

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Scientific Discovery and Technological Innovation: An Eclectic Odyssey Into Olefin Metathesis Chemistry

Herbert S. Eleuterio<sup>a</sup>

<sup>a</sup> Petrochemicals Department Hickory Run, Wilmington, Delaware

**To cite this Article** Eleuterio, Herbert S.(1991) 'Scientific Discovery and Technological Innovation: An Eclectic Odyssey Into Olefin Metathesis Chemistry', *Journal of Macromolecular Science, Part A*, 28: 9, 907 – 915

**To link to this Article:** DOI: 10.1080/00222339108054068

**URL:** <http://dx.doi.org/10.1080/00222339108054068>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **SCIENTIFIC DISCOVERY AND TECHNOLOGICAL INNOVATION: AN ECLECTIC ODYSSEY INTO OLEFIN METATHESIS CHEMISTRY**

HERBERT S. ELEUTERIO

Petrochemicals Department  
Hickory Run, P.O. Box 80723  
Wilmington, Delaware 19880-0723

Thirty-three years in applied chemistry has taught me that technology is an endless marathon. Before we revisit that topic, I want to share insights into the discovery process in the physical sciences in a way that should make you wonder, "What role and function might I play in the scientific discovery process?" And should prompt you to ask, "How can I best contribute to the process of innovation and invention?" so that chemists can continue to produce "better things for better living."

Our odyssey begins in 1955 and starts with research carried out in the exploratory group of Du Pont's Polychemicals Department. Personal preference as well as constraints of time compel me to pick and choose from several hundred patents and publications published over some 30 years. Of necessity, this presentation shall be an eclectic chemical odyssey.

I was one of several chemists assigned to find economically attractive process options for making polypropylene of any desired crystallinity index from propylene and coordination-type catalysts. My immediate objective was to scout reaction conditions and catalyst combinations that might increase polymer crystallinity. Beyond a given molecular weight, the physical and mechanical properties of polypropylene correlated with crystallinity. In turn, crystallinity was presumed to be a function of the substituents along the polymer backbone.

My unassigned longer-range interest was to understand the mechanistic details of the reaction. In 1955, the polymerization was thought to

proceed in the following manner. Initiation begins with the coordination of the olefin by a transition metal complex. An alkyl group displaced the coordinated olefin. Adsorption and displacement of monomer repeated in the propagation step. Termination seemingly involved adventitious reaction with impurities, disproportionation to olefin and metal hydride, or chain transfer to monomer. Chain transfer to monomer was mechanistically the most challenging and least understood step.

Four reaction paths were considered likely. Pathway [1] is labeled normal propagation. Pathway [2] generates an electron-deficient center, which can be satisfied in one of two ways. Pathway [4] gives rise to "dead" polymer with vinylidene end-group plus an active catalyst site. Pathway [3] involves alkyl group transfer. Propagation can continue but the polymer chain would carry with it a quarternary carbon atom. Let's take a closer look at the hydride ion transfer to the monomer step. If the bond in the one o'clock position breaks, chain termination results. On the other hand, if the bond at 11 o'clock breaks, then "abnormal" propagation results. The experimental evidence that pathway [3] might occur was based on infrared data derived from examining samples of polypropylene with different crystallinity indices.

A correlation relating crystallinity to an infrared band at  $8.15 \mu$  was developed. The band at  $8.15 \mu$  is characteristic of a carbon atom substituted with four alkyl groups. Molecular models showed that one quarternary carbon per 20 propylene units totally disrupted the polymer's spiral structure. The experimental data supported the notion that structural differences might account for differences in crystallinity for polypropylenes prepared from titanium tetrachloride and lithium aluminum alkyl catalyst combinations. These observations were written up for external publication in mid-1956. To date, the paper remains unpublished. This paper was the first of many that were tabled due to patent litigation involving Du Pont, Montecatini, Standard Oil of Indiana, and Phillips Petroleum.

