PERSPECTIVES: POLYMER SYNTHESIS

Catalysts Rise to the Challenge

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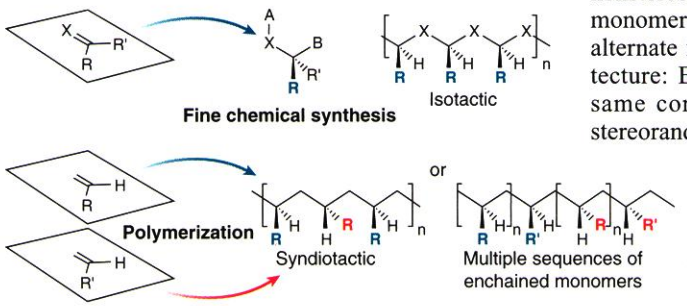
The efficient synthesis of molecules with well-defined three-dimensional architectures and hence specific properties faces a formidable challenge: the control of stereochemistry (the spatial arrangement of atoms in molecules). The synthesis of fine chemicals such as drugs usually requires chiral molecules to have a defined absolute configuration. In contrast, the physical properties of macromolecules such as plastics are determined mainly by the relative stereochemistry of adjacent locations in a polymer chain.



Stereoselective synthesis. A key goal in fine chemical synthesis is the stereoselective addition of A-B to one face of a substrate. The stereoselective enchainment of multiple monomers follows similar principles (**top**). However, polymerization requires controlling the stereoconfiguration of the sequence of monomer units in the polymer (**bottom**).

Despite these differences, similar synthetic strategies have evolved in the two areas. Chiral coordination compounds have been developed that activate substrates and control the stereochemistry of key bond-forming steps. The work of Knowles, Kagan, Sharpless, and Noyori (*1*) was complemented by that of Brintzinger, Ewen, and Kaminsky, who showed that chiral C_2-symmetric metallocenes were effective catalysts for the stereoselective conversion of propylene to highly isotactic polypropylene, an important commercial thermoplastic (*2*). In an isotactic polymer, all substituted carbons have the same stereoconfiguration (see the first figure).

Strategies for controlling the stereoselectivity of polymerization reactions thus have much in common with stereoselective transformations of small molecules. But polymerization catalysis presents challenges not normally encountered in small molecule synthesis. For example, how can one control the relative configurations in a sequence of stereocenters?

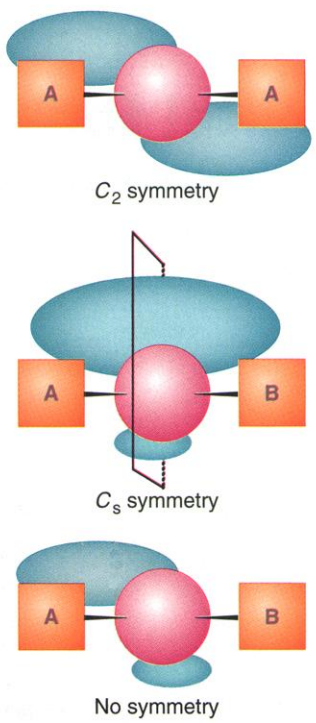
Ewen, Razavi, and co-workers have developed a clever method for doing so (*3*). They have synthesized syndiotactic polypropylene (an architecture in which the configuration alternates at every stereocenter) with a catalyst that changes its stereoselectivity with each insertion event. The C_s-symmetric catalyst has two coordination sites related by a mirror plane of symmetry (see the second figure). The alternating insertion of the monomer at one site and then the other leads to a sequence of alternating stereocenters of opposite configuration (*2*).

This example illustrates the role of catalyst symmetry in stereoselectivity. Many coordination compounds contain two (or more) coordination sites that can bind and activate substrates or monomers. In C_2-symmetric complexes, these coordination sites are rendered equivalent by symmetry (see the second figure). To some extent, the fact that most catalyst to date have C_2 symmetry is a testament to our inability to control the locus of the key bond-forming reactions in coordination compounds with multiple sites. For polymerization catalysis, the presence of multiple coordination sites presents opportunities to perform different reactions at these sites, leading to new and interesting polymer architectures.

One can imagine an almost infinite series of architectures in which sequences of differing stereochemical configurations are strung together in unusual combinations—all with different physical properties. Our ability to control both the stereoselectivity of single insertion events and the sequence of stereoselective events at the same time remains rather limited, but several strategies are beginning to emerge.

One strategy uses catalysts containing two coordination sites where one of the sites is stereoselective and the other is nonstereoselective (*4*, *5*). Insertion of the monomer at these two sites in a rigorously alternate fashion creates an unusual architecture: Every other stereocenter has the same configuration and every other is stereorandom. A series of insertions at one site, followed by a series at the other site, generates a stereoblock structure of isotactic and atactic (stereorandom) sequences. Polypropylene stereoblock materials exhibit interesting elastomeric properties (*2*, *4*, *5*).

Another approach to controlling the sequence of stereoselective events uses conformationally dynamic catalysts that change their coordination geometry, and thus their stereoselectivity, with time (*6*, *7*). For example, unbridged metallocenes containing 2-arylindene ligands can access chiral and achiral coordination geometries and have been shown to generate stereoblock polypropylenes with elastomeric properties (*6*).



Symmetry of coordination complexes. In a catalyst with C_2 symmetry, coordination sites A are identical. In a catalyst with C_s symmetry, coordination site A is related to B by a mirror plane. In a catalyst without symmetry, the two sites are different.

