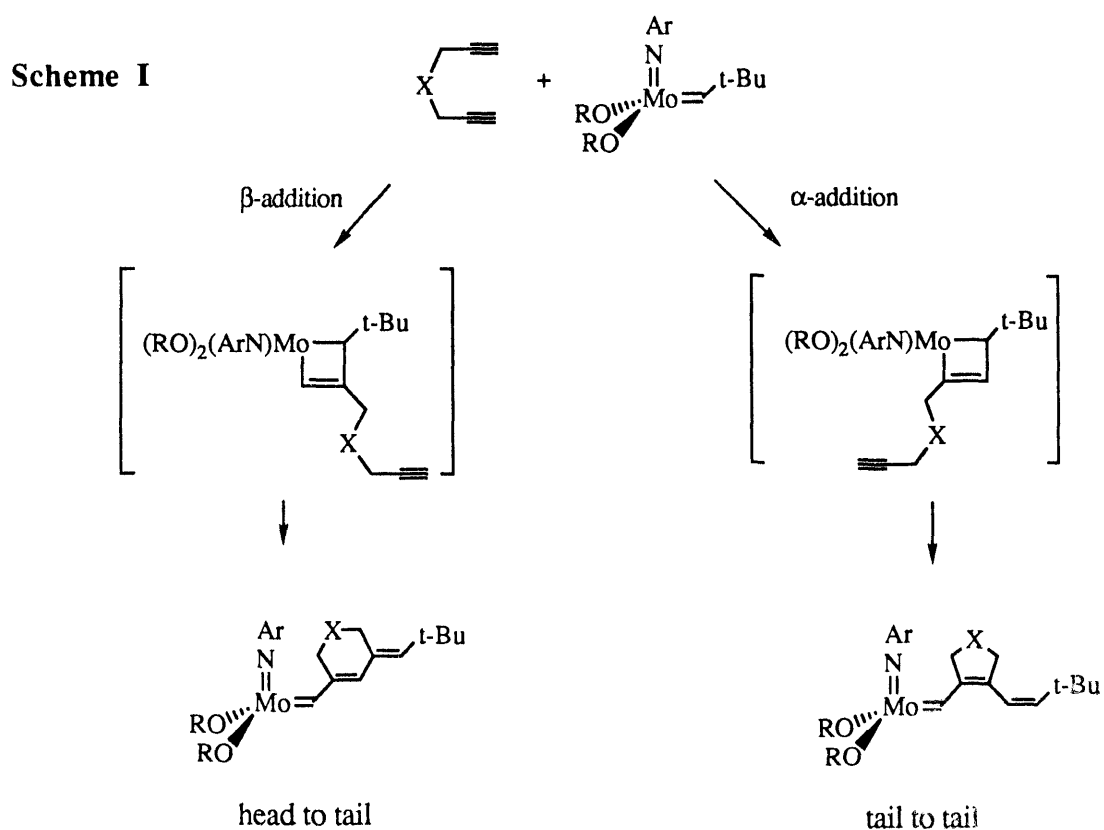
The living cyclopolymerization of dipropargyl derivatives has been reported for diethyl dipropargylmalonate ($X = C(CO_2Et)_2$; Scheme I; #225). We have found that α addition and β addition take place approximately to an equivalent degree, on the basis of the ^{13}C NMR chemical shift for the quaternary carbon atom in the five or six-membered ring, and in the presence of ethylene have isolated a molecule that contains a six-membered ring that is formed when ethylene cleaves the cyclized species from the metal in a chain transfer-like reaction. On this basis also we can say that the polymer prepared from this monomer using *classical* catalysts contain mostly *five*-membered rings, not *six*-membered rings, as proposed in the literature. We are in the process of attempting to design a catalyst which will produce polymer that contains only type of ring. We prefer that to be the six-membered ring, since non-linear response of an all trans polyene is likely to be significantly greater than a polyene that contains cis linkages (five-membered rings). Polyenes made from the diethyl dipropargyl monomer are now in the hands of Dr. Joe Zyss, who will be determining the third order hyperpolarizability in solution as a function of chain length.

We have found that several other ester derivatives can be polymerized smoothly, among them t-butoxy and menthoxy. We will vary the size of the alkyl group in the ester in order to determine how steric factors influence the relative rates of cyclization. The menthoxy derivative is potentially especially important, since a large chiral group could force the polyene to coil in one direction to give a chiral helical form that would have a second order response. Two other derivatives that have been polymerized successfully are $X = C(CH_2Otosyl)_2$ and $X = C(CH_2OTMS)_2$.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED





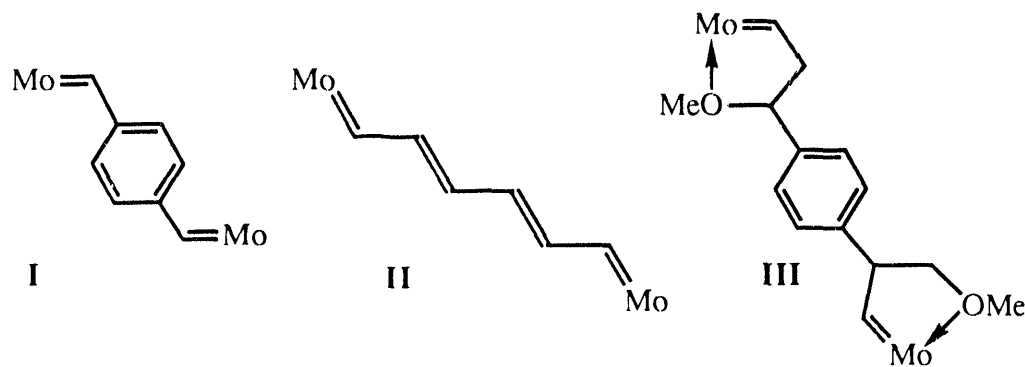
Paper #229 reports some older results that have been discussed in previous progress reports.