This was a terribly exciting time to be doing polymer chemistry. Almost daily our experimental results challenged the conventional wisdom of the polymer scientists. As Sherlock Holmes once observed: "It is a capital mistake, my dear Watson, to theorize before one has data. Insensibly one begins to twist facts to suit theories instead of theories to suit the facts." To this day, many questions that were being asked remain unanswered.

One day my supervisor asked me to help respond to a patent examiner's objection of a Du Pont patent application that involved the polymer-

ization of ethylene with a supported nickel oxide catalyst. The desired experiment was carried out as described in the patent. The results were transmitted in an affidavit to the U.S. Patent Office.

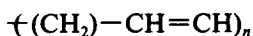
At about this time, I was assigned to a semiworks task force whose purpose was to test a polymerization process for preparing highly crystalline polypropylene.

In contrast to polyethylene, the literature available in the fall of 1956 was vague as to what type of polymer would be obtained from propylene polymerized with supported transition metal catalysts. To satisfy my own curiosity, I tried an experiment using a propylene feed with a metal hydride-promoted molybdena on alumina catalyst as disclosed in a U.S. patent assigned to Standard Oil of Indiana. A rubbery-like product that resembled amorphous polypropylene was obtained. Much to my surprise, an infrared scan of a pressed film showed a doublet at 13.7–13.9  $\mu$  that was not present in the infrared spectra of polypropylene. A doublet in that region of the infrared meant a sequence of methylene groups. My first thought was contaminated propylene. I repeated the experiment. The results were the same; apparently a propylene-ethylene copolymer was being made from propylene. To be absolutely certain, I asked the operator of the high-pressure lab to sample the propylene fed as well as the off-gas after the pressure drop stopped. The operator was insulted and incensed. Mass-spec analysis of the off-gas indicated propylene, ethylene, and butene-1; whereas the propylene feed was better than 97% propylene, the other 3% was nitrogen and propane.

Propylene was being selectively scrambled under remarkably mild reaction conditions. In order to capitalize on the unusual catalytic behavior of this catalyst, experiments were tried with olefins that had not previously been polymerized by coordination-type catalysts, namely, internal olefins and cyclic olefins.

*Cis*- and *trans*-2-butene was converted to a mixture that contained propylene and a C<sub>5</sub>H<sub>10</sub> fraction, *Trans*-2-butene gave *trans*-2-pentene. From *cis*-2-butene, mass-spec analysis indicated *cis*-2-pentene and, surprisingly, 1,2-dimethyl cyclopropane.

Cyclopentene was polymerized to an amorphous rubber-like solid polymer. Chemical, x-ray, and infrared data suggested that the repeating unit was a pentamer.



Norbornene also gave a rubber-like polymer. Analytical data sug-

gested a repeating unit of cyclopentane rings linked through 1,3-vinyl groups. Note that ring opening was thought to occur at the bridge head carbon.

Since carbene-type intermediates were implicated in the 2-butene experiments by the presence of cyclopropane, known methylene acceptors such as tetramethyl ethylene and cyclohexene were used as reaction solvents with propylene as the monomer. Mass-spec analysis indicated that methylene-enhanced reaction products were in fact formed. The  $C_7H_{12}$  cracking pattern from the cyclohexene experiment was similar to that of an authentic sample of norcarane. However, even if carbenes were involved in scrambling linear olefins, the mechanism of the ring-opening polymerization of cyclopentene was puzzling. It appeared that the double bond had been snipped in half by the catalytically active site and then neatly resealed to produce a linear unsaturated polymer. Double bonds simply did not behave this way! To establish that "carbene-type" intermediates were mechanistically responsible would require time-consuming isotopic labeling experiments which would not per se be definitive. Although the chemistry was recognized as novel with much up-side theoretical and synthetic potential, a decision was made to terminate the work by writing a summary report along with appropriate patent notes. Of the patent notes submitted, one claiming an olefins process for upgrading propylene to higher-valued products was rejected with the comment that "Du Pont was not in the oil business." Another note claiming novel compositions of matter and processes for their preparation from cyclic olefins first surfaced as a German patent issued Jan. 7, 1960. An abstract of this patent appeared in *Chemical Abstracts* in 1961. Publication of the propylene scrambling reaction was set aside because some of the results were considered relevant to pending polypropylene patent applications. Some of these polypropylene cases were tied up in patent disputes that were not resolved until 1980. Certain aspects of these patents are still being litigated.

