Fullerene Polymers from Solid Precursors?

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One of the many speculations that quickly followed on the heels of the Krätschmer-Huffman process for producing large quantities of C_{60} "buckminsterfullerene" was the possibility of stitching the molecules together to create a linear chain polymer, a "pearl necklace" of buckyballs (Fig. 1A). In addition to being chemically elegant and intrinsically beautiful, such a material might be expected to exhibit interesting electronic and nonlinear optical properties. Traditional solution-phase routes to fullerene polymerization have thus far resulted only in mixtures of incompletely characterized species with a high degree of cross-linking. In this issue, the report by Iwasa *et al.* (*1*) reinforces two previous results that suggest that this goal might be achieved by starting from a fullerene solid precursor.

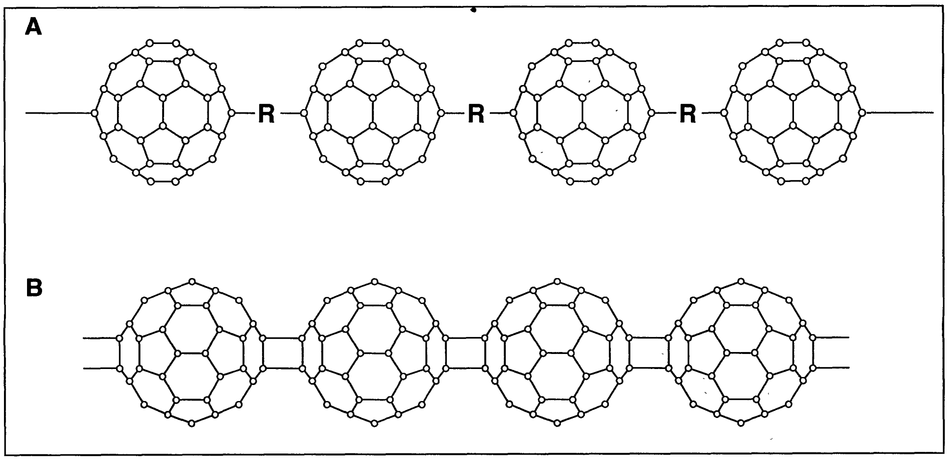

Fig. 1. Hypothetical fullerene polymers. Solution reactions of C_{60} and another molecule might produce something like the upper structure in (**A**), which shows an adduct R bridging adjacent fullerenes in a cyclopropane bonding configuration (R bridges a hexagon, with hexagon fusion on each molecule). All carbon chains obtained by [2 + 2] cycloaddition (**B**) may be implicated in the three experiments described here.

The first, a photo-induced polymerization, was reported in these pages last year (*2*). Laser irradiation of thin C_{60} films yielded a toluene-insoluble product in which the icosahedral symmetry characteristic of the C_{60} molecule was strongly perturbed. The proposed mechanism, [2 + 2] cycloaddition by the conversion of double bonds on adjacent molecules to a four-membered ring (Fig. 1B), would be forbidden for the ground state of neutral C_{60} by the usual rules of organic reactions. Oligomers as large as $(C_{60})_{20}$ were observed in laser desorption mass spectrometry. [The irradiation of thin films with low-energy electron beams induces a similar effect (*3*).] The precursor for the second example (*4–6*) is the high-temperature cubic phase of the intercalation compound RbC_{60} (*7, 8*). The cooling of this material below 400 K results in an orthorhombic distortion (that is, a compression of the cubic lattice along one of the <110> directions), a shortest interfullerene distance of 9.12 Å (compared to 10.04 Å in solid C_{60}), a perturbed molecular symmetry, and a conduction electron spin resonance signature reminiscent of quasi–one-dimensional organic metals. Finally, the treatment of solid C_{60} at 500° to 800°C and a hydrostatic pressure of 5 GPa followed by a return to ambient conditions leads to a toluene-insoluble rhombohedral phase (that is, a distortion along <111>) with a 9.22 Å intermolecular spacing and spectroscopic signatures of molecular symmetry reduction (*1*).

