

## WHAT, IF ANYTHING, CAN CHEMISTRY OFFER TO FRACTURE MECHANICS?

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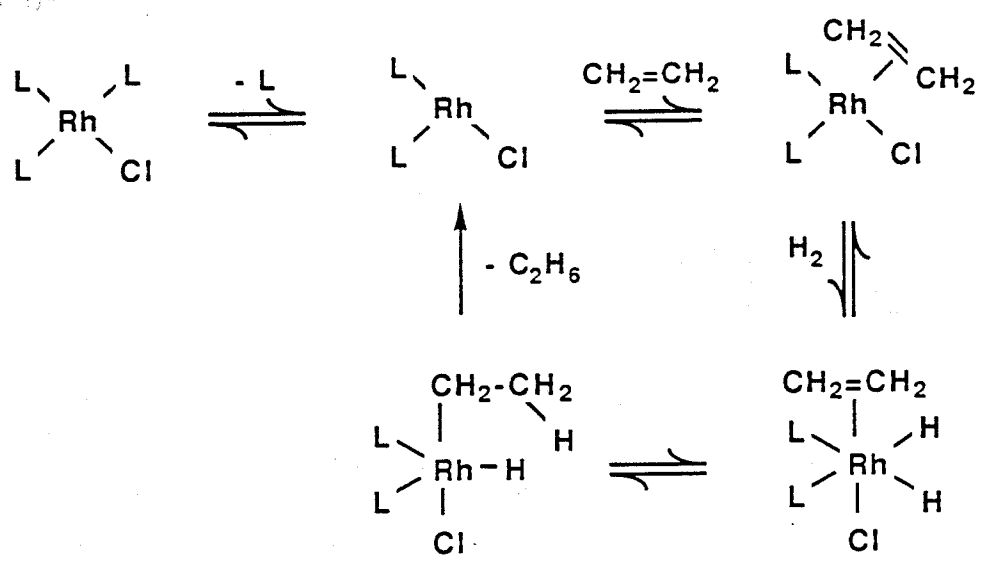
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Chemistry is primarily concerned with the structures and properties of bonds between atoms and with relating these bonds and their properties to the structure, reactivity, and other properties of molecules. The principle concerns of chemistry have thus been individual molecules and molecular reactivity. Attention is now slowly turning to the structure, reactivity, and properties of solids: that is, to collections of molecules and to very large molecules. Why slowly? Certainly not because the problems in the solid state, or more broadly in materials science, are unimportant. The objectives of rationalizing properties such as tensile modulus, fracture strength, corrosion resistance, electrical conductivity using atomic-level structural information, dielectric constant, and thermal conductivity are clearly simultaneously immensely interesting scientifically and important technologically.<sup>1,2</sup> They are also, unfortunately, very difficult to attain. Moreover, the difficulty often is of an annoying sort--that is, it is associated with defects. The properties of large, regular ensembles of atoms and bonds can often be calculated with a high degree of precision using standard techniques of statistical mechanics.<sup>3</sup> What cannot be readily calculated is the often critical influence of unknown impurities or defects of unknown composition and structure on the properties of interest. In general, only average or highly perfect structure is available. Even in cases where impurities are intentionally introduced (as in the doping of semiconductors), the measured properties of the final material represent an average of the constituent structures. Detailed structural information concerning defects is only now becoming available.<sup>4</sup>

Fracture represents a particular problem for chemists. The calculation of tensile modulus of a single crystal is a tractable problem, given sufficient information about structure and single-bond properties. The calculation of the stress at which failure occurs in a real brittle solid is not. Fracture is fundamentally a kinetic problem and is intimately associated with rates of crack initiation, crack stopping, loading, and energy dissipation. The thermodynamics of fracture--that is, the energy required to create the new fracture surfaces--is one limiting useful quantity, but not, in general, of high predictive value. Understanding the relation of defects in real solids to the ultimate materials properties of these solids at the level of individual bond properties is a challenge of large magnitude.

