Branching Out into New Polymer Markets

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One dependable route to the development of a novel, commercially important polymeric material, a substance that will grasp the attention of industrial scientists, is to use commercially available monomers to produce distinctive new materials. Incremental changes in the properties of old materials can sometimes extend commercial markets, but dramatic changes in properties can open up whole new markets. This has now been done by Fréchet and co-workers, who, on page 1080 of this issue, describe a fascinating new concept for making use of readily available monomers to synthesize inexpensive new polymeric materials (*1*). The process by which they do this is branching, or manipulating the topology of the polymer chain.

Branching exerts tremendous influence on material properties. The chemical, physical, mechanical, and rheological properties of a material correlate closely with the nature, degree, and distribution of chain branching. For example, polyethylene (PE), one of the most commonly used bulk polymers because of its excellent balance of cost and performance characteristics, can be used in widely different applications when chain branching is varied in degree and kind (Fig. 1). Completely linear PE, also known as high-density polyethylene (HDPE), has a crystalline melting point of 135°C and is used for applications where structural integrity is of utmost importance, such as crates and pallets, bottles, toys, and housewares. A slightly branched version of PE, commonly referred to as low-density polyethylene (LDPE), has a melting temperature of 115°C and is used in applications where low-temperature toughness and flexibility is important, such as pipe and packaging applications. Very recently, an amorphous PE was developed (*2*) that is so highly branched that it cannot crystallize and, as such, makes possible a number of heretofore unimaginable applications for PEs, such as very low temperature elastomers and damping materials. All of the above are PEs but their applications are diversified as a result of their disparate performance characteristics.

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Recently a new class of branched polymers, called dendrimers, has emerged (*3–8*). Dendrimers are highly branched polymers, sometimes of precisely defined structure, that emanate from a central core. Dendritic materials have captured the imaginations of many scientists far afield from polymer science. This interest, primarily due to the globular, three-dimensional structure of these materials, has allowed dendrimers to be considered for use in applications ranging from drug delivery to nanoscopic building blocks for the design of new materials. Although there have been numerous advances in potential specialty applications for dendrimers, the process required to produce them has involved the use of tedious, solvent-intensive, multistep syntheses and reagents that are expensive relative to common vinyl monomers such as ethylene and styrene. As a result, the future of dendrimers to significantly impact commodity applications has been bleak. However, this gloomy, short-sighted perspective for the use of dendrimers in commodity applications has always tainted the dendrimer field as a whole, which is the easiest of critiques one can level at a new field and the hardest to defend. This negative view also reflects the type of sentiment that is commonly used to fuel today's fervor for "downsizing" long-term, basic science research programs across the country. And to those of you who had a research program in dendritic materials and pulled the plug on it because of the emerging view of the high costs associated with conventional methodologies to synthesize dendrimers, it is time to brush the dust off the old laboratory notebooks because Fréchet's approach should make dendrimers much more accessible and attractive.

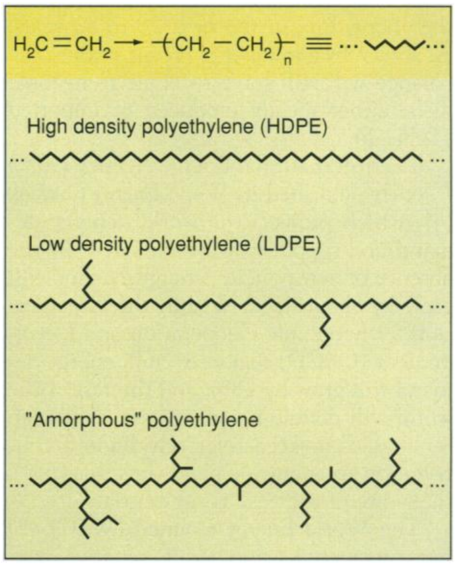

Fig. 1. Polyethylene with different degrees of branching. Ethylene chains are represented as in the top of the figure. Linear or high-density PE has no branching. Slight branching gives low-density PE, whereas amorphous PE is characterized by extensive branching.

The "self-condensing" vinyl polymerization method introduced herein by Fréchet and his co-workers appears to offer a readily implementable paradigm for making dendritic materials from commercially available

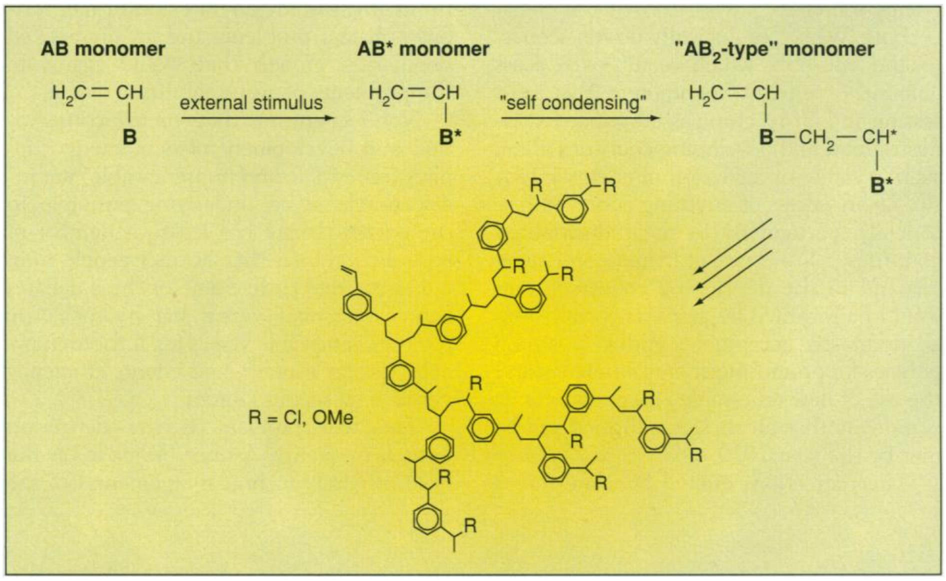

Fig. 2. Self-condensation route of Fréchet *et al.* (*1*). An AB vinyl monomer is activated by an external stimulus to generate an AB* monomer that is capable of "self-condensing" to form an AB_2-type monomer, which is further capable of "self-condensing" to generate a dendritic macromolecule.