Copolymerization of two or more different monomer types presents further challenges because the catalyst must select different monomer units in defined sequences and insert them stereoselectively into the polymer chain. The alternating, stereospecific polymerization of olefins and carbon monoxide yields a stereoregular and chiral polymer that can be made as a single enantiomer (*8*). Related efforts with ethylene/olefin copolymers have led to interesting new stereoregular copolymers (*9*).

The challenges of stereoselective copolymerization can also be met by drawing on ideas from small molecule catalysis, where kinetic resolution can generate chiral products by selectively transforming chiral substrates from a mixture (*10*). On

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the basis of this concept, Coates and coworkers have devised catalysts that can select different sequences of lactide (a cyclic dimer of lactic acid) stereoisomers to create a variety of regular structures, including R-S-R-S (syndiotactic), R-R-S-S-R-R (disyndiotactic), and R-R-R-R-S-S-S-S (stereoblock) (*11*). This novel strategy enables the creation of new architectures from chiral monomers.

The control of stereochemistry and the controlled introduction of functional groups are of paramount importance for the synthesis of pharmaceutical and agrochemical intermediates. Combining these properties in one catalyst remains one of the central challenges in polymerization catalysis. Olefin polymerization catalysts have high stereoselectivities but are notoriously intolerant of functional groups. Recent advances in generating catalysts with higher functional group tolerance have been made with late transition metals (*12*). These catalysts activate olefins in polar and in some cases aqueous media, but few are also highly stereoselective. Promising examples of catalysts that combine stereoselectivity with high functional group tolerance include chiral catalysts for stereoselective metathesis reactions (*13*, *14*), stereoselective palladium catalysts for the synthesis of stereoregular, chiral polyketones (*8*), and stereoselective zirconium and lanthanide catalysts for acrylate polymerizations (*15*).

The control of polymer chain length is also critical in polymer synthesis. Major advances have been made in the development of living polymerization strategies (so called because the catalyst or polymerization initiator remains active at the end of the growing polymer chain). These strategies permit control of the molecular weight and molecular weight distributions and allow for the synthesis of block copolymers. Few systems are both living and stereoselective (*16*, *17*), however, and simultaneous control of molecular weight and relative stereochemistry remains an important goal in polymerization catalysis.

The pace of development in stereoselective catalysis for both fine chemical and polymer synthesis has been breathtaking, but formidable challenges remain. For the next generation of synthetic macromolecules with ever more closely defined properties and functions to become a reality, stereoselective and living cationic or radical polymerization schemes must be developed, highly functionalized olefin copolymers must be synthesized, and new polymer architectures must incorporate defined sequences of monomer units, functional groups, and stereocenters.

References and Notes

1. The 2001 Nobel Prize in Chemistry was awarded to Knowles, Sharpless, and Noyori for their contributions to stereoselective catalysis (see www.nobel.se/chemistry/laureates/2001/).
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PERSPECTIVES: ECOLOGY

Beta Diversity in Tropical Forests

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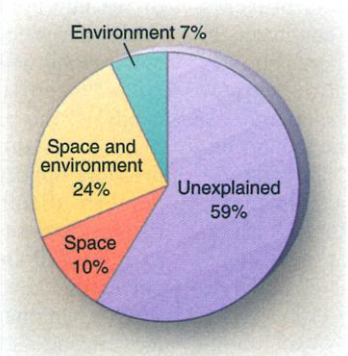
The tropics support more than 200,000 species of flowering plants including many tree species (*1*). Yet even between different geographical areas, species composition may vary dramatically. For the tropical forests of Africa, Asia, and the Americas greater than 10^6 km^2 in size, overall or gamma diversity varies from perhaps 30,000 to 120,000 species of flowering plants (*2*). It is well established that smaller forest plots ranging from 0.001 to 0.01 km^2 in area contain from 30 to 300 tree species (alpha diversity) (*3*). Less information is available for beta diversity, which describes how species composition varies from one area to another. On page 666 of this issue, Condit *et al.* (*4*) present a new analysis of beta diversity in which they compare the species composition of forest plots that are located at distances of 10^{-1} to 10^3 km apart in the neotropics of Panama (southern Mesoamerica) and in Ecuador and Peru (western Amazon).

Condit *et al.* explore how similarity in tree species composition from plot to plot declines as the distance between the plots increases. Regions in Panama and the western Amazon that are 10^4 km^2 in area support 3500 to 5000 tree and shrub species (*5*). Yet at smaller scales (10^{-2} km^2), the western Amazonian forests support 2 to 10 times as many species as do the Panamanian forests (*6*). It is possible to obtain rough values for beta diversity from the quotient of gamma and alpha diversity. This method predicts a relatively low beta diversity for the western Amazon, which Condit *et al.* confirm. However, this prediction is not in line with earlier views of strong beta diversity in western Amazonian forests (*6*). The higher beta diversity in Panama presumably reflects greater spatial variation in geology and climate and a lag in forest recovery after the marked temporal variations in climate during the last glacial cycle.

The investigators (*4*) compared their observations to predictions derived from a neutral model that takes into account dispersal capacity but ignores environmental and historical events controlling species distribution. Their data compare well with the neutral model at intermediate distances (0.2 to 50 km) between plots, underscoring the potential importance of dispersal as a key process in the structuring of tropical forest diversity (*7*). At smaller distances, they observed much greater similarity in species composition



Tropical forest diversity. Variance in tree species similarity among plots in Panamanian tropical forests. Distance and environment explain minor portions of the variation in species similarity. The bulk of the variation remains unexplained.

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