Macromolecular Architecture for the 21st Century

Otto Vogl[a]

[a] Polytechnic University, Brooklyn, New York, USA

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OTTO VOGL

Polytechnic University
Six MetroTech Center, Brooklyn, New York 11201, USA

INTRODUCTION, EARLY DEVELOPMENTS, AND USE OF MATERIALS

The success of civilizations and technologies has always depended on the efficient use of the available materials.

In the early days of man, tens of thousands of years ago, *stone* in its various forms and shapes was the primary material of use. This period became known as the *Stone Age*. In its original form of naturally shaped pieces, stone was used for general purposes, food preparation and cooking, and for defense. Specialty stone was split and formed into flints, these sharp pieces were used for cutting, as knives, for spear heads, and as arrowheads for hunting.

Various *composite materials* were also used during this period: straw, bones, and bricks in their varied forms. Nature provides us with a variety of composite materials such as wood, bamboo, and shells.

We have witnessed the discovery of an excellently preserved Stone Age man, "Ötzi," revealing many facts of how man lived in the Alps thousand of years ago. Ötzi was recovered after 5000 years entombed in a glacier; he was essentially intact with hair skin, clothing, and hunting equipment.

The next important category of materials came later—the *metals*. Nobel metals were the first to be discovered and used because they occur in nature as metals. Artifacts of gold were the first metal objects known.

Copper was the first metal obtained from its derivatives and gave its name to the period that used copper as the main material of survival, hunting, and warfare. Over the years man learned that alloys of copper with tin, zinc, and other metals were superior to copper because of such properties as hardness, ease of working, durability, and beauty. Hence, the *Bronze Age* was born.

The ultimate metal used by mankind became iron. Working of iron required higher temperatures and longer heating for the liberation of the metal from its

oxides and carbonates. Ultimately the basic process of producing iron metal from iron ore was relatively simple and could be carried out in large smelting ovens. Iron ores are available in abundant quantities on earth and are easily mined. Consequently the metal iron as the prime material has dominated our way of life for the last 3000 years, and we say "We have been living in the *Iron Age*."

By the end of World War II, metals and their alloys almost entirely dominated the materials, particularly where the rate of development — the preparation of materials with new material properties — was concerned.

Some advances had also been made in the ceramic sector, although not much fundamental progress had been made in the preparation of cement and mortar. Although much is now known about tile technology, ceramic glazing, earthenware, and porcelain manufacture, for centuries only slow (but steady) progress had been made since the Middle Ages.

Over 150 years ago people started to pay attention to some naturally occurring materials and their modifications that were found to have useful and desirable material properties. Natural rubber, cellulose, and some natural fibers, such as wool and silk, caught the attention of a number of entrepreneurs and chemists.

It had been found that "organic" compounds could be made from "inorganic" salts based on a Wöhlers chemistry. Organic reactions, especially organic substitution reactions, could be carried out on natural materials, such as sulfur curing of rubber and the "nitration" of cellulose to nitrocellulose — *celluloid*. The first real polymer — baekelite — a phenol/formaldehyde resin, was discovered before the turn of the century. The basic structures of proteins as poly(α-amino acids) and of sugars and cellulose as polysaccharides were determined.

In 1920 the concept of macromolecules, linear giant molecules, whose individual units were connected by sigma bonds was proposed by Staudinger. Macromolecular behavior attempted to explain the problem of highly viscous solutions, and the behavior of colloids. At that time, what we now know as macromolecules were considered to be colloidal associates, in part because colloid chemistry was a very important part of physical chemistry.

The struggle between the followers of the macromolecular idea and the followers of the "associates idea" lasted for about 10 years, during which time more and more "associates" members abandoned this idea. It is ironic that the "associates" idea in a much more realistic form has reemerged in the idea of associations of "properly fitting" molecules and macromolecules, spawned by the phenomenal arrangement of perfectly fitting polymer "units" that can reassemble spontaneously only because of configurationally and conformationally fitting entities — the nonastructures. These are efficient assemblies on the (macro)molecular scale.