Paper #233 reports the casting of films of 7,8-bistrifluoromethyl-tri-cyclo[4.2.2 (2,5)]deca-3,7,9-triene onto platinum microelectrode arrays and subsequent heating to give polyacetylene in the molecular weight range from 400 to 6500. These films have been characterized by *in situ* measurements of conductivity as a function of electrochemical potential in liquid SO_2 /electrolyte. The results show a steady increase in conductivity with average chain length for samples with chain lengths in the range 11 to 60 double bonds, above which conductivity levels off as chain length continues to increase. All samples exhibit a finite potential window of conductivity which increases in width in the range 11 to 60 double bonds and does not change further with increasing chain length.

Paper #236 reports a nonlinear optical analysis of a series of triblock copolymers

containing a known distribution of polyene sequences. These data suggest that the third order hyperpolarizability increases by the power 3.6. These studies have now been extended and clearly show for the first time that γ levels off when the number of double bonds reaches a nominal level of approximately 200 double bonds. We also have found, surprisingly, that γ for a polyene prepared in a polynorbornene matrix is approximately an *order of magnitude greater* than γ for a polyene prepared in a polyMTD (MTD = methyltetracyclododecene), and is also less sensitive to oxygen. *No phase separation is observable*. We attribute this difference in the magnitude of γ to the relatively low T_g of polynorbornene ($\sim 30^\circ\text{C}$) compared to polyMTD ($\sim 230^\circ\text{C}$), a circumstance that allows the polyene that is generated via the "Feast" method to equilibrate more completely with the "host" polymer. Other recent results in the process of being published include the finding that γ for "fixed length" polyenes in similar circumstances is of a magnitude consistent with what was predicted from the data obtained on materials that contain a known distribution of polyenes.

Paper #240 reports (*inter alia*) bifunctional hexafluoro-*t*-butoxide Mo species (such as I, II, or III), and their use as initiators in ROMP reactions. Some of these initiators have been



used to form polyenes, either "fixed-length" or a distribution of chain lengths, for evaluation in nonlinear optical studies. One of the most important aspects of this paper is that Mo hexafluoro-*t*-butoxide catalysts in 1,2-dimethoxyethane give essentially monodispersed polymers in a living polymerization reaction. This finding was the logical extension of the finding that Mo hexafluoro-*t*-butoxide catalysts in 1,2-dimethoxyethane are the only successful ones for

cyclopolymerization of dipropargyl derivatives described above.

We are in the process of writing a large paper on the synthesis of "hybrid" polyacetylenes, random or block copolymers that contain unsubstituted polyene sequences as well as sequences made from diethyl dipropargyl malonate. Such polymers are still soluble and currently are being examined in terms of γ in solution.

In the coming year there is a good possibility that a collaboration to measure nonlinear effects will open up here at MIT. In that case we expect evaluations to proceed much more quickly. One important new direction in the next year will be the preparation of polyenes that contain silver clusters in order to determine the magnitude of the expected "nanocluster enhancement" of γ , a result that can now be anticipated because of the success of the ROMP technology for making polyenes with well-characterized catalysts.

Publications appearing in the last year.

225. "Living Cyclopolymerization of Diethyl Dipropargylmalonate by $\text{Mo}(\text{CH-t-Bu})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ in Dimethoxyethane"
Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763-2765.
229. "Linear Optical Properties of a Series of Linear Polyenes: Implications for Polyacetylene"
Chance, R. R.; Schaffer, H.; Knoll, K.; Schrock, R.; Silbey, R. *Synth. Met.* **1992**, *49-50*, 271.
233. "The Effect of Chain Length on the Conductivity of Polyacetylene. Potential Dependence of the Conductivity of a Series of Polyenes Prepared by a Living Polymerization Method"
Park, L. Y.; Ofer, D.; Schrock, R. R.; Wrighton, M. S. *Chem. Mater.* **1992**, *4*, 1388.
236. "Nonlinear Optical Analysis of a Series of Triblock Copolymers Containing Model Polyenes; The Dependence of Hyperpolarizability on Conjugation Length"
Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, *115*, 860.
240. "The Synthesis of Five- and Six-Coordinate Alkylidene Complexes of the Type $\text{Mo}(\text{CHR})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2\text{S}_x$ and Their Use as Living ROMP Initiators or Wittig Reagents"
Fox, H. H.; J.-K. Lee; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

**DATE
FILMED**

1 / 21 / 94

END