By way of example, Scheme I shows a sketch of a chemical process that is very much simpler than fracture, but at the outer limit of what is presently considered a practical level of complexity by individuals concerned with detailed rationalization of reactivity in terms of bond making and bond breaking processes. This scheme outlines a homogeneous catalytic cycle: that of the hydrogenation of ethylene by hydrogen using a rhodium-based catalyst.<sup>5,6,7</sup> In some distant way, this catalytic process and fracture of a rhodium single crystal share a number of common features. Both involve the creation of vacant coordination sites on rhodium (in the

805\*



Scheme I. Schematic mechanism for hydrogenation of ethylene by dihydrogen catalyzed by soluble rhodium(I) complex:  
 L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P.

case of fracture, by cleaving rhodium-rhodium bonds; in the case of the catalytic cycle, by dissociation of a phosphine ligand L from the rhodium center). Both involve "reconstruction" around the rhodium following the bond breaking: that is, the immediate environment of the atoms remaining bonded to the rhodium shifts to minimize the free energy of the system. Both involve adsorption of new molecular species onto the vacant site on rhodium (in the case of fracture, dioxygen and water from air; in the case of catalytic hydrogenation, ethylene and hydrogen). In both various transformations subsequently occur that involve these adsorbed species. For the hydrogen reaction, all of these transformations are critical to the overall functioning of the catalytic system. For fracture, it is unclear how many of these reactions (if any) are critical to the question of the stress under which the crystal fractures or yields. In the case of fracture, we acknowledge that we have very little idea of the relative rates, reversibility, or energetics of individual steps in the process leading to the breaking of individual rhodium-rhodium bonds, and less idea whether this process--as opposed, say, to failure in adhesion between rhodium and an embedded particle or breakage of a surface film--is the step that ultimately determines whether fracture occurs under given circumstances. We also stand little chance of modelling effectively catastrophic fracture in a single crystal using a homogeneous organometallic system since no organometallic compounds are known that undergo multiple (i.e. 10-10<sup>3</sup>) sequential metal-metal bond scissions.

In contrast, in the catalytic reaction, we believe that we have a very good idea of what happens and know in fair detail which steps determine the overall catalytic throughput in the system. The details of our understanding of the catalytic system are unimportant for this discussion, but from these details, and related details drawn from a large number of other studies,<sup>8</sup> it is possible to draw several cautionary inferences about conclusions from atomic-level investigations of catalysis. These cautionary inferences can certainly be extended to the more complex process of fracture as well.

1) *Any intermediate that can be observed is irrelevant.* This inference is semi-facetious, but it has a hidden grain of truth. That is, any species that can be detected in this type of catalytic cycle is probably present in sufficiently high concentration and is sufficiently stable and long-lived that it does not represent the highly reactive species that determine the course of catalysis. The same generalization may hold for many materials systems having properties dominated by defects. Often only the small, hard-to-detect anomalies in structures are the ones that truly determine the systems properties; the more easily accessible average or theoretical structure represents only a limiting value and is not directly helpful in determining real properties.

2) *Entropy may be as important as enthalpy.* The correctness of this statement for a system involving dissociation of ligands (as in the catalytic cycle in Scheme I) is self-evident, but the fact remains that a great deal of theory in catalysis is still focused on enthalpic considerations and ignores entropic ones.<sup>9</sup> The reason for this disregard of entropy is, of course, that it is much more difficult to calculate the entropy of a process than it is to calculate the enthalpy. In certain systems, disregard of entropy is probably permissible; in others, particularly where solvents or solvent effects are involved or where association or dissociation is important, entropy may dominate. Particularly for considerations of fracture in organic solids, entropy may prove to be as important as it is in catalysis.

3) *New catalysts are developed empirically.* Despite a long and highly successful (from an academic point of view) effort to understand and rationalize catalysis,<sup>10</sup> new catalysts are usually developed by trial and error: that is, by preparing new, thermodynamically stable compositions of matter and passing reactive mixtures of substances over these catalysts to detect reactions that depend upon the catalytic substances.<sup>11</sup> Theoretical considerations and mechanistic understanding has proved highly valuable in catalysis in *incremental* improvement of existing systems; it has not proved useful in inventing new ones. In an analogous sense, mechanisms and theory may be highly useful in rationalizing and incrementally improving the properties of some materials systems, but probably will not lead to new ones in the immediate future.

4) *Mechanisms are based on or inferred from studies of kinetics.* In complex systems, it is difficult enough to rationalize the energetics of starting materials and products based on their structures, much less to infer structures and energies of intermediates lying between starting materials and products, and even less the structures of transition states connecting these intermediates.<sup>12</sup> Although obtaining information concerning a complete reaction coordinate for a process is always difficult, it is also necessary to have a real understanding of the process. The word "process" implies a kinetic phenomenon: that is, the transformation of the system from one state to another during a time that is significant to the observer. It is not possible to rationalize a process without understanding the rate of the process, and thus the details of the structures and energetics of the intermediates lying between starting materials and products. Fracture is, of course, a process, and must ultimately be approached in the same way, if it is to be explained in full atomic detail.

