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ROMPing to Nobel success

The beginning of the 'Plastic Age' is something of a moveable feast, but by one measure its centenary is imminent, for it was in 1907 that Leo Baekeland invented Bakelite, the first fully synthetic commercial polymer. If that messy phenolic resin is a far cry from today's precisely tailored advanced polymers, this year's Nobel prize in chemistry reveals one reason why. The development of stable and reliable catalysts for alkene metathesis by Richard Schrock[1] and Robert Grubbs[2], following key mechanistic work by Yves Chauvin[3], is treasured by synthetic organic chemists everywhere — but it had its origins in the petrochemicals industry and was at first the province of chemists concerned with making polymers.

METATHESIS IN ACTION: A HIGH-PERFORMANCE GOLF CLUB MADE FROM POLYDICYCLOPENTADIENE.

Metathesis now allows organic chemists a gentle touch in constructing the most complex of molecules, such as pharmaceuticals and natural products. Yet it continues also to play a major role in polymer chemistry. In particular, the technique known as ring-opening metathesis polymerization (ROMP) can supply block copolymers with precisely controlled dimensions, leading for example to nanoparticles with biomedical applications such as drug delivery.

Metathesis fits well with current efforts to find mild, 'green' processing routes to materials and other products. The shortcuts that it opens up improve the efficiency and thus the environmental friendliness of synthetic strategies; better still, some ROMP reactions can be conducted in aqueous media.

It was at the research laboratories of DuPont, the cradle of the US plastics revolution, that metathesis first emerged. This class of reactions involves the exchange of substituents between two molecules that both contain carbon–carbon double bonds. For propylene, this means swapping a methyl group on one molecule for a hydrogen atom on another, yielding ethylene and butylene. That process was reported by Herbert Eleuterio and co-workers at DuPont in 1956, using a catalyst of a molybdenum compound supported on alumina[4]. This rearrangement of hydrocarbons resulted in the creation of a propylene–ethylene copolymer.

It is telling that in 1966 the reaction attracted the interest of Guilio Natta, the Italian chemist who won the 1963 Nobel prize (with Karl Ziegler) for work on the catalytic synthesis of alkene polymers with controlled molecular structures. Natta initiated the use of metathesis for polymerization of cyclic hydrocarbons: ROMP, in other words.

But it wasn't until Chauvin's work in the early 1970s, on the role of the metal-atom catalyst in the exchange of molecular partners[3], that the curious reaction became transformed into rational science. Schrock was working at DuPont when he made the first stable version of the organometallic compound that Chauvin proposed as the crucial reaction intermediate. At the Massachusetts Institute of Technology, Schrock later made a whole series of such compounds, and found that those of molybdenum and tungsten were particularly effective at catalysing metathesis[1].

Grubbs took an interest in metathesis in the early 1970s, but his key contribution came 20 years later when he found that ruthenium-based catalysts (first explored in Natta's work) were stable in air and were less apt to attack vulnerable side groups on the reactants[2]. One of the additional boons of Grubbs' catalyst is that it tolerates the complex formulations often used in industrial polymer synthesis: fillers, stabilizers and other additives.

Among the advanced polymers now made by ruthenium-catalysed ROMP are polyoctenamer, used in tennis balls and to stabilize rubberized asphalt concrete in road surfaces, and metathene, a tough waterproof material used in bathroom fixtures. Grubbs' work lies behind the California-based company Materia, which markets polydicyclopentadiene, a tough, all-purpose, injection-mouldable thermoset resin used in a variety of sports products. But according to SonBinh Nguyen at Northwestern University in Illinois, a materials chemist and former student of Grubbs, "the major applications of metathesis in materials chemistry are still waiting to be discovered, particularly in the electronics and biological sector." ROMP is currently being used to make products ranging from polymer resists for silicon lithography to drugs that combat Alzheimer's disease.

Perhaps the most telling message of this year's Nobel award is that it emerged from unambiguously applied science — from a time when industrial laboratories were free to explore and pursue interesting science without any clear indication of an application. Metathesis went from industry to academia, and then back again in a more useful form. One might wonder whether industrial research has sufficient freedom for such a thing to happen today.

References

1. Wengrovius, J. H. *et al. J. Am. Chem. Soc.* **102,** 4515–4516 (1980).
2. Fu, G. C. *et al. J. Am. Chem. Soc.* **115,** 9856–9857 (1993).
3. Chauvin, Y. & Hérisson, J.-L. *Macromol. Chem.* **141,** 161–167 (1971).
4. Eleuterio, H. S. *J. Mol. Catal.* **65,** 55–61 (1991).