the growth of marram grass *Ammophila arenaria*, which is followed in sequence by fescue *Festuca rubra* and sand sedge *Carex arenaria*, with sea couch *Elymus athericus* at the landward edge of the dune. But what causes the marram grass to become prone to invasion by the fescue, and the fescue by the sand sedge? Traditional explanations have included resource depletion, alteration of the physical environment, accumulation of metabolic toxins and the action of species-specific herbivores[7]. Van der Putten *et al.* now suggest that the breakdown of inhibition may be caused by soil-borne plant diseases.

The idea that soil-borne pathogens play a role in plant succession is not new. This is what Clements[2] was writing in 1928: "Parasitic fungi. . . restrict or prevent [establishment] either by the destruction of invaders or by placing them at a disadvantage with respect to the occupants" (page 78). "The most usual effect [of pathogens] is a decrease in number or dominance by which the species assumes a less important role. In the majority of cases no direct influence is discoverable, the effect being merged in the general outcome of competition" (page 91). What is exciting about the present study is the elegant test of the issues involved.

Van der Putten and colleagues carried out an ingenious series of reciprocal transplant experiments using sterilized and unsterilized dune sand. Two-week-old seedlings, raised from local seed, were planted into replicated series of pots containing sand collected from beneath each of the main dominant plant species; the sand in half of the pots was sterilized by gamma irradiation. They discovered that biomass production of each plant species was reduced by the soil-borne diseases of its successors but not by the diseases of its predecessors. This implies that soil-borne diseases affect both the rate and the direction of succession of foredune plant species.

If species-specific plant pathogens were the only mechanisms operating to break the inhibition imposed by dominant species, then the possibility of cyclical successions would arise. Suppose that species A is replaced by B, and B by C, but that by the time that C has attained dominance, the pathogens of A have died out, so that C can be invaded and replaced by A. The fact that we do not find marram grass invading lawns of sand sedge demonstrates that plant pathogens are only part of the story in sand-dune succession. The competitive ability of marram derives largely from its ability to withstand burial by sand, and in more stable soil conditions this competitive edge is lost so that marram could not re-invade, even if sufficient time had passed for its pathogens to have disappeared. There is also an important element of facilitation in the dune succession because, in the absence of soil stabilization by the marram grass, the community could not be invaded by the other plant species. Thus, if the pathogens of marram grass were too effective, there wouldn't be any sand dunes for the other species to inhabit.

It remains to be seen how often species-specific soil pathogens are responsible for breaking the competitive stranglehold of early successional dominants. Long-term field tests involving pathogen exclusion using fungicides would be illuminating, although it is not clear how the effects of excluding pathogens and mutualist mycorrhizal species could be teased apart. Pathogens are most likely to be important in successions driven by inhibition rather than by facilitation, and in systems exhibiting strong dominance rather than in species-rich seral stages.

More generally, the hope is that rather than simply adding yet another element to the long and growing list of complex and interacting factors, this study may help to reinforce the message that competitive ability is not a species-specific trait; it depends on the other species and on the circumstances (both biotic and abiotic) under which the struggle for existence is taking place. There is always more than one thing happening in succession, yet we may find that the variety of community dynamics reflects correlations among a small subset of ubiquitous mechanisms. ☐

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1. Van der Putten, W. H., Van Dijk, C. & Peters, B. A. M. *Nature* **362**, 53–56 (1993).
2. Clements, F. E. *Plant Succession and Indicators* (H. W. Wilson, New York, 1928).
3. Gleason, H. A. *Bull. Torrey bot. Club* **53**, 7–26 (1926).
4. Connell, J. & Slatyer, R. *Am. Nat.* **111**, 1119 (1977).
5. Noble, I. R. & Slatyer, R. O. *Vegetatio* **43**, 5–21 (1980).
6. Gray, A. J., Crawley, M. J. & Edwards, P. J. *Colonization, Succession and Stability* (Blackwell, Oxford, 1987).
7. Tilman, D. *Resource Competition and Community Structure* (Princeton University Press, 1982).

