

Electrically conducting polymers: An emerging technology

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During the last two decades, electrically conducting polymers have evinced much interest. Known also as synthetic metals, these polymers combine the electrical properties of metals with the advantages of polymers. Some special characteristics of these polymers, strategies to design novel low band gap polymers, and the possible use of these exciting materials in various technological applications and devices in academic and industrial research laboratories are discussed here.

POLYMERS are a familiar part of everyday life and, because of the ability of chemists to tailor-make their properties, have found widespread applications. Until recently, these applications capitalized on advantageous properties such as chemical inertness, greater workability and durability. By contrast, the most valued electrical property of polymers was their capacity to inhibit conductivity, that is, act as insulators, and little work was done to examine and understand the fundamentals in order to enhance electrical conductivity in polymers. Beginning in the 1970s, a resurgence of effort occurred in the study of polymers as electronic materials. Known as electrically conducting polymers, they are attracting considerable research interest, both industrial and academic; not just because of their electronic conductivity and its theoretical applications for charge transport within organic systems, but also because their structural features give rise to additional properties of ion transport, redox behaviour, electrochemical effects, photoactivity, catalytic properties, and electronic junction effects, which are added to light weight, flexibility, non-metallic surface properties, and other polymeric physical properties. The potential for molecular engineering of the desired properties and the low cost of polymers have made them extremely attractive materials for electrically-conductive applications.

In the mid-1970s, considerable attention was directed towards the study of conducting polymers following the discovery of Shirakawa *et al.*¹ and Ito *et al.*², who found that polyacetylene (CH)_x could be prepared as film having a metallic lustre. In 1977 it was discovered³ that the conductivity of polyacetylene could be increased by 13 orders of magnitude by doping it with various donor or acceptor species. Polyacetylene (PA) is a simple conjugated organic polymer which occurs in *cis* and *trans* forms. Pure

cis- and *trans*-PA have room temperature conductivity values of 10⁻¹⁰ and 10⁻⁵ (ohm cm)⁻¹, respectively, which can be increased to 10³ (ohm cm)⁻¹ when a thin film of *cis*-PA is treated with an oxidizing agent such as iodine solution or a reducing agent such as a solution of sodium metal in mercury. The BASF A.G. in Germany has succeeded in preparing doped PA with a conductivity of about 147,000 (ohm cm)⁻¹. Japanese scientists have reported a conductivity of 9 × 10⁵ (ohm cm)⁻¹ for their samples of doped PA.

One of the drawbacks of PA is its instability in air⁴. This spawned efforts to uncover other polymers that exhibit similar properties. By 1979 many novel systems such as poly(*p*-phenylene) (PPP), poly(*p*-phenylene vinylene) (PPV), polypyrrole (PPY), polythiophene (PTP), polyfuran (PFU) and their derivatives were discovered. Structures of some of the conducting polymers are shown in Figure 1. None of these polymers has, however, reached the high conductivities of doped PA. It has also been found that while both, oxidation and reduction processes are possible for polyacetylene, and oxidation process is the one more easily achieved for heterocyclic polymers.

Conjugated polymers can be doped to a state of high electrical conductivity (to make electrically conducting polymers, the necessary condition being of conjugation, i.e. the alternation of single and double bonds along the polymer backbone). The unique electronic properties of conjugated polymers are derived from the presence of π -electrons, the wave functions of which are delocalized over long portions of the polymer chain, when the molecular structure of the backbone is planar. The essential properties of the delocalized π -electron system, which differentiate a typical conjugated polymer from a conventional polymer with σ -bond are as follows⁵:

- i) The electronic band gap E_g , is relatively small (~ 1.0 to 3.5 eV), leading to low energy electronic excitations and semiconductor behaviour.