Staudinger had made the bold statement years ago that the peculiar phenomena that had been described in various ways could be best explained by assuming the existence of large molecules — both linear and crosslinked — macromolecules that consisted of thousands of "monomer" units connected with sigma bonds — not associates of small molecules.

RESOURCES AND DEVELOPMENTS

The rapid development of polymer science and polymer technology rapidly developed because of continued new, fundamental, and essential discoveries at a

crucial time and the efficient utilization of these discoveries and the materials available.

The rapid progress of polymer development was driven by continued progress in the chemistry of polymerization, which was achieved at the right time. Processes and fabrication techniques were perfected and markets for the desirable plastics products were opened. In the United States, thermoplastics alone has reached a volume of sales of over 30 million tons, and the United States market consists of about a quarter of the world market. The plastics market development depended on the invention of new polymers with new balances of properties. PVC and PMMA were developed in the late twenties and early thirties, polyethylene in the midthirties but were not fully commercialized until the early fifties. Polyurethanes and nylons were discovered in the late thirties; Teflon and useful polyesters appeared a little later. The point that I wish to make is that we have enjoyed commercially for 50 years a constant flow of new polymers, and new fabrication techniques that could form novel polymer materials with new properties and new technologies.

The worldwide production of plastics is about 150 million tons. Many of our present plastic materials are based on oil as the raw material. This most important raw material for plastics production, about 80% of the total, is derived from oil-cracking ethylene and 1,3-butadiene. When we consider that the annual harvest of oil is about 3 billion tons, the plastics use of oil is ~5%, another 5% is used for the production of chemicals, but 90% of oil is used as fuel and burned directly for energy production.

Plastics production and utilization have an important impact on the economy. It is estimated that, in the United States, about 200 billion dollars worth of merchandise is produced that can be directly related to polymers and plastic materials; 4% of the gross national product of the United States. This includes not only the production of the polymers themselves but also the production of plastics products, from the polyolefins and polystyrene for packaging materials to children's toys to skis, ski boots, and tennis rackets.

The world population is nearly 6 billion inhabitants and the world plastics production is about 150 million tons; the average use of plastic material would then be 25 kg per person per year. This is, of course, an average: Industrialized nations use about 100 kg per person per year and others less. The United States produces nearly 140 kg per person per year of plastics materials, Finland 110 kg/person/year. China's usage of plastics is growing rapidly and the present amount of plastics used is in excess of 5 kg/person/year. The projected growth of plastic production and use worldwide is directly related to the increase of the use of plastic materials in both industrialized *and* in Third World countries. The total weight of plastic materials could reach a level of between 400 to 600 million tons per year by the year of 2030—still only 20% of the present day oil production! While 20 years ago the worldwide estimate for oil reserves was 100 billion tons, today it might be 5 times that amount; only, oil is becoming more difficult and expensive to harvest.

Plastics production, as mentioned before, is about 150 million tons per year, worldwide. Over the years the production and use of metal materials has also increased. Nevertheless, plastics production passed the production of nonmetal materials (aluminum, copper and its alloys) in 1972. In 1978 the production of plastic materials passed the production of iron (ferric metals) in terms of volume. For space-filling utilization, plastic materials with sufficient strength are the materials

of choice; metals, with their much higher density, offer little competition. Iron and its alloys have densities 5–6 times that of our "commodity" plastics. Consequently, the weight of iron products is much higher than their plastics equivalents.

It is customary to think of renewable resources rather than oil for plastics production. Forty billion tons of carbon dioxide are converted annually by photosynthesis into the so-called biomass, primarily polysaccharides. This is 12 times the tonnage of the oil we are harvesting world-wide per year. Of these 40 billions of material produced by photosynthesis from carbon dioxide, about 8 billion tons is useful wood; the rest is ill-defined but recyclable "biomass." Our annual plastics production and use is less than 2% of the production of useful wood (about 7 billion) and only about 0.3% of the production of biomass per year.

