Makoto Kumada (1920–2007)

Makoto Kumada, Professor Emeritus of Kyoto University, passed away on June 28, 2007, at the age of 87 from kidney failure. Kumada is known worldwide as the father of polysilane chemistry and also as one of the discoverers of modern transition-metal-catalyzed cross-coupling reactions.

Makoto Kumada graduated from Kyoto University in 1943 and worked for Toshiba Electric Co., Ltd. until 1950, when he started the academic career as an assistant professor at the newly established Osaka City University. In 1962, he moved to Kyoto University as a full professor.

Kumada's polysilane chemistry can be traced back to the discovery in 1945 of the "Rochow direct process" (Eugene G. Rochow) for the production of methylchlorosilanes from elementary silicon and chloromethane in the presence of copper as catalyst around 300 °C. Kumada was interested in the undesired high-boiling-point by-products (still-pot residue) formed as waste in the industrial Rochow process used by Toshiba from 1950. The dawn of the polysilane chemistry is described impressively in his essay in 2003:[1]

"*On a very cold winter morning of 1953, when performing fractional distillation of an exhaustively methylated product from the fraction boiling around 150 °C, I observed a distillate boiling at about 112 °C crystallized just at the exit of the distillation column, thanks to the laboratory not being heated. It took no long time before this crystalline substance, with b.p. 113 °C and m.p. 13 °C, proved to be hexamethyldisilane $Me_3SiSiMe_3$.*

"I remember clearly that I jumped up with joy when I recognized it, because although this had been a known compound since 1912–1913, only a very limited range of studies with very small quantities of this compound had been reported, and now it became possible to prepare, with great ease, this lowest member of the peralkylated polysilane family in large quantities by using, as starting material, the still-pot residue from the Rochow process. I was proud of getting several hundred grams of hexamethylsililane for the first time throughout all ages and countries."

In the following years, Kumada and his co-workers became pioneers of polysilane chemistry. A representative result is the thermal rearrangement of $Me_3SiSiMe_3$ to $Me_3SiCH_2SiMe_2H$ (now know as the Kumada rearrangement) discovered in 1958, which later served as a model reaction for the first stage of the Yajima process for the production of silicon carbide fiber from solid methylpolysilanes. Another striking discovery is the photochemical generation of silylene species from polysilanes in 1971, which was crucial for the synthesis of the first crystalline disilene by West et al. in 1981.[2] This synthesis involved the dimerization of silylenes generated photochemically from trisilane.

Apart from the polysilane chemistry, Kumada also made many contributions to organosilicon chemistry in general, as represented by the first report on the catalytic asymmetric hydrosilylation of olefins in 1971 and the synthetic application of hexacoordinate organopentafluorosilicates in 1978.

As described by Kumada,[3] Corriu and Masse (University of Montpellier), and Tamao, Sumitani, and Kumada (Kyoto University) almost simultaneously in 1972 disclosed a very efficient method for selective carbon–carbon bond formation by nickel-catalyzed cross-coupling of Grignard reagents with sp^2-hybridized carbon halides. In this articel he also notes the key importance of Akio Yamamoto's observation in 1970 of the reaction between [Ni(C_2H_5)$_2$(bpy)] (bpy = bipyridyl) with chlorobenzene as the motivation for Tama's idea of a Ni-catalyzed Grignard cross-coupling reaction, as well as for the remarkable current development of transition-metal-catalyzed cross-coupling reactions in general. The Kumada group extended this chemistry to catalytic asymmetric cross-coupling reactions by developing a series of chiral ferrocenylphosphines as ligands.

In 1967, Makoto Kumada was awarded the Frederic Stanley Kipping Award in Organosilicon Chemistry. He was thus the first Japanese scientist ever to win a national award of the American Chemical Society. At a special symposium organized in his honor by Alan MacDiarmid at University of Pennsylvania, Kumada talked about polysilane chemistry. Just after his talk, Eugene Rochow praised him by joking, "We must refine the direct process to produce the high boiling reside as the main product!" The Silicon Symposium in North America, the biennial European Silicon Days, and similar meetings in Japan originate from this special symposium.

Less known is an episode that could be seen as a catalyst for the awarding of 2000 Nobel Prize in Chemistry to Alan MacDiarmid for the discovery of conducting polymers: In 1975, Alan MacDiarmid was a guest of Kumada at Kyoto University for a few months, during which time he also visited Tokyo Institute of Technology, where only by chance he met Hideki Shirakawa, who had prepared polyacetylene films. They soon started the collaborative research that finally lead them to Stockholm.

More than 40 world-leading scientists presented their messages to celebrate Kumada's retirement from Kyoto University in 1983. These are compiled in a commemorative booklet. Among them, Alan wrote: "Your kindness in inviting me and my wife to spend a semester with you at Kyoto University in 1975 actually turned out to be one of the most important events in my life, a turning point in my career. In one way, it was perhaps a sad turning point, since unexpectedly it took me away from silicon chemistry, but if it had not been for your invitation I would not have become involved in the conducting polymer field." All the messages equally praise Kumada's personality and scientific spirit: "You are truly a scholar and gentleman" (Henry Gilman), "I appreciate even more your ability to connect your scientific activities with an attitude of warm and kind humanity" (Gerhardt Fritz), "Instead of providing a long, long list of compounds, let me select just one but very important class out of the manifold: the polysilanes" (Hans

Bock). Leo H. Sommer presented him with a poem:

Look back with much pride
On years so well spent:
Your students and their students
Will now carry the torch
In carbon–silicon land
The light from the torch
Will ever enlarge that land.

I worked with Makoto Kumada in his laboratory for more than 20 years and learned a lot, not only about chemistry but also about mental attitude as a scientist: He often said, "Original research will finally be highly appreciated" and "The laboratory is a sacred training room only for researchers of prepared mind."

The world has lost a great scientist.

Kohei Tamao
Frontier Research System, RIKEN

[1] M. Kumada, *J. Organomet. Chem.* **2003**, *685*, 3.
[2] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.
[3] M. Kumada, *J. Organomet. Chem.* **2002**, *653*, 62.

DOI: 10.1002/anie.200704157