Three years after the abstract of the German patent appeared, researchers here and abroad reported the "disproportionation of olefins" and "the ring-opening polymerization of cyclic olefins." Olefin "metathesis" reactions fall into three categories: exchange, ring-opening polymerization, and degradation. That this chemistry captured the imagination and interest of many industrial and academic researchers worldwide is summarized in several review articles. An article authored by Professor Ivin, in Ivin and Saegusa's book [13], which reviews the ring-opening polymerization literature, is exceptionally well done in terms of both historical accuracy and completeness.

Carbene-type intermediates are, in fact, mechanistically involved. Since 1975, the experimental evidence has heavily favored the metal-carbene species. Of all the articles that address the mechanistic features of olefin disproportionation, I prefer Katz' review in *Advances in Organometallic Chemistry* [15]. Olefin "metathesis" is a textbook example illustrating that novel investigative methods are central to the advancement of science.

As it turns out, norbornene polymerizes in the same fashion as cyclopentene; that is, rupture had reassembly of the double bond. The catalytically active sites have been directly observed using NMR techniques. Recently these species have been isolated and identified using an experimentally clever combination of a reactor probe and ESCA analysis. After 30 years, the metalcarbene-catalyzed olefin chemistry seems to be reasonably well understood. Like any first-rate mystery, however, a few intriguing pieces of the puzzle are still missing. A piece of the puzzle not missing is the role that this chemistry has played in the scientific renaissance in the field of catalysis, organometallics, and polymerization, a renaissance that began in the 1950s catalyzed by a profusion of inexpensive and reliable analytical instruments.

Not only has this reaction advanced science, it has had practical value as well. Bayer, Goodyear, Montecatini, British Petroleum, CdF Chimie, and Chemische-Werke-Huls have piloted and/or commercialized processes and products based on this catalysis. Late in 1986, Lyondell announced construction of an olefins plant based on Phillips Petroleum technology. Shell International has developed rhenium catalysts for diene synthesis. Shell calls its development effort the *FEAST* project. FEAST is an acronym for further exploration of advanced Shell technology. The project's aim is to sell new intermediates worldwide for use in specialty polymers. The synthetic versatility of this reaction has exceeded my expectations. A variety of novel compositions of matter have been synthesized. Vestenamer and Norsorex are being sold commercially by the French as specialty elastomers. *Trans*-polypentenamers whose properties bear a remarkable resemblance to natural rubber fell victim to the energy crisis and subsequent restructuring of the global tire market. There is renewed interest. Several companies are testing various polyalkenamers in polymer alloys, polymer blends, and engineering plastics end-uses. Hercules and Goodrich have developed proprietary catalysts for polymerization of dicyclopentadiene in (RIM) applications.

Given that technological advances depend on human creativity, as an industrial researcher, I have had a long-standing interest in the process of scientific discovery and technological innovation. In a PNAS article

[21], Nobel Laureate Herb Simon states, "What chiefly distinguishes creative thinking from more mundane forms are the willingness to accept vaguely defined problem statements and gradually structure them, a continuing preoccupation with problems over a considerable period of time and an extensive background knowledge in relevant and potentially relevant areas."

Professor Simon's focus on human creativity was on basic research and individual characteristics. He cites the following: tolerance of ambiguity, persistence, knowledge, problem formulation, communication, and chance as relevant to the discovery process. Two articles in *Nature* [19] speak to individual as well as institutional factors that affect the discovery process in the sciences.

In the first article, Lederberg reminisces on the circumstances that surrounded the discovery of genetic recombination of bacteria. In an accompanying article, Zuckerman and Lederberg analyze the process of scientific discovery from the perspective of sociologist-observer and scientist-participant. Paraphrasing their remarks:

Premature discoveries . . . are either passively neglected or actively resisted at the time they are made. Discoveries are premature because they are conceptually misconnected . . . made by an obscure discoverer, published in an obscure place or are incompatible with prevailing doctrine.