ORGANIC CHEMISTRY

Polymer science branches out

Philip Hodge

AFTER years of seeking, for the most part, to synthesize polymers in the form of simple long linear chains, polymer scientists are turning their attention to more elaborate topologies. Dendritic polymers, or 'dendrimers'[1], are one novel type that has attracted a great deal of attention in recent years. Formally speaking, dendrimers are the result of several chains growing from a core molecule. As the chains become longer and further removed from the core they branch regularly and frequently so that the ever-increasing volume that is available is filled by an ever-increasing number of growing chains. Ideally all the chains grow equally and the final product is a close-packed molecular ball with many surface end groups. Hawker and Fréchet[2] at Cornell University have developed a new approach to dendrimer synthesis which not only makes the dendrimers more accessible and more defect free, but which also allows blocks of copolymers to be assembled in one dendrimer.

One reason for the interest in dendrimers is that their architecture is so different from that of the traditional linear step-growth polymer. An ideal molecule of the latter type is one long chain with only two end groups. If the polymer has a substantial molecular weight, the end groups and their functionality, if any, are usually of little importance. The linear chains will usually exist in solution as flexible loose random coils. In contrast, the dendrimer has many short chains, a very high degree of branching and many chain ends (typically hundreds). In solution, it forms a tightly packed ball. The end groups at its surface are the main feature a dendrimer presents to other molecules.

Dendritic polymers were first described by Tomalia[3] and co-workers in

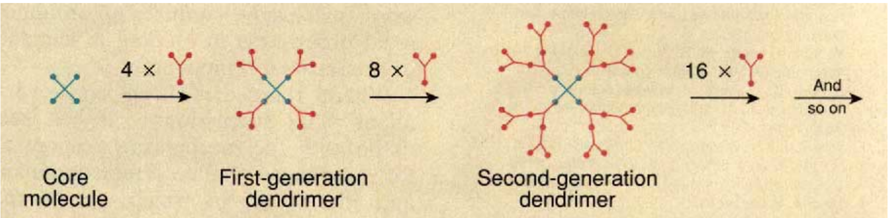

FIG. 1 The 'divergent' synthetic approach — building up a dendrimer from the inside out to create a 'starburst'. The blobs indicate the site of activity (actual or potential), or the site of a linking reaction.

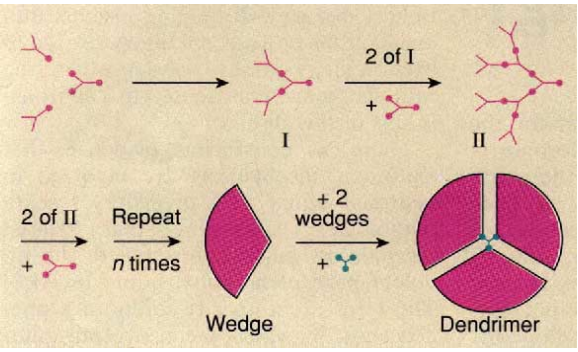

FIG. 2 'Convergent' synthetic approach — assembling a dendrimer in segments. The monomer units that will make up the outer layer have only one site where links can be formed, so the successive steps of the synthesis build up a segment from the outside in. Finally, the 'wedges' are linked at their apices to a core molecule.

1986. They used a divergent synthetic approach: starting at the core and working outwards. The basic idea, which has since been developed and widely exploited, is shown schematically in Fig. 1. It starts with a multifunctional core molecule: in this illustration the core has four functionalities. These are then reacted with four monomer molecules, each of which has two functionalities which will allow further monomer molecules to become attached, so giving the first-generation dendrimer. The process is then repeated for several generations.

In reality, the linking process is more complex than this and 'blocking groups' must be used to control which groups react at each stage. The cycle of reactions leading to each generation of dendrimers is completed as a series of practical steps before the next cycle of reactions is commenced. The total number of monomer molecules added soon becomes very large: after five generations the dendrimer contains more than a hundred monomer units, which would be a respectable number for many linear polymer chains. Using this divergent synthetic approach it is possible to prepare up to ten-generation dendrimers with molecular weights of up to 700,000 and with more than 3,000 end groups per molecule. But there are snags. For example, the conversion of one generation into another may not be complete, and it is difficult to detect whether this is so. If it is incomplete, separation of the resulting mixture of dendrimers is virtually impossible.

Instead, Hawker and Fréchet have synthesized dendrimers using a convergent approach. Here the synthesis starts at what will eventually become the periphery of the dendrimer and progresses inwards. Successive reaction cycles ('blocking groups' are also needed here) generate a 'wedge' with a reactive group at the apex (Fig. 2). The last step of the synthesis is to attach several wedges, by means of their apical functionality, to a multifunctional core molecule.