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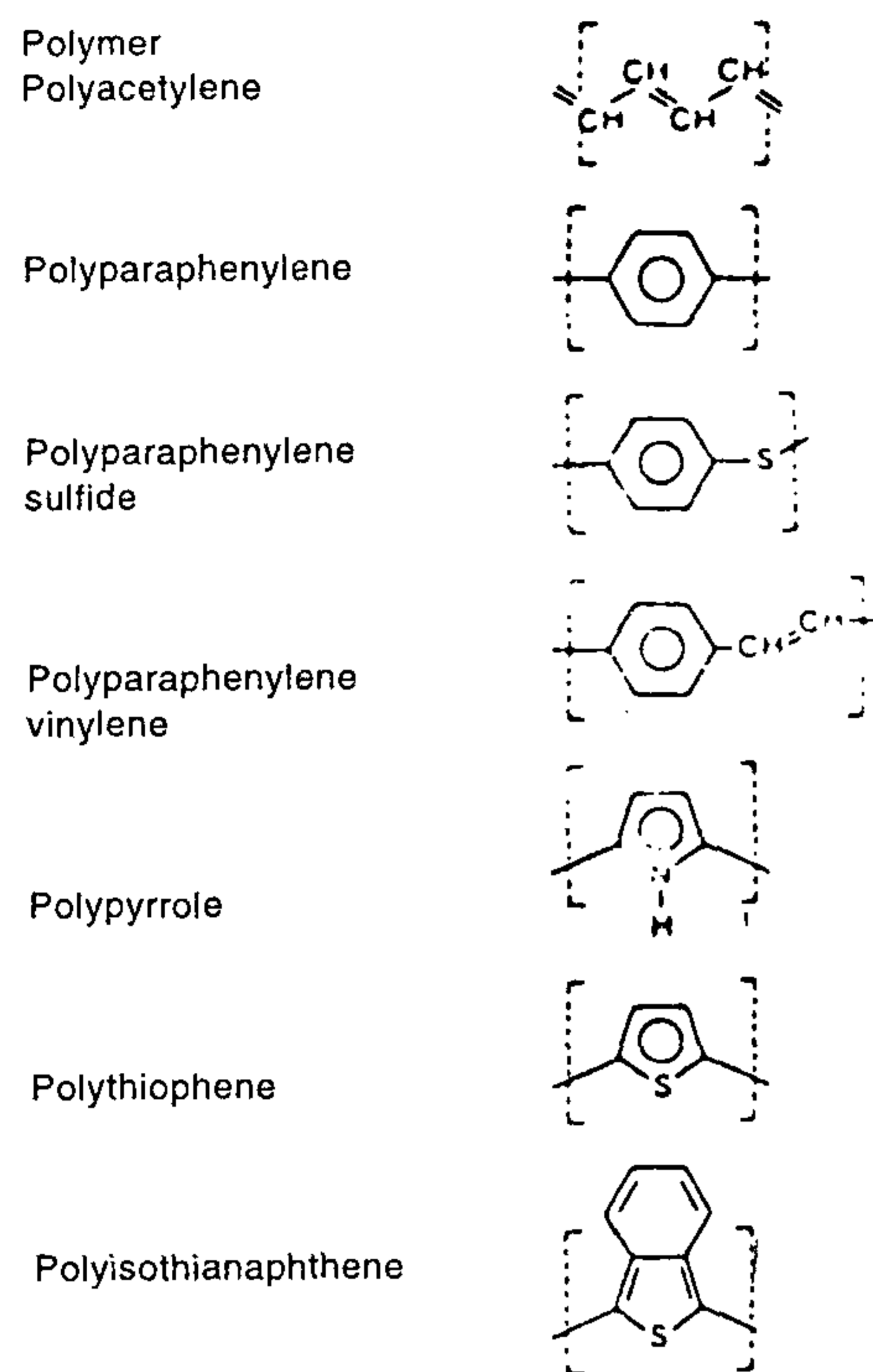


Figure 1. Structures of some organic conjugated polymers.

- ii) The polymer molecules can be rather easily oxidized or reduced, usually through charge transfer with molecular dopant species.
- iii) Carrier mobilities are large enough for high electrical conductivities to be realized.
- iv) Charge-carrying species are not free electrons or holes as is the case with inorganic semiconductors but quasi-particles such as solitons, polarons and bipolarons which may move relatively freely through the material.

Through doping, the electronic and optical properties of conducting polymers can be controlled over the full range from insulator to metal. Doping can also be carried out by chemical means by direct exposure of the dopant to the polymer in the gas or solution phase or by electrochemical means (oxidation and reduction). Radiation can also induce conductivity in polymers.