Why do we use plastic materials rather than other materials like wood, metals, and ceramics? In most cases they are cheaper, easier to produce (especially to mass produce) and easier to shape into desired, unusual forms. The final objects are safer and — ultimately — easier to dispose of.

In our present world, plastic products have a most significant and essential impact in the *maintenance and improvement of human life*. They are used for *nutrition*, for *food production and storage*, for *health care and medicine*, for *transportation*, for *construction*, for *energy production and utilization*, and last but not least, for *leisure activities*. We could not imagine the high performance of the equipment that is now used in modern sport activities, from tennis to golf, from soccer to football and basketball, not to forget the winter sports like skiing, mountain climbing without the up-to-date high performance equipments based on the strength and light weight of plastics materials, the highly advanced composites in skis, tennis racquets, and golf clubs, the Teflon-covered nylon parkas, the polyurethane ski boots. Telecommunication and computers would not exist without specialty polymers.

We could not imagine health care as we know it today without the safe, sealed equipment of disposable syringes, sterile tubings, and containers. It would be impossible to have telecommunication without the plastics involved in their production and utilization. It would be difficult to build enormous building complexes without oligomeric and polymeric agents that control and facilitate the flow of concrete.

COMMODITY PLASTICS AND ADVANCED POLYMER MATERIALS

Several classifications of polymeric materials, or better, materials derived from macromolecules, have been in use for decades. For the purpose of this article I will divide the plastic materials into *commodity plastics* and *advanced polymer materials*. Commodity plastics usually include the "big four": polyethylene, polypropylene, poly(vinyl chloride) and polystyrene. The price of these materials is about $2.00 per kilogram and they are produced in about 20 million tons per year. Sometimes we divide the polyethylene into high density (linear) and low density (branched) polyethylene. Together with the acrylics and other vinyl polymers, they dominate the plastics market in terms of volume and constitute about 80% of the total plastics market. These commodity materials have dominated plastics production for the last 40 years. There has not been a large-scale polymer developed in the last 20 years, and we probably cannot expect any new large-scale polymer in the foreseeable future.

In addition to the traditional commodity plastics, in the 60s and early 70s a then new category of polymers was introduced that could compete directly with metals because of their easier fabrication techniques—that of plastic processing—*engineering plastics*. They have a somewhat higher combination of properties, higher use temperatures (above 150°C), and higher modulus. These engineering plastics included polyacetals, some nylons, some aromatic polyesters, polycarbonates, and in the higher range of properties (and price) polysulfones, polyetherketones, and polyetherimides. In all these cases matching of the major properties *or the major desired property*—at a tolerable price level—demonstrated even more than usual that the market and the application determines which material is used for the required application.

As property demands were sometimes relaxed for many applications, and properties could be sufficiently improved by reinforcing or blending with other plastic materials, the price requirements became dominant. Polypropylene is the classic example. Production of polypropylene has been growing rapidly over the last 20 years. It is now being produced at a level of nearly 25 million tons per year and is still growing at the present time at almost 10% per year. Polypropylene has properties that are sufficient for the basic requirements for engineering plastics and it also is cost efficient.

For many years propylene could not be polymerized to high molecular polymers. It was then found that it could be polymerized to a stereoregular so-called isotactic polymer, a polymer that crystallizes in a helical structure. Initially it had to be made in solution at about 10,000 parts of polymer per part of catalyst. Now we have learned to make the polymer in the liquid monomer propylene itself or in the gas phase. We have learned how to produce polypropylene as highly (nearly 100% specific) stereospecific or, if necessary, not very highly stereospecific polymers. We have learned to produce polypropylene at nearly 100 times the catalyst efficiency of 40 years ago and can now leave the catalyst in the polymer. The effort worldwide to optimize catalyst efficiency with regard to grams of polymer per gram of catalyst has achieved phenomenal proportions as has the control of molecular weight and molecular weight distribution, tacticity and tacticity distribution.

