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FINAL REPORT

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"Ring Opening Metathesis Polymerization"

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The central theme of this research is ring opening metathesis polymerization of norbornenes and substituted norbornadienes by well-characterized imido alkylidene catalysts of the type $M(CHR)(NR')(OR'')_2$ (where R, R', and R" are some alkyl or aryl groups), or most recently (as yet unpublished) alkylidyne alkylidene rhenium catalysts of the type $Re(CHR)(CR')(OR'')_2$

Initially we focused on developing catalysts that would tolerate functionalities (such as carbonyl groups). Full papers have now appeared (papers 7, 8, and 9; technical reports 10, 11, and 12; preliminary communication 3). The findings concerning the polymerization of 2,3-bistrifluoromethylnorbornadiene suggested that the polymer was virtually all trans and tactic. It is now believed to be syndiotactic. Such materials are highly polarizeable above T_g (200 °C). A significant fraction of the present effort is being expended toward understanding how this stereoselectivity arises and how it can be controlled by changing the nature of the catalyst.

Initially we strove to develop a method of cleaving the polymer chain from the metal and starting a new chain, since the catalysts was relatively tedious to prepare. Papers 2 and 5 dealt with cyclopentene and styrene-based chain transfer agents, respectively. After the development of a simple synthesis of the molybdenum catalyst, catalyst longevity (i.e., reuse) became less crucial. Therefore the development of chain transfer agents was de-emphasized.

The synthesis of star polymers and block copolymers was another significant development in the past grant period (paper 6). Such techniques now make it possible to prepare amphiphilic start shaped polymers (paper in press).

Four papers are in the offing that concern the synthesis of side chain liquid crystal (SCLC) polymers by ROMP techniques. At least one wholly new type of SCLC polymer has been prepared, and several relatively rare examples of block copolymers that contain a SCLC block.

Investigations into the synthesis of chiral catalysts and the polymerization of chiral monomers are continuing. So far polymers have been prepared from chiral monomers but a chiral catalyst has not been synthesized. Research in this direction is an important part of the present research program. Chiral catalysts should be able to "correct" their stereochemical "mistake" and thereby produce much more tactic and stereoregular polymers than analogous achiral catalysts.

Technical Reports and Published Articles 1989-1992:

1. "Living Polymerization of 2-Butyne Using a Well-Characterized Tantalum Catalyst" **(Technical Report #4)**
Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

2. "Evaluation of Cyclopentene-Based Chain-Transfer Agents for Living Ring-Opening Metathesis Polymerization" **(Technical Report #5)**
Schrock, R. R.; Yap, K. B.; Yang, D. C.; Sitzmann, H.; Sita, L. R.; Bazan, G. *Macromolecules* **1989**, *22*, 3191.

3. "Living and Highly Stereoregular Ring-Opening Polymerization of 5,6-Difunctionalized Norbornadienes by a Well-Characterized Molybdenum Catalyst" **(Technical Report #6)**
Bazan, G.; Schrock, R. R.; Khosravi, E.; Feast, W. J.; Gibson, V. C. *Polymer Commun.* **1989**, *30*, 258.

4. "Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition Metal Alkylidene Complexes " **(Technical Report #7)**
Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158.

5. "Chain Transfer Agents for Living Ring-Opening Metathesis Polymerization Reactions of Norbornene" **(Technical Report #8)**
Crowe, W. E.; Mitchell, J. P.; Gibson, V. C.; Schrock, R. R. *Macromolecules* **1990**, *23*, 3536.

6. "The Synthesis of Star Block Copolymers by Controlled Ring-Opening Metathesis Polymerization" **(Technical Report #9)**
Bazan, G. C.; Schrock, R. R. *Macromolecules* **1991**, *23*, 817.

7. "Living Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized Norbornadienes by Mo(CH-t-Bu)(N-2,6-C_6H_3-i-Pr_2)(O-t-Bu)$_2$" **(Technical Report #10)**
Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112* , 8378.

8. "Polymerization of Functionalized Norbornenes Employing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ as the Initiator" **(Technical Report #11)**
Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.

9. "Living Ring-Opening Metathesis Polymerization of 7-oxa-2,3-Difunctionalized Norbornenes and Norbornadienes by Mo(N-2,6-C_6H_3-i-Pr_2)(CHCMe$_2$R)(O-t-Bu)$_2$ and Mo(N-2,6-C_6H_3-i-Pr_2)(CHCMe$_2$R)(OCMe$_2$CF$_3$)$_2$" **(Technical Report #12)**
Bazan, G. C.; Oskam, J. H.: Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

Manuscripts submitted.

"Synthesis of Amphiphilic Star Block Copolymers Using Ring Opening Metathesis Polymerization"
Saunders, R. S.; Cohen, R. E.; Wong, S. J.; Schrock, R. R. *Macromolecules*

"Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis Polymerization. 1. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length (n = 2-8) on the Thermotropic Behavior of the Resulting Polymers"
Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules*

"Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis Polymerization. 2. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length (n = 8-12) on the Thermotropic Behavior of the Resulting Polymers"
Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules*

"Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis Polymerization. 3. Influence of Molecular Weight, Interconnecting Unit and Substituent on the Mesomorphic Behavior of Polymers with Laterally Attached Mesogens"
Pugh, C.; Schrock, R. R. *Macromolecules*

"Synthesis of Side Chain Liquid Crystal Polymers by Living Ring Opening Metathesis Polymerization. 4. Synthesis of Amorphous and Side Chain Liquid Crystal AB Block Copolymers"
Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules*

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