Design of novel low band gap polymers

One of the fundamental challenges of the field of conducting polymers has been the design of low band gap polymers⁶. The polymers with most wide applications such as polypyrrole or polythiophene have band gaps in

the range of 2.0–3.5 eV and are, therefore, in comparison with inorganic semiconductors (Si, for example, with a band gap of 1.1 eV sets the standard) classified as wide band gap semiconductors. Conjugated polymers with a small band gap can offer a lot of advantages. They can be i) intrinsically good electrical conductors or semiconductors without the need of any doping; ii) transparent in either the intrinsic or doped state and; iii) of great interest as new polymeric materials for non-linear optics (because of fewer contact problems) and other properties.

To be successful in designing low band gap polymers, it is necessary to have a complete understanding of the relationship between the chemical structure of a polymer and its electronic and conduction properties. Once such information is available, the desired electronic properties can be obtained by molecular design followed by specific synthesis. Over the years a great deal of understanding of this relationship has been achieved with the help of quantum-chemical calculations of the ground state properties of the undoped conjugated polymers. It is now, for example, fairly well established that in the case of conjugated polymers with degenerate ground state (e.g. *trans* polyacetylene (PA)), the band gap decreases as a function of decreasing bond-length alternation along the backbone⁷. In polymers with nondegenerate ground state such as polypyrrole, polythiophene, etc. on the other hand, the band gap is generally found to decrease with increasing quinoid contributions to the ground state of the polymer⁸. Various routes are presently followed for designing low band gap polymers, using the aforementioned guidelines. These include substitution⁹, ladder structures formation¹⁰, topological consideration¹¹, copolymerization¹² and bringing together of conjugated donor and acceptor-like moieties¹³ in a conjugated chain. Table 1 contains some of the low band gap conjugated polymers which have already been synthesized.

Applications

Stability in air and processing characteristics of electrically conducting polymers have been the main barriers to their commercialization. Doped PA, for example, is very reactive toward oxygen and moisture – it rapidly suffers irreversible loss of conductivity in the atmosphere. Some other polymers such as polypyrrole, polythiophene, polyaniline, polyphenylene – vinylene exhibit much greater stability toward ambient conditions. While not as conductive as PA, they do well enough for many applications. The second key issue in conducting polymer technology is ease of processing. The first conducting polymers were hard to process because of their insolubility and infusibility. But considerable progress has been made in the past few years. Several conducting

Table 1. Some low band gap conjugated polymers

Name	Structure	Band gap (eV)
<i>Trans</i> -PA		1.5
Polythiophene		2.1
Polyisothianaphthene		1.0
Polyisophthothiothiophene		1.4
Poly[α -(5,5'-tetrathio-phenenedyl) benzylidene]		0.75-1.1
Poly(dithieno-[3,4-b:3',4'-d]-thiophene)		1.0
Poly-4H-cyclo-penta dithiophene-4-one		1.2
Polydicyanomethylene-cyclopenta-dithiophene		0.8
Polysquaraines		0.5
Polyazopyrrole		1.0

polymers can now be prepared as dispersions and applied as coatings while others can be prepared from processible precursor polymers. Many of the polymers can now be blended with conventional thermoplastics such as polyethylene or polyvinylchloride to produce partially conducting materials that are readily processed.

The most common application of conducting polymers is their use as electrodes in light weight and rechargeable batteries. In polymers where both p- and n-doping processes are feasible, the possibility exists of their use as both positive and negative electrodes in the same battery system. Such batteries are lighter in weight, have a longer life and are devoid of toxic materials. The invention of polymer batteries has been heralded as the invention that would make electric car a reality as the light weight polymer batteries would not weigh a car down to the extent as the heavy lead acid batteries would do.

The Bridgestone Corporation of Japan have developed coin-type rechargeable polymer lithium batteries with a conducting polymer polyaniline and the high capacity lithium aluminium alloy as the two electrodes. The characteristics of these batteries are low self-discharge, high voltage and long-term reliability. One of the unique features of this rechargeable polymer lithium battery is that it can be used as a power source in combination with solar cells. This feature opens up many new possibilities for application as a power source. The operation of electronic clock, watches, calculators, remote control devices of audio-visual units, etc. stand to benefit from this technology.