We can now make polypropylene with a controlled degree of stereoregularity—and stereoregularity with regard to the distribution of irregularity! We have learned to make syndiotactic polypropylene. This polymer has a considerably different combination of properties from the isotactic polymers (the repeat unit of the crystalline form is 4/1 as compared to 3/1 for the isotactic polypropylene).

We have learned how to make isotactic polypropylene (with third generation catalysts) directly in the bulk density that is desired and in the oval "pellet" form that is required to feed the polymer particles directly into the extruder for extrusion or injection molding. We have learned to make copolymers and alloys by these highly specific catalysts directly, and we have learned to some extent to influence and control the crystallization behavior of polypropylene.

NEW ASPECTS AND DIRECTIONS FOR THE FUTURE

A much smaller group, but a highly profitable group of advanced and high performance polymeric materials, are the functional and the specialty polymers. These are polymeric materials that fill specific functions of material properties. This

category is growing in importance, but the volume of these materials is relatively small as compared to that of commodity plastics. We call high performance polymers those that are produced in thousands of tons a year. The most important and most publicized of these categories are the polyimides. Beyond the polyimides are even more exciting materials of sophisticated polymers that are called smart polymers. We think that some of these polymers can act almost as living systems.

A long list of polymers falls into the category that are made by macromolecular architecture and design. Some of the characteristics include high performance, which might mean high stiffness and high durability.

While commodity plastics consist of 80% of the volume and have sufficient performance for most needs at affordable prices, they are produced from monomers that have been synthesized by optimal technical processes. A considerable amount of research and development effort is still attempting to achieve the production of the cheapest and purest monomer for polymerization. And then the polymers of the ultimate properties must be synthesized at the highest yield with the most desirable combination of properties and at the lowest cost.

As we touched upon, the production of a "polymer" by the most direct way is essential to produce a product that is sellable comparatively at the best profit. The use of blending and making alloys is an efficient modern way of utilizing commodity plastics for the production of maximum performance materials. To have a cost-effective polymeric material in use form we need to include not only the cost of the starting material and the final product but we also have to include the cost of installation and maintenance or disposal. As the cost of qualified labor goes up, the cost of installation and replacement as well as disposal also goes up. Sometimes we can afford a more expensive material if we do not have to replace it very often.

Production Efficiency

The requirement for the future of chemical and polymerization processes is clearly in the direction of *no stress on the environment*. This means that all future processes should be catalytic processes because we cannot afford any more undesirable waste products that might be produced by processes involving stoichiometric reactions. This accounts not only for chemical processes in the production of monomers but also for the production of polymers that might involve an inordinate amount of solvents or poisonous catalysts.

The present process to produce methyl methacrylate involves the hydrolysis of acetone cyanhydrine with sulfuric acid. This reaction produces one mole of ammonium sulfate tainted with cyanide ions. No technically successful substitute has been found in the last 40 years in spite of many tries. A recent patent suggested that we might have a possible catalytic example for a new synthesis of methyl methacrylate based on methyl acetylene. A catalytic reaction has been described that gives methyl methacrylate from methyl acetylene, carbon monoxide, and methanol in 95% yield using special platinum catalysts. Methyl acetylene is not synthesized from oil but from coal, and coal is much more plentiful as compared to oil.

New Polymer Structures

We normally think of polymers as linear polymers. We now can make block polymers, especially with systems of "living polymerizations," but also branched

polymers. Although branched polymers with short and long branches are best known for polyethylene, the most widely used approach to make branched polymers is by copolymerizations using macromonomers.