vinyl monomers and their derivatives. In hindsight, the concept outlined by Fréchet is relatively simple. In principle, this new polymerization method is quite versatile as it should be compatible with the wide range of chemistries associated with vinyl monomer polymerizations, although this first report (1) is focused on cationic processes. The method involves the activation of an AB vinyl monomer by an external stimulus, which in this case involved the addition of a Lewis acid to the monomer, which generates a B* moiety that is capable of initiating the polymerization of a vinyl monomer (Fig. 2). The self-condensing then begins with the addition of the B* moiety across the double bond of another AB* monomer unit to afford a dimer that contains one conventional propagating center and one B* center capable of further initiation. At this stage, this dimer now contains two active centers possessing essentially equivalent reactivities and one double bond. As such, this AB monomer has now been transformed into an AB_2-type monomer, which is known to give rise to hyperbranched "dendritic" polymers. Subsequent condensations lead to highly branched polymeric materials with high molecular weights through simple vinyl additions.

Considering the universality of self-condensing vinyl polymerizations, it will not be long before we see a plethora of new materials based on this innovative achievement. It should not be too difficult to extrapolate to such new materials as dendritic perfluoropolymers, liquid crystalline polymers based on simple vinyl monomers (9), thermoplastic elastomers, and perhaps even a new version of PE.

The challenges that now remain include the extension of this work to mechanisms other than propagating carbocations, such as radicals; the use of light and thermal energy as external stimuli; the development of synthetic methodologies for the creation of new "self-condensing" monomers from other readily available monomers; and the creative combination of "self-condensing" monomers with conventional monomers to generate unique materials with significantly new properties.

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Snowshoe Hare Populations: Squeezed from Below and Above

Nils Christian Stenseth

All ecologists favor long-term studies and in this respect differ from chemists, physicists, most other biologists, and all politicians. But, like other scientists, ecologists prefer to do experimental work. ... We must combine these two approaches to solve the major ecological questions (1, p. 3).

The cyclical population density of the Canadian snowshoe hare (*Lepus americanus*), with high densitites occurring every 9 to 11 years, is a classic example of the multiannual cycles in many vertebrate populations of the boreal zone (2–4). Although the cycles in the hare population are cited in almost all introductory biology texts, their cause has been obscure. Food, predators, disease, and sunspots have all been put forward as essential, but there has been no agreement as to which factors best explain the cycles. Now, Krebs and his co-workers, on pages 1112 to 1115 of this issue (5), report a technically unique and important experiment indicating that the hare population cycle results from a food-hare-predator interaction.

The new results show that the effects of food and predation on population density are nonadditive. Food augmentation and exclusion of mammalian predators separately caused about a twofold increase in the abundance of individual hares, whereas combined addition of food and reduction of predation increased the population density by a factor of 10. Krebs and co-workers therefore argue that neither plant-herbivore nor predator-prey interactions are by themselves sufficient for cycling. Although this notion is consistent with the earlier suggestion of Keith (4) that the periodic fluctuations in the hare population are due to a dynamic interaction between predators and food shortage during winter, the new results do not necessarily support Keith's proposed sequential two-level interaction that assumes food shortage to be temporarily followed by predation.

The validity of the proposed three-trophic-level hypothesis may be tested independently by examining long-term monitoring data of snowshoe hare populations (6). If a three-level interaction is truly responsible for generating and maintaining the observed dynamics, the relevant time series should exhibit dimension (7) three or higher. Indeed, the structure of the hare time series is consistent with dimension three (8) and is therefore consistent with the proposed three-level hypothesis. In theory, a three-dimensional structure in the time series could also arise because of several other three-factorial explanations; however, the extraordinary consistency between the experimental and the time-series data greatly strengthens the plant-hare-predator hypothesis. This consistency is emphasized by the facts that (i) the experimental and the time series data are independent sources of information; (ii) by combining these two data sources, insights derived from experimental manipulation can reinforce insights from statistical analyses of observed patterns; and (iii) the new experimental results allow a biological interpretation of the estimated dimensional structure of the time series.

Indeed, this synthesis is an example of the integrated, dual approach to ecology advocated by Krebs in 1991 (1). I agree with Krebs (1, p. 3) that "monitoring of populations is politically attractive but ecologically banal unless it is coupled with experimental work to understand the mechanisms behind system changes." Further, the utility of experimentally deduced mechanisms, like the new work of Krebs *et al.* (5), is greatly enhanced if these mechanisms can be shown, as I have attempted above, to generate the patterns they are supposed to explain.

Many Northern microtines—lemmings and voles—also exhibit periodic fluctuations in their population densities (10). The estimated dimension of the time series for small rodents is typically two (11), suggesting that the microtine cycle may be caused by fewer processes than are involved in the snowshoe hare cycle. Krebs favors a structurally simpler hypothesis—the so-called Chitty hypothesis (12)—for the microtine cycle, consistent with the estimated lower dimensionality of the microtine time series. This hypothesis assumes that some population-intrinsic factor by itself causes the density cycle. But much experimental and theoretical evidence suggests that the Chitty hypothesis cannot explain the cycle (10, pp. 70–73); extrinsic factors also seem essential (10, 13). Perhaps

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