For a discovery to qualify as post mature . . . it must have three attributes. In retrospect, it must be judged to be technically achievable at an earlier time with methods then available. It must be judged to be understandable, capable of being expressed in terms comprehensive to working scientists at the time, and its implications must have been capable of having been appreciated.

Although I was brought up in the 90% perspiration/10% inspiration school of creative endeavor, I agree with Simon and Zuckerman that there is more to it than that. In addition to the individual and institutional factors discussed by Simon and Zuckerman and Lederberg, my own experience suggests that pluck, adaptability, resilience, and sponsors have a role in the scientific discovery process. Experimental luck is cited as having played a major role in Lederberg's work. Lederberg had a 1 in 20 chance in picking the right strain of *Escherichia coli* for his genetic experiments! I learned earlier this year that "a pound of pluck is

worth a ton of luck." A clear-cut example of pluck was the discovery of high-temperature superconductivity by two IBM researchers. These two researchers had the courage of their convictions and were able to beat the "IBM R&D project selection system."

The metallocarbene scrambling of olefins began with a mundane request to repeat a patent disclosure. Curiosity about the behavior of propylene over a heterogeneous catalyst and finding a mixture of olefins was indeed serendipitous. Had I not been plucky, however, I would have not made the discovery. The section manager had mandated that no experimental work be carried out with supported transition metal catalysts. In my opinion, the catalyzed scrambling of olefins is an example of a postmature discovery. It is reasonable to assume that others before me may have prepared similar materials and either missed the 13.7–13.9 doublet or moved on to a more "fruitful" research area.

On the other hand, the catalyzed ring-opening cleavage of the cyclopentene double bond to a linear unsaturated polymer is an example of a premature discovery. Not only was it found by an obscure discoverer (me), but it was also incompatible with the prevailing doctrine as to how double bonds reacted. In fact, one outside consultant refused to believe the experimental results and vehemently persuaded the section manager to assign a colleague to prove that the reaction was thermodynamically impossible. I believe that "chance favors the prepared mind." Prepared, in my lexicon, means not only informed but having an open mind. A closed mind is a barrier to scientific discovery.

Adaptability, that is, the ability to structure open-ended problems along with the ability to sort out and adapt to the "right" information, is an important attribute. The most successful problem solvers I have known are willing to try to master whatever needs to be mastered to achieve a solution and are able to adapt to and overcome artificial institutional barriers. Mastery may simply mean "to know enough so that you know what you don't know." Many distinctions between science and applied science are at best bookkeeping exercises. When carried too far, they may become institutionalized and stifle creativity. Discretionary time, time in which "bootleg" experiments on unassigned projects can be tried, was an important factor in the metallocarbene-catalyzed reaction of olefins.

I prefer resilience to persistence because resilience connotes the dynamics of the discovery process. Human creativity involves not only intellectual interactions, but more often than not, psychological and societal encounters as well.



Success in the applied sciences is the result of complex technical, economic, and psychosocial interactions requiring close cooperation among many disciplines. When funds are tight, these interactions more closely resemble psychological warfare. Discovery and technological innovation are often depicted as steps in a linear, sequential process. In an industrial research setting, they are more likely to be step changes and discontinuities. An indicator of resilience is system robustness. The ability to recover from insult can determine the fate of an idea, the outcome of a venture, or the career path of an individual.

Advances in experimental information-rich techniques contribute significantly to system robustness. The presence of so many first-class research facilities scattered throughout the world assures system robustness. The creative responses to the scientific challenges posed by the ring-opening polymerization of cyclic olefins, as well as the high degree of originality shown in the application of this chemistry, attest to system robustness in catalysis, reaction mechanisms, synthetic chemistry, and polymer science. In art and in music, successful creative individuals have traditionally enjoyed the backing of a patron. In the physical sciences, ideas and/or projects often survive only when a champion or sponsor is found.