A problem that occurs repeatedly in trying to apply chemical considerations based on bonding to the consideration of processes as complicated as the fracture of organic solids is that of the proper size of the domain that must be considered in discussing the critical phenomena

underlying the process of interest. A certain amount of success has been achieved in attempting to model the surface of heterogeneous catalysis using soluble organometallic clusters.<sup>13</sup> The fraction of an organic solid involves considerably more complexity. A covalent organic solid is a collection of a very large number of individual, directed, covalent bonds (for example, for diamond,  $\sim 2 \times 10^{23}$  bonds/cm<sup>3</sup>); and fracture involves a small fraction of these bonds, but still a large number of them (at least  $10^{14}$ /cm<sup>2</sup>). A molecule involves a much smaller number of bonds ( $10-10^4$ ) of which only 1-5 might break or form in a typical reaction. Simply on the basis of the number of bonds involved, fracture represents a much more difficult problem. In trying to understand fracture, chemists must first begin to address the problem of the quantity of the solid--that is, the number of bonds and atoms--that must be considered in atomic detail to prove or disprove any hypothesis concerning correlations between atomic and macroscopic structure. Is fracture initiated by the failure of a single bond? By concerted failure of 100 bonds? By failure of all of the bonds in a region of  $10^3$  nm<sup>2</sup>? *How large is the problem?* And what are the characteristics of the region to be examined (whatever its size)? And how are these characteristics to be identified? The interior of a perfect single crystal? The region surrounding a crack tip? A representative region in an oxide-covered surface? The region including a critical void or microscopic embedded particle? Since fracture is often dominated by defects, the anomalies in structure are often the most important features of the system. These anomalies are also, of course, the most difficult features to detect and characterize, and thus to discuss in chemical detail.

Given the severe problems in making plausible connections between atomic level information in solids (at any level of theory or experiment) and macroscopic materials properties of that solid, what can chemistry realistically be expected to offer to fracture and materials science? In fact, should chemistry be expected to be an active participant in this area at all? In broad terms, the answer to the latter question is certainly "yes." Organic solids (particularly polymers) are the most rapidly evolving of the important classes of structural materials. Composites often contain organic components, and critical auxiliary components in materials (adhesion promoters, barrier film forming agents, corrosion inhibitors) are often molecular entities. Moreover, chemistry has and will continue to make important contributions to a number of areas of materials science entirely apart from organic solids: organometallic precursors for sol-gel-derived ceramics<sup>14</sup> and pre-ceramic precursors<sup>15</sup> for ceramics provide examples.

In more specific terms, we suggest a number of areas in which current events in chemistry offer analytical techniques, synthetic procedures, or conceptual insights of real relevance to fracture:

1) *Control of interfaces and thin films.* Fracture is a process that creates new interfaces; initiation of fracture often occurs at interfaces. Understanding the influence of environmental effects on the energetics of interfaces, and the kinetics of their creation, is a subject of real opportunity for chemistry.<sup>16</sup> The characterization and control of surface films as passivating systems, or as weak or strong components<sup>17</sup> in a system are also, in principle, under synthetic control. Adhesion promoters and compatibilizing agents for many heterogeneous systems can be designed using chemical techniques.<sup>18,19</sup>

2) *Analytical methods.* One of the areas of most rapid advance in chemistry and physics has been the development of new analytical techniques applicable to the study of materials at the microscopic scale. The range

of vacuum physics spectroscopies<sup>21</sup>--X-ray photoelectron spectroscopy, Auger spectroscopy, secondary ion mass spectroscopy, Rutherford backscattering spectroscopy,<sup>22</sup> and many others--make it possible for the first time to characterize in useful detail many materials systems. Transmission electron microscopy can now image single atoms in many circumstances.<sup>23</sup> New techniques, especially scanning tunneling microscopy<sup>24</sup> and force balance methods,<sup>25,26</sup> offer an unprecedented degree of detail concerning structure and potential functions for surfaces.

The large majority of the new instrumental techniques are most easily applicable to surfaces or thin films. Many important materials properties originate, of course, in some part of the system other than the surface. There are slowly emerging new techniques for examining structure in a microscopic scale deeper in a solid. Most of these techniques are based on the availability of high intensity X-ray sources. EXAFS,<sup>27</sup> low-angle X-ray reflectography,<sup>28,29</sup> and X-ray tomography<sup>30</sup> all provide examples. In certain types of systems, techniques such as nuclear magnetic resonance spectroscopy can also be applied to examining the interior structure of solids,<sup>31</sup> as can certain of the newer acoustical methods.