In all three examples, the prima facie evidence for polymerization is the decreased interfullerene distance, suggestive of chemical bonding, and the concomitant lowering of the molecular symmetry. All three precursor solids are orientationally disordered. Disorder is clearly a prerequisite for polymer formation in the laser irradiation process; double bonds on adjacent molecules must come into alignment for cycloaddition to occur, and the probability of having double bonds on adjacent molecules in an eclipsed configuration is vanishingly small in the ordered state (below 260 K for pure C_{60} at atmospheric pressure). All three processes require some input to overcome a reaction barrier: the photo-induced population of a singlet excited state followed by rapid intersystem crossing to the triplet (*2*), compression close to the limit of molecular integrity (*1*), or transferred charge leading to new orbitals that no longer violate the usual rules (*6*). In the Iwasa experiment, the molecules are brought closer together by direct (presumably hydrostatic) pressure, while orientational disorder is maintained by working at elevated temperature (*9*). In the RbC_{60} case, the precursor cubic phase is orientationally disordered with an extra pseudo-π electron per molecule. There is also some compression; the lattice constant is considerably smaller than that of C_{60} because the Rb^+ ions are confined to the large octahedral sites and the Coulomb attraction between Rb^+ and C_{60}^- acts as an "internal" pressure (*7*). All three processes lead to toluene-insoluble metastable structures that revert to C_{60} (or to cubic RbC_{60}) at 200° to 300°C.

Although none of these results would be considered definitive by polymer scientists, they are certainly suggestive. Many questions remain. How does a cubic system pick out a specific direction along which to nucleate the growth of a linear polymer? Nothing is known about the structure or morphology of photo-polymerized C_{60}. The rhombohedral distortion in the high-pressure experiment is the most sensible way to reduce the free volume from the cubic precursor. On the other hand, because the chain direction in Fig. 1B is a twofold axis of rotation, infinite chains of this sort cannot exist in a rhombohedral lattice. The low-temperature orthorhombic distortion of RbC_{60} does not suffer this problem, but there is no obvious driving force for it to occur. In all three cases it is difficult to rationalize a free energy of formation $F = U - TS + PV$. The internal energy U of the putative polymer would be reduced relative to the cubic precursors by the formation of intermolecular bonds but would be increased by distortions of some of the carbons away from their C_{60} positions (*10*). The PV term would be reduced as well. The volume per C_{60} in RbC_{60} decreases from 689 Å^3 in the cubic phase at 200°C to 657 Å^3 in the orthorhombic structure at 21°C; a better comparison in the Iwasa ex-

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periment is between normal and rhombohedral pressure-temperature–quenched C_{60} at ambient conditions, 709 Å^3 and 603 Å^3, respectively. These effects would be partially offset by the reduced (negative) contribution from the entropy term TS associated with the onset of orientational order. Calorimetry experiments on RbC_{60} show small reversible heats of transition that are more likely associated with first-order orientational ordering transitions than with bond formation or large volume changes (*7*). A calculation of $(C_{60})_2$ dimers (*11*) shows no carbon distortions and an 8.5 Å center-to-center distance, equal to the undistorted C_{60} skeleton diameter (about 7 Å) plus a C–C single bond length, considerably smaller than the observed values. Also in the RbC_{60} case, polymer formation on cooling from 150°C competes with phase separation into C_{60} and R_3C_{60}; in the potassium analog, slow cooling leads to phase separation, whereas quenching produces a similar metastable orthorhombic structure but with a larger minimum inter-ball distance 9.61 Å (*12*). There is ample motivation to tackle these issues; particularly intriguing is the possibility that the mono-anion polymer is metallic while the mono-anion cubic van der Waals solid is not.

It is also probably true that we have not heard the last from practitioners of the more traditional polymerization reactions. The ever-growing list of mono-functionalized fullerenes will certainly present opportunities for rational polymer synthesis using solution techniques. In the best of all possible worlds we will end up with two families of fullerene polymers: the all-carbon versions described here and those originally envisioned with heteroatom linkages between molecules.