A completely new branch of polymer chemistry consists of highly branched polymers and dendrimers, nearly spherical structures rather than linear macromolecules. Highly branched polymers are made from monomers that have three functionalities, and two of these functionalities are the same. Dendrimers are more regular and are usually synthesized from segments that are ultimately put together to form spherical structures. In both of these cases we are speaking of "generations of spheres" rather than of degree of polymerization. Spherical "polymers" and highly branched polymers (or polymers with long branches) as compared to linear polymers have drastically different properties because the "entanglements" do not play the important role that has been known for a long time for strictly linear polymers.

Polymers with Ultimate Properties

Up to now we have been discussing linear polymers and polymers with a more spherical structure and have not mentioned polymer composites and network polymers. The classical traditional filled polymer networks are glass fiber reinforced polyesters and phenol and urea-formaldehyde resins.

With the availability of Kevlar and carbon fibers as reinforcing materials, new dimensions have been added for the preparation of composites. The primary matrices for advanced materials based on composites are primarily based on epoxies and, to a much smaller extent and only for higher performance requirements, on polyimides. The new plane introduced by the Boeing Corporation, the B777, has about 28% plastic material and plastic composites. The F16 fighter bomber has about 48%. The reason why we like to replace the metals aluminum and magnesium and replace them with plastic composites is to reduce the weight of the planes and, consequently, lower their fuel consumption.

Polymers for advance composites (beyond the properties that can be obtained by optimized epoxy chemistry) are oligomers with maleimide, benzocyclobutene, and acetylene end groups which are ultimately crosslinked when cured. The epoxies, as matrix materials, dominate the fiber-reinforced advanced materials market. The world capacity and use is about 500,000 tons of epoxies of various degrees of sophistication.

Very recently it was found that it is possible to synthesize giant cycles of organic compounds, particularly oligomeric polycarbonates, polyesters, and even polyetherimides. These giant cycles can be ring-opened to linear polymers of very high molecular weight. They can also be polymerized in the presence of carbon fibers (or other fibers used for advanced composites) to prepare composites with unusually high performance characteristics. The reason why such large macrocycles are desirable is because the density change between macrocycles and polymer is small, and consequently the shrinkage as a consequence of the polymerization is low. With low shrinkage, very little stress is introduced in these materials and maximum properties can be obtained.

Polyethylene as a major plastic has been with us for more than 40 years, and 40 million tons of polyethylene is being presently produced and used. Polyethylene has a linear *zigzag* crystal structure. It is one of the few polymers that has this kind

of structure conformation (most polymers have a helical conformation). Linear polyethylene has a degree of polymerization of about 10,000; ultrahigh molecular weight polyethylene about 100,000.

Super high molecular weight polyethylene has been used for two basic applications in its *extended chain form*. High modulus polyethylene fibers have been produced by gel spinning. Polyethylene can also be crystallized as extended (not the regular folded) chain polyethylene by pressure crystallization. This form of polyethylene has entirely different properties but must be fabricated by machining.

Fluorocarbon polymers have always occupied a special place in polymer science and for polymeric products. Because of their special characteristics *and* high costs they have limited utility, but when their properties, like oxidation resistance, resistance to degradation, and retention of colorlessness, are needed, they are irreplaceable. Recent needs for specific applications required amorphous transparent fluorocarbon polymers of high glass transition temperature. Vinylallylether and copolymers of tetrafluoroethylene and 2,2-di(trifluoromethyl) 4,5 difluorodioxolene seems to have given the answer. The requirements for such fluorocarbon polymers were apparently needed for optical applications.

NEW POLYMER STRUCTURES AND CONCEPTS

Liquid crystals and liquid crystalline polymers have occupied the imagination of scientists, since the first liquid crystalline polymer solution of poly(*p*-phenyleneterephthalamide) was recognized at DuPont in the mid-60s and the first liquid crystalline polymer melt was seen in a copolymer of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid.