An important problem in the area of analytical methodology remains, however, the imaging of the interior structure of solids. Techniques such as single-fiber pullout<sup>32</sup> (based on optical dichroism of poorly understood origin) are primitive but provide one of the few available windows into the changes accompanying strain in the interior of solids.

3) *New materials and structures.* Chemistry continues to provide techniques of unparalleled utility and flexibility for the preparation of many new types of materials, especially those based on organic or organometallic precursors. Polymer alloys and phase-separated systems provide one outstanding example;<sup>33</sup> high-strength polymer fibers<sup>34,35</sup> based on liquid crystals provide a second. The expertise is available in chemistry to make almost any conceivable structure; the guidance needed to use this synthetic expertise efficiently is not.

4) *Control of impurity and defects; new processing techniques.* It goes without saying that chemistry is an essential element in materials processing. Detailed studies increasingly suggest that the strength of many high-performance fibers (for example, PAN-based carbon fibers or poly"dimethylsilane"-silicon carbide fibers) is dominated by impurities in the polymer<sup>36</sup>: gel or dust particles being particularly important. Thus, the preparation of highly uniform systems, and the processing of these systems to give defect-free structures is an area in which chemistry and chemical engineering can play an important role.

5) *Conceptual models.* The value of even simple chemical theory in understanding local properties of materials is clear.<sup>37</sup> Organometallic chemistry offers an enormous range of possible structures for metal-containing systems, and thoughtful examination of these illustrations provides at worst a highly developed intuition concerning structural types that appear to be energetically favored. More complex theory offers greater detail, but typically at the cost of examining a smaller system.

One of the major problems in theory is, in fact, to find the best strategies for integrating the many different types that are presently available, ranging from *ab initio* theory for very small isolated systems at the one extreme through semi-empirical and molecular mechanics calculations, thorough statistical methods, to finite element calculations. How does one transfer results from each level of detail to the next highest level of systems integration? What features are essential to be transferred correctly, and which can be neglected?

Given the problems faced in connecting (or even recognizing!) relations between microscopic structure and macroscopic properties, it is perhaps no wonder that the most important advances in chemistry as applied to materials have come on the one hand from strongly physical methods for analysis or theory that provide static structural detail concerning solids, and on the other hand from largely empirical synthetic or preparative activity that has provided new solids to be examined for useful properties. The connection between these analytical/theoretical methods and the synthetic methods has been extremely limited.

We suggest that an alternative, hybrid approach--the so-called "physical-organic" approach--is just beginning to be applied usefully in materials science. This approach integrates synthesis and physical measurements: hypotheses concerning the relation between structure and properties are tested by synthesizing new structures, rather than by taking advantage of higher precision and greater detail in physical measurement. This method is particularly useful when applied to organic or organometallic materials, where it is possible to achieve very high variability in structure with relatively modest synthetic effort. The physical-organic approach is fundamentally science by analogy: it does not generate quantities of numbers in a form satisfying to those who are trained in the physics paradigm. It has, however, proved highly successful in solving complex problems in chemistry and biology, especially concerning the kinetics of organic reactions, catalytic mechanisms, and rational drug design.<sup>38</sup> We illustrate this approach with a project in progress in our own laboratory.

The objective of this work is to prepare new organic solids having particularly high thermal stability, resistance to chemical corrosion, hardness, and thermal conductivity. The basis for this project is a qualitative consideration of the extraordinary breadth of properties displayed by organic solids containing only carbon and hydrogen (Figure 1).

