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Book reviews

Metallocene-based polyolefins—preparation, properties and technology, Vols 1 and 2
J. Scheirs and W. Kaminsky (eds)
John Wiley and Sons, Chichester, 2000
Vol. 1, 526 pages; Vol. 2, 571 pages. £275 (two volume set)
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The ready availability of ethylene, propylene and various other α-olefins from the oil industry means that if polymers can be prepared from them efficiently the products will be relatively inexpensive. Hence the polymerization of these olefins has occupied an important position in polymer chemistry for many years and currently approximately 40 million tons of such polymers are produced annually. The area has had an interesting history, one which has seen relatively long fallow periods suddenly followed by great advances.

Ethylene was initially polymerized in the 1930s by a standard type of free-radical-initiated polymerization. Unfortunately, high pressures and temperatures were required and, due to the side reactions inherent in free-radical polymerizations, the polymers produced had highly branched structures. This meant that the polymer chains did not pack together well (hence the description low-density polyethylene (LDPE)) and the product had relatively poor material properties. Against this background the reports in the 1950s from Ziegler in Germany and Natta in Italy that ethylene and propylene could actually be polymerized at ambient temperatures and pressures using a heterogeneous catalyst prepared from a transition-metal halide, usually $TiCl_4$, and an aluminium alkyl, for example $AlEt_3$, seemed almost unbelievable. It led to the first major revolution in the field; subsequently Ziegler and Natta received the Nobel Prize for their discoveries. The polymer produced from ethylene in this way was free of branching so the polymer chains packed together well and the mechanical properties were much better than those of LDPE. The product is usually called high-density polyethylene (HDPE). Furthermore, the product from propylene was found to be stereoregular—a great novelty at that time. Whilst Ziegler–Natta catalysts are very important and have been used commercially to great effect for many years, the fact they are heterogeneous is in some ways a problem. Typically they contain several ill-defined catalytic sites whose performances differ. Tuning catalyst performance tends to be rather hit-and-miss and catalysts are not always easily reproduced.

In the mid-1970s Breslow showed that a new type of catalyst, prepared from bis(cyclopentadienyl)titanium dichloride and dimethylaluminium chloride plus a small amount of water, was quite effective for the polymerization of ethylene. A year later Sinn and Kaminsky showed that adding the water to the alkylaluminium before the addition of the metallocene produced a highly active catalyst system with commercial potential. The second major revolution had begun!

The developments in this second revolution are the subject of the two volumes of *Metallocene-based polyolefins*. The books are edited by John Scheirs, a well-known industrially based researcher, and Walter Kaminsky of the University of Hamburg, who, as noted above, made the breakthrough which ushered in the second revolution. Both the industrial and academic aspects of the subject are comprehensively and authoritatively covered in 46 chapters written by 121 authors from both academia and industry in 11 countries (none from the UK!). The chapters are well written, produced and referenced. They chart progress made from the heterogeneous multi-site catalysts of the Ziegler–Natta era to the development of exceedingly active soluble single-site catalysts which often do not need methylaluminoxane as a cocatalyst. The most active catalysts now produce more than 500 000 g of polymer per gram of metal. The solubility of the catalysts assists a detailed study of their key features and performance, which then usually prompts the rational design, often with the aid of modelling, of still better catalysts. The later chapters in Volume 2 consider the rheology and processing of the various polymers.

These are exciting times for the polymerization of α-olefins and the revolution is still not finished. New catalysts based, for example, on nickel and iron complexes continue to be discovered. We can soon expect to have commercial catalysts which are not moisture-sensitive and which will allow functional monomers to be polymerized. It is clear that anyone working on the polymerization of α-olefins should have these two volumes on their bookshelf as they are a wonderful source of information on this very important and active area of polymer science and technology.

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