Psychologists point out that an individual's career typically evolves through four identifiable, often overlapping stages: apprentice, independent contributor, mentor, and sponsor. Briefly, the relationships in these stages entail learning, collaborating, helping others, and setting a course. After guiding me through the apprentice and contributor phases, Harold Hart, my doctoral thesis advisor, became my mentor-sponsor from whom I learned that research was fun and with whom I first experienced the joy of scientific discovery.

Early on, I asserted that technology is an endless marathon. In Kafkaesque fashion, every time the runners approach the finish line, the finish line moves away. Runners drop in, runners drop out, runners trade places. No runner ever wins! Runners with a limited view are beaten out by those with a vision! An interdisciplinary education in science and engineering keeps the competitors in the running!

As we near the end of our odyssey, I wish to mention one other sponsor, the Du Pont Company, who provided me with outstanding physical and people resources. Du Pont also gave me the opportunity to participate in a rich research tradition in materials science. Materials science is now perceived as an umbrella discipline that encompasses several branches of science but whose core is made up of chemistry, physics, and engineering. Du Pont's Polychemicals Department commitment to

materials synthesis, materials science, and materials engineering as an explicitly stated multidisciplinary objective dates back to 1950, when its research division was first formed. This early recognition of the benefits of interdisciplinary research teams is a tribute to the foresightedness of Du Pont management. It is professionally gratifying to be among those Du Ponters who have explored uncharted areas in science and technology. Among those who helped me find my way were Don Johnson, infrared spectroscopy, Ada Ryland, mass-spec and x-ray crystallography, Paul Till, polymer physics and polymer morphology, and Bill Truett, who was helpful in many ways.

### REFERENCES

- [1] R. L. Banks, *Ind. Eng. Chem.*, **3**, 170, 1960.
- [2] C. W. Bunn, *J. Appl. Physics*, **25**(7), 840, July 1954.
- [3] N. Calderon, *Accts. Chem. Res.*, **5**, 127, 1972; *Chem. Week*, June 3, 1987.
- [4] A. Clark, *Ind. Eng. Chem.*, **48**, 1152, 1956.
- [5] H. S. Eleuterio, *Chem. Abstr.*, **55**, 16005, 1961.
- [6] H. S. Eleuterio, U.S. Patent 3,074,918, 1963.
- [7] H. S. Eleuterio, Ger. Patent 1,072,811, 1960.
- [8] E. Field, U.S. Patent 2,691,647, 1954.
- [9] P. G. Gassman, *J. Am. Chem. Soc.*, **107**, 2380, 1986.
- [10] R. H. Grubbs, *C & E News*, **65**, 41, April 27, 1987.
- [11] R. H. Grubbs, *J. Am. Chem. Soc.*, **107**, 3377, 1985.
- [12] J. P. Hogan, R. L. Banks, W. C. Lanning, and A. Clark, *Ind. Eng. Chem.*, **47**, 752, 1955.
- [13] K. J. Ivin and T. Saegusa, *Ring Opening Polymerization*, Chapter 3, Elsevier, New York, 1984.
- [14] K. J. Ivin, *Olefin Metathesis*, Academic Press, New York, 1983.
- [15] T. J. Katz, *Adv. Org. Met. Chem.*, **16**, 283, 1978.
- [16] C. Kirkland, *Plastics World*, **50**, September 1990.
- [17] G. Natta, G. Dall'Asta, and G. Mazzanti, *Angew. Chem. Int. Ed.*, **3**, 723, 1964.
- [18] J. A. Osborn, *J. Am. Chem. Soc.*, **109**, 900, 1987.
- [19] J. Lederberg and H. Zuckerman, *Nature*, **324**, 627, Dec. 18, 1986.
- [20] D. B. Silica, *Invention Tech.*, **45**, Spring/Summer 1990.
- [21] H. A. Simon, *Proc. Natl. Acad. Sci. USA*, **80**, 4590, 1983.
- [22] W. L. Truett, *J. Am. Chem. Soc.*, **82**, 2337, 1960.
- [23] *Wall Street Journal*, Aug. 20, 1987.