This novel synthetic approach has several advantages, not the least being the ease of purification at each step. Because each step involves adding two large units to a smaller bifunctional unit, the desired product has a molecular weight very different from those of the units from which it is constructed. It is thus relatively easy to purify the desired product. The efficiency of the reactions is also easily monitored spectroscopically at each stage. These features help greatly to minimize the occurrence of 'defects' in the final structure.

An example of the power of the convergent approach is the synthesis of segment-block dendritic copolymers (Fig. 3). These are obtained simply by attaching different wedges to the same core molecule. Clearly the chemistry of the latter has to be such that the number of wedges added at each stage is controlled, but this is not difficult. Using this approach Hawker and Fréchet have synthesized a segment-block dendrimer with a molecular weight, M_n, of 5,364 which has one ether-linked segment and two ester-linked segments.

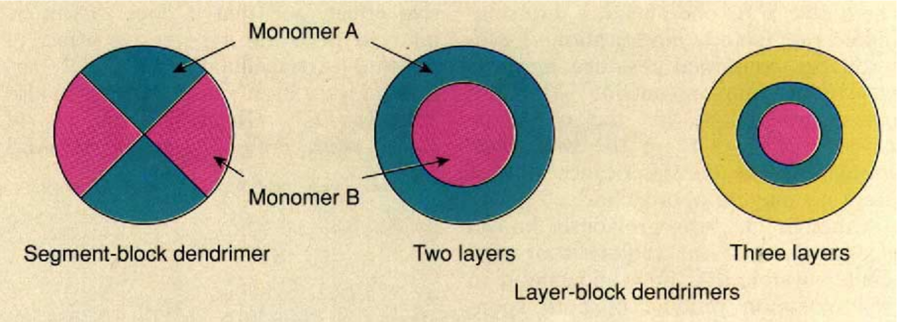

FIG. 3 Dendrimers synthesized by the convergent approach can be made up of blocks of different monomers.

The copolymers can be made to lie in concentric spheres rather than adjoining segments. Hawker and Fréchet's example is the synthesis of a layer-block dendritic copolymer with a molecular weight, M_n, of 10,242. The inner two layers were ester-linked and the outer three ether-linked. In such layer-block dendrimers, the chain length of each block may be very small but the layer is a whole shell. In conventional linear polymers, the chain lengths of blocks are long but they have no 'width'.

Interest in dendritic polymers will continue because the degree of structural control available is much higher than with linear polymers. Especially attractive features are monomer sequence control in copolymers and molecular weight control.

What possible applications are there for dendrimers? One possibility is a drug delivery system. This might be a layer-block dendrimer with surface groups that make the polymer water-compatible, ester linkages to make it biodegradable, and inner layers built of appropriate amounts of drug so that when the polymer degrades a uniform supply of the drug is delivered.

Segment-block dendrimers might find uses in enzyme reaction studies. Micelles, which are loose spherical arrangements of amphiphilic molecules with the lipophilic groups inside and the hydrophilic groups outside, have long been used in such studies. A molecule generally slips in between the lipophilic groups with the active part in the hydrophilic region. The hydrophilic head groups contain chemically reactive sites. In future, dendrimers might be prepared in such a way that small molecules could creep into clefts between segments. The system could be more highly organized, have better recognition and be more permanent than micelles.

Novel materials might be obtained by close-packing dendrimers, then cross-linking them through surface functionality. And if the ins and outs of dendrimers begin to lose their novelty, other topologically fascinating polymers abound. Interest is now growing in other types such as rotaxanes (where a large cyclic compound is strung like a bead on a polymer chain), cyclic polymers, and catenanes (two cyclic polymers linked like a true chain). Polymer science, like the dendrimers themselves, is branching out in all directions. ☐

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1. Tomalia, D. A., Naylor, A. M. & Goddard, W. A. III *Angew. Chem. Int. Edn Engl.* **29**, 138–175 (1990).
2. Hawker, C. J. & Fréchet, J. M. J. *J. Am. chem. Soc.* **114**, 8405–8413 (1992).
3. Tomalia, D. A. *et al. Macromolecules* **19**, 2466 (1986).