References and Notes

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9. Y. Iwasa *et al.* also found a new cubic phase with "normal" inter-ball distances by quenching from 5 GPa at a lower temperature, 300°C, and 5 GPa. The pressure dependence of the C_{60} ordering temperature [G. A. Samara *et al.*, *Phys. Rev. B* **47**, 4756 (1993)] indicates that at 300°C the molecules are orientationally ordered while 800°C is sufficient to induce orientational melting at 5 GPa. This finding is consistent with high-pressure polymerization at the higher, but not at the lower, temperature.
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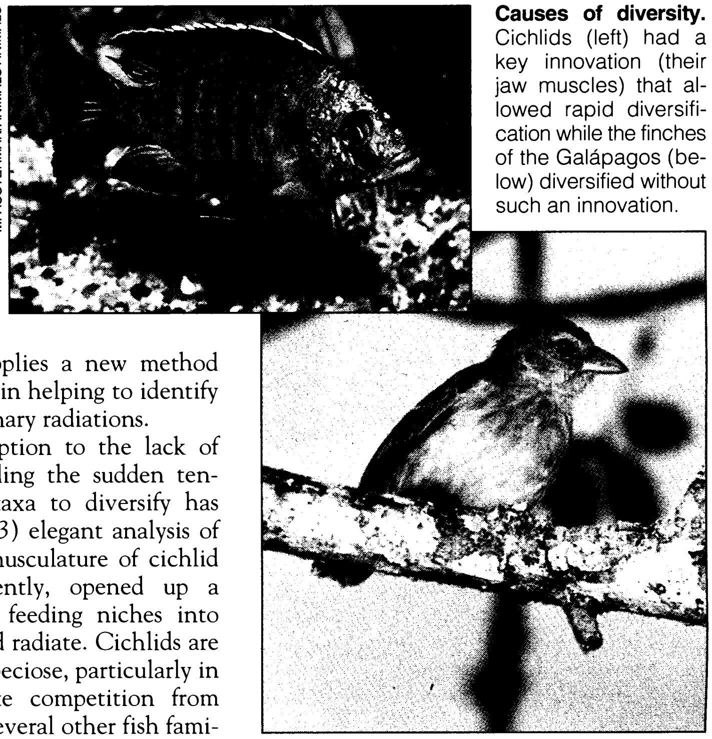
13. I acknowledge useful discussions with B. Harris, M. Kertesz, S. Pekker, P. Stephens, K. Subbaswamy, and O. Zhou.

Getting to the Roots of Flowering Plant Diversity

Sean Nee and Paul H. Harvey

The fossil record tells us that speciation and extinction rates have, on occasion, changed dramatically. Much has been written recently about possible causes of mass extinctions, particularly the one at the close of the Cretaceous period, which has been claimed to be associated with the impact of a sizable asteroid and the loss of humankind's beloved dinosaurs. Rather less attention has been paid to the reasons for suddenly increased rates of diversification in particular lineages. A paper by Sanderson and Donoghue in this week's *Science* (*1*) applies a new method that may prove useful in helping to identify the causes of evolutionary radiations.

One notable exception to the lack of success in understanding the sudden tendency of particular taxa to diversify has been Karl Liem's (*2, 3*) elegant analysis of changes in the jaw musculature of cichlid fishes which, apparently, opened up a whole new range of feeding niches into which the group could radiate. Cichlids are now extraordinarily speciose, particularly in African lakes, despite competition from species belonging to several other fish families. The change in jaw musculature in cichlids may therefore have been a so-called key innovation. Such key innovations are not prerequisites for adaptive radiations. For example, there was not necessarily anything special about the species of finch that originally invaded the Galápagos Islands and led to the radiation known as Darwin's finches (*4*). Notwithstanding the occasional importance of such vicariance events or changes in the environment that may turn a mundane character into a key innovation, it is natural to seek traits associated with the origin of a radiation. The first step in such an analysis is to pinpoint the origin of the radiation as accurately as possible. One reason is that the number of candidates for the key innovation can be minimized if the number of differences between a radiating taxon and its nonradiating relatives can be reduced. Because closest relatives generally share the greatest number of characters, the comparison should be made between the closest relatives possible. Sanderson and Donoghue provide a powerful and elegant procedure for achieving that end.



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Causes of diversity. Cichlids (left) had a key innovation (their jaw muscles) that allowed rapid diversification while the finches of the Galápagos (below) diversified without such an innovation.

The aim is to identify nodes in a phylogenetic tree from which one daughter lineage shows higher rates of branching than the other. The source material, then, is the number of descendent clades arising from each daughter branch of a node. Even if two clades do not differ in features promoting diversification, large inequalities in clade size can arise by chance, prompting one to ask whether observed differences are statistically anomalous with reference to a particular null model. Sanderson and Donoghue are, in essence, asking two questions. First, are the angiosperms significantly more diverse than their sister group the Gnetales? Second, is there a significant difference in diversity between the two most basal angiosperm clades? A positive answer to both questions, which is what they obtain, implies that some angiosperms acquired features or inhabited environments

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