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FINAL REPORT

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New Polymers Made with Well-Characterized Organometallic Catalysts

Richard R. Schrock, Department of Chemistry, 6-331, Massachusetts Institute of Technology,

77 Massachusetts Avenue, Cambridge, MA 02139

In the first publication we reported that Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ was a good catalyst for the ring opening metathesis polymerization of *endo,endo*-5,6-dicarbomethoxynorbornene to give homopolymers with polydispersities in the range 1.11-1.22, as well as block copolymers containing *endo,endo*-5,6-dicarbomethoxynorbornene and norbornene with similar low polydispersities.

In the second publication we reported additional details of the metathesis of functionalized monomers by molybdenum, and also that 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene could be ring opened and the polymer cleaved with pivaldehyde to give (after pyrolysis) soluble polyenes, (t-Bu)(CH=CH)$_{2x+1}$(t-Bu). Triblocks containing a 40-ene (average) central chain, capped by two polynorbornene chains also were prepared.

In the third we applied some of the principles of Mo and W chemistry to Ta. Ta(CH-t-Bu)(DIPP)$_3$(THF) (**1**), Ta(CH-t-Bu)(DMP)$_3$(THF) (**3**; DMP = 0-2,6-C$_6$H$_3$Me$_2$), and Ta(CH-t-Bu)(TIPT)$_3$(THF) (**5**; TIPT = S-2,4,6-C$_6$H$_2$-i-Pr$_3$) were prepared by straightforward methods. These species react with olefins to give metallacyclobutane intermediates, e.g., **1** reacts with norbornene to give an isolable tantalacyclobutane complex, Ta[CH(C$_5$H$_8$)CHCH(t-Bu)](DIPP)$_3$. Norbornene is polymerized by Ta[CH(C$_5$H$_8$)CHCH(t-Bu)](DIPP)$_3$ in a reaction that is zero order in norbornene to give essentially monodisperse polynorbornene. The TIPT system behaves similarly, and in this case secondary metathesis (after NBE has been consumed) is negligible. Several crystal structures were reported.

In the fourth publication we reported that $Ta(CHCMe_3)(DIPP)_3(THF)$ (DIPP = 2,6-diisopropylphenoxide) reacts with one equivalent of 2-butyne, diphenylacetylene, bis(trimethysilyl)acetylene, or 2-methyl-1-buten-3-yne to give THF-free metallacyclobutene complexes, and that addition of pyridine to two of these metallacycles yields vinyl alkylidene complexes that react with up to 200 eq of 2-butyne readily to give living polymers. $Ta\{[C(Me)C(Me)]_xCHCMe_3\}(DIPP)_3(py)$, from which the organic poiymer can be cleaved by treatment with benzaldehvde and shown to have a very low polydispersity (< 1.05). This work establishes that it is possible to polymerize acetylenes in a living fashion, and incorporate them into block copolymers made from cyclic olefins by ROMP.

In the fifth publication we examined potential chain transfer (CT) reagents for removing a growing polymer from living ROMP catalysts. Although 1-(2-cyclopentenylmethyl)-2-phenylethene will react with $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ to give $W(CHPh)(NAr)(O\text{-}t\text{-}Bu)_2$ in 60% yield, other potential chain transfer (CT) reagents for W catalysts fail to varying degrees for a variety of reasons. The most significant problem is that the double bond in the alkenyl side chain of the alkenylcyclohexene (the rearrangement product of the CT reagent) ultimately reacts with a relatively small alkylidene ligand (e.g., a propylidene ligand) in the just-formed initiator. We conclude that although the principle is valid, the double bond in an ideal CT reagent would have to be considerably more reactive than that in a cyclopentene, and/or the catalyst would have to discriminate more efficiently between the double bond in the cyclic olefin and that in the side chain.

In the sixth publication we show that 5,6-dicarbomethoxynorbornadiene or 5,6-bis(trifluoromethyl)norbornadiene can be polymerized by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ in a well-behaved living manner to give essentially monodisperse homopolymers that have a high degree of stereoregularity. Attempts to polymerize these monomers using $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ were unsuccessful.

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2. "Controlled Ring-opening Metathesis Polymerization by Molybdenum and Tungsten Alkylidene Complexes"
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3. "Preparation and Reactions of Tantalum Alkylidene Complexes Containing Bulky Phenoxide or Thiolate Ligands. Controlling Metathesis Activity and Mechanism Through Choice of Anionic Ligand."
   Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.*

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Names of Personnel:

J. S. Murdzek, R. R. Schrock, S. A. Krouse, K. Knoll, K. C. Wallace, K. B. Yap, L. R. Sita, G. Bazan.