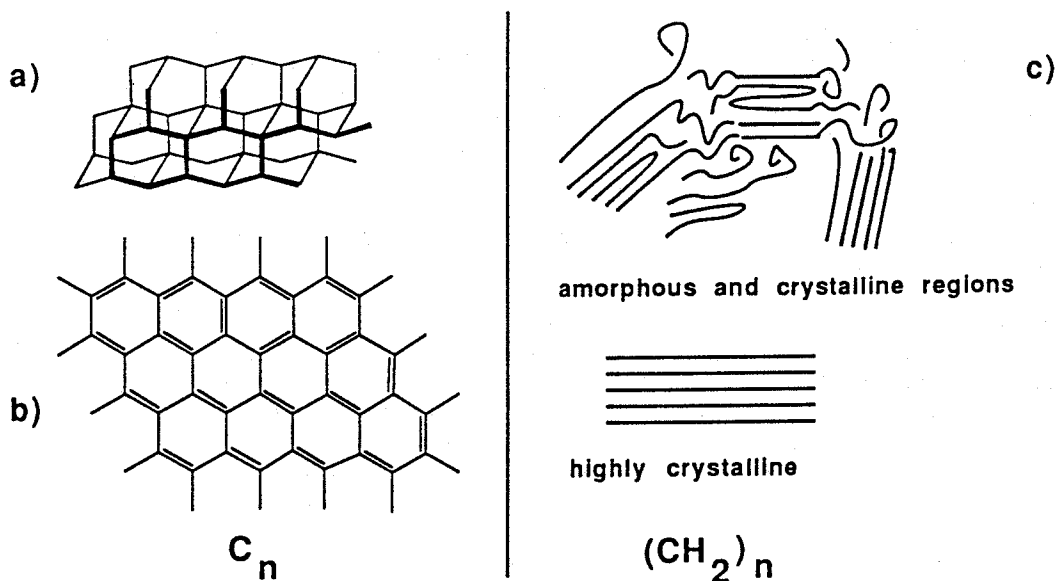


Figure 1. Organic solids containing only carbon and hydrogen: (a) diamond; (b) graphite; and (c) schematic representation of an organic polymer such as polyethylene showing amorphous and crystalline regions.

At one extreme is diamond. Diamond is both the hardest known solid and the best thermal conductor at room temperature. It is an electrical insulator and can be optically transparent. It contains a very high density of directed, strong,  $sp^3$  carbon-carbon bonds. It is brittle in fracture. Graphite represents a second extreme. It has very high tensile modulus in the graphitic plane, and very low modulus perpendicular to it. It is sufficiently slippery to be used as a lubricant. It is an excellent electrical conductor, and a black solid. Polyethylene and related compounds represent a third example. This class of polymers are typically waxy solids with a density of  $\sim 1.5 \text{ g/cm}^3$  (as compared with  $2.3 \text{ g/cm}^3$  for graphite and  $3.5 \text{ g/cm}^3$  for diamond). They are soft, insulating (both thermally and electrically) materials that can be processed readily.<sup>39</sup> They are typically semi-transparent. Their structures consist of a mixture of amorphous and crystalline regions, and physical properties depend strongly on the relative proportions of these regions and on the orientation of the crystalline regions. Typical polyethylene film has low tensile strength. Ultra-drawn polyethylene has very high tensile strength.

The concept that aligned, covalent bonds form the basis for structurally useful solids has, of course, been heavily exploited in making the current generation of engineering plastics.<sup>40</sup> Figure 2 gives examples.

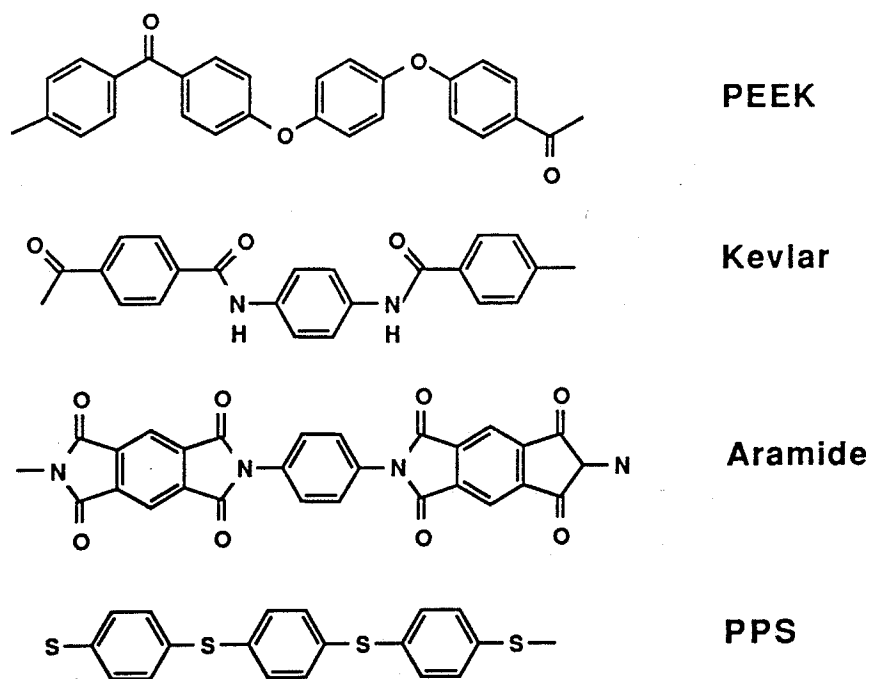


Figure 2. Examples of current generation of engineering plastics.