Both types of polymers are liquid crystalline polymers whose liquid crystallinity is caused by the specific structure (a stiff segment of the "mesogenic unit of about 20–30 Å) of the polymer main chain. Liquid crystallinity can also be observed by a mesogenic structural element of the side chain. To have the useful properties of liquid crystalline polymers (main chain or side chain liquid crystallinity), it is usually necessary to introduce "disruptive groups" such as flexible spacers or structural irregularities to "break-up" the regularity of the mesogenic sequence. If the polymers are too regular and consequently stiff, the result is a nonfabricable "brickdust" polymer. As a consequence, a precise balance (ratio) between effective mesogenic groups and spacer and other irregularities is essential to achieve optimum properties; in the case of liquid crystalline polymers, this provides the widest liquid crystalline temperature range.

Spacer groups also play a very essential part in the effectiveness of the physiological activity of proteins and polysaccharides. The side chain lengths of the methylene groups in glutamic acid, asparagine, and arginine are carefully tailored by Nature. For example, to control the stability of the iron–oxygen complex in hemoglobin, they have four methylene groups in the prosthetic group, not two and not three! We know that we have to have three methylene groups for the polymerization of epoxides with terminal functional groups and four methylene groups for the polymerization of α-olefins with terminal functional groups.

Stabilization against the effect of photodegradation and photooxidative degradation plays an important part in our lives, especially in the outdoor environment.

For a long time we have been involved in the photostabilization of polymers, especially in the long-term photostabilization. For this purpose we have prepared polymerizable and polymer-bound UV stabilizers to avoid the loss of low molecular weight stabilizers that are used because of the ease of blending them into plastics materials.

More recently we have focused our interest on the design of stabilizing systems which are arranged by self-assembly on the surface of polymers, where the stabilization is most needed, namely by *morphology engineering*. The photostabilizer consists of the UV absorbing part of the molecule, a polymerizable group, and the "self-assembling" group, in our preferred case fluorocarbon side chains of 10-14 difluoromethylene side chains or silicon chains of corresponding chain lengths.

Another approach that we pursued with Rabek and Rånby was to place the polymerizable UV stabilizer where it is needed: on the surface. We achieved surface grafting by surface photografting which was done by using a photosensitizer for the UV grafting which had its UV absorption maximum at the wavelength where the polymerizable UV absorber had its UV absorption minimum. Grafting of polymerizable UV stabilizers onto several polyolefin surfaces was successfully demonstrated.

DISPOSAL OF PLASTIC MATERIALS

As we produce plastic materials, we also have to be concerned with the disposal of these plastic materials, either from an excess of production or from used and aged polymer materials. In the City of New York the plastic component of the municipal waste is about 8%.

Four possible ways of *disposing of plastic materials* have been proposed, with a combination of some of these techniques as a possibility in special cases. The first method, which is most frequently discussed, is *recycling*. Present evaluations indicate that recycling can only be used for 15-20% of the polymer materials, and only for special type of polymers. Highly aged and degraded polymers have lost most of their desirable properties and cannot be utilized. In the United States, disposal of plastic materials (together with other waste materials) by using *landfills* is done extensively, but can be done only as long as there is enough suitable room for this type of disposal. In Europe, disposal of plastics materials by *composting* is frequently proposed, and even used in some cases and some places.

The simplest way of disposing of used plastics materials is by *combustion*. This method also allows us to regain some of the materials value in the form of energy. In Japan, where land is very precious, most refuse, including plastic materials, is being burned. Even in the City of Vienna, Austria, the percentage of combustion of refuse has increased from 40 to 70% in 5 years. Such developments make one wonder if it would not be prudent to concentrate our research on plastics disposal on the design of highly efficient incinerators.

Disposal of waste material, including plastic materials, is a very emotional problem, and it is complicated to come to a uniform and most efficient solution for plastics disposal. There seem to be different approaches and possible solutions for the various materials, depending on the amounts and the locations. We must be continuously concerned, not only with the most efficient production but also for the disposal of plastic materials now and in the next century.