The qualitative physical-organic basis for this class of polymers is straightforward. All consist of highly stable, aromatic units joined in a relatively rigid form by strong covalent bonds. The examples shown represent a small number of those currently being developed; the major distinctions between them have less to do with ultimate physical properties than with economics and processability. This class of polymers has, as a group, three disadvantages. The first is that almost all are very difficult to process. The second is that most are formed in the liquid

crystalline state, in order to obtain maximum tensile strength along the axis of the aligned, extended polymeric chains. Since interchain interactions are weak, they are typically weak perpendicular to the direction of preferred orientation, and fibers prepared from these materials tend to fail in compression. This perpendicular weakness is also reflected by limited resistance to damage by organic solvents. Finally, the ceiling operating temperatures of these materials (~350 °C) will probably not be sufficient for many future needs.

We and others<sup>41</sup> have set out to explore the idea that introducing heavy cross-linking between chains may provide a way of preparing three-dimensional, highly cross-linked solids having high strength and good solvent resistance. Our approach (Figure 3) has been to prepare polymers

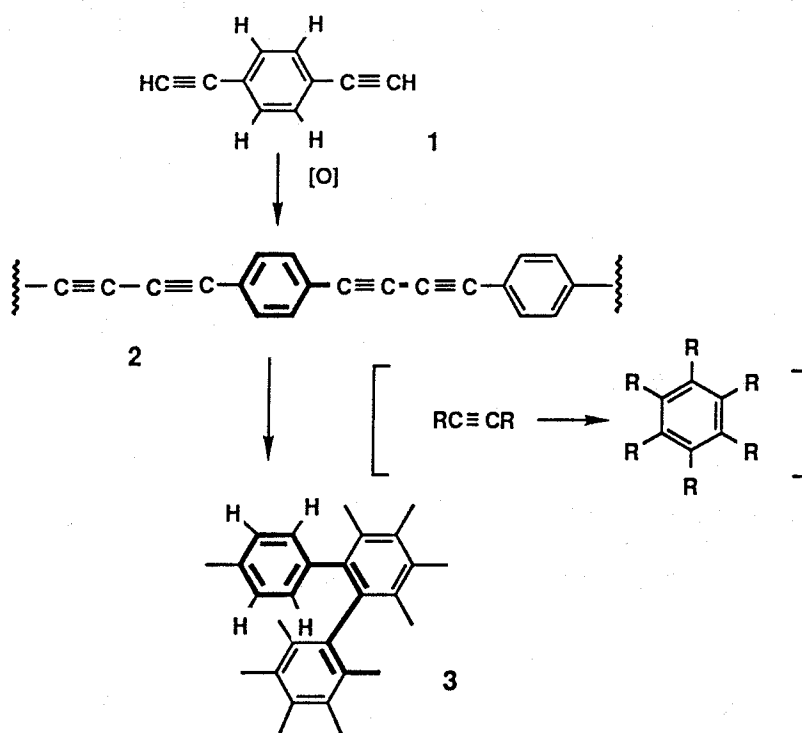


Figure 3. Synthesis of dense carbon solids from acetylenic precursors. Under appropriate processing conditions, the linking diacetylene units in 2 may be cyclotrimerized to yield highly cross-linked structures such as 3.

having a high density of diacetylene ( $\text{C}\equiv\text{C---C}\equiv\text{C}$ ) units. Properly formulated, these polymers can be processed, molded, and then cross-linked either catalytically or thermally. The resulting solids have, in fact, a high density of covalent bonds, and can be considered to be a type of glassy carbon. Preliminary results indicate that these solids are very stable thermally, very resistant to damage by solvents, and (for organic materials) very hard.



The detailed results of this project are less important than the approach. The project is based on reasoning by analogy, and has very little quantitative calculation involved. The process involves an examination of a group of interesting materials--diamond, graphite, and polyethylene--and the inference from these structures of structural features that may underly the desirable physical properties. These hypotheses are tested by synthesizing new solids incorporating as many of the structural features identified by examination of existing systems as possible.

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