Recently, batteries with a full solid state configuration have also been realized using the electrically conducting polymers. The absence of liquids or gases in the solid state cell leads to high durability and reliability, properties which may become precious when safety is essential. Further, the solid state batteries from the thin films of conducting polymers may provide plasticity, a feature which would be highly welcome in various applications.

The doping processes of certain conducting polymers are accompanied by changes in colour. This effect has been conveniently exploited in the realization of electrochromic display (ECD) devices. An ECD device changes colour on the application of an electric potential. Thin films of a conducting polymer polythiophene, for example, are red in the doped state and deep blue in the undoped state. However, the fact that a material changes colour is not sufficient to permit its use in a display system, its switching time between these two states must be very short and it should maintain these properties in spite of intensive use. In the case of polythiophene, switching time around 30 milliseconds and a stability exceeding one million doping/undoping cycles have been measured. This value corresponds to about 2 years of operation for a frequency of one cycle per minute. Some of the applications of the ECDs include timetables in airports and train stations, calculators, computers, clocks and any other piece of equipment that utilizes a liquid crystal display.

The fact that many conducting polymers are semiconductors in the undoped or lightly doped state has promoted proposals for their use in microelectronics. Both industrial and academic groups are pursuing their use in semiconductor devices and especially field effect transistors (FETs)¹⁴. For a FETs active layer – the semiconducting layer between the source and drain electrodes – micrometer thick films are required. Advances during the last few years have made it possible to prepare this level of thinners from polymers with standard techniques such as spin coating and thermal evaporation. The carrier mobility of the order of 10^{-1} cm²/V-s in such FETs has been achieved. This development shall soon open the way to uses such as flat-panel colour displays for computers and possibly flat colour televisions when tied to a liquid crystal matrix.

Light emitting diodes (LEDs) have also been fabricated from conjugated polymers using poly (*p*-phenylene-vinylene) as the emissive layer¹⁴. Flexible, almost entirely metal-free LEDs have been developed and such feats have been made possible by, among other reasons, the advances in the chemistry of 'processable conjugated polymers' over the past several years and the focussed work on the physics of electroluminescence in these materials. These polymer-based LEDs could be competitive in display applications in the future because

of the potential ease, low cost of fabrication and large surface area of devices based upon processable polymers.

Another useful application of conducting polymer films is in the field of gas separations. Selective control of gas permeability is facilitated by the doping, undoping and redoping process of emeraldine films. In the last few years, polyaniline has emerged as the class of conducting polymers with the highest potential for technological applications as this material combines ease of processability, ease of synthesis, satisfactory environmental stability and chemical versatility. Polyaniline is found to be suitable for a number of applications in computer manufacturing processes. Polyaniline can play significant roles in the lithographic processes used to fabricate integrated circuits. Thin films of conducting polyaniline are found to be effective discharge layers for electron-beam lithography. Polyaniline provides attractive chemical flexibility and processing options, including secondary doping. It also provides an opportunity for use in welding of thermoplastics and thermosets.

Electrically conducting polymers which can be processed thermoplastically and possess the advantageous mechanical behaviour and corrosion stability of plastics would open up an entirely new field of applications. Cables for conducting electricity, wall papers which allow electrical heating, optical fibres covered with conducting polymers for many sensors, electrostatic devices for ion injection in air, antenna for satellite reception, new materials for antistatic equipment are only some few fields in which electrically conducting polymers would find a big market. The polymerization and doping of conducting polymers on such fabrics as nylon, cotton and polyester to produce fabrics with a range of conductivities under the trade name Contex has been achieved. These materials are under intense study for use in future aircraft and tanks. They could also be used for heated clothing, shielding computers against electromagnetic interference, static dissipation in high speed missiles and conveyor belts that handle static-sensitive electronic and flammable articles. Electrically conducting polymers are also regarded as candidates of high potential for passivating layers with respect to photocorrosion of photoelectrodes. Films of polypyrrole have already been tested as coatings for certain semiconductor electrodes.

Other speculative applications of these conducting polymers include such diverse areas as solar cells and drug delivery systems for the human body. Although conducting polymers can absorb sunlight, their conver-

sion efficiencies fall far below those required for effective solar cells. Their potential in drug delivery depends on the redox properties of a polymer implanted in the body. If a drug molecule, e.g. heparin penicillin, could function as a dopant ion, the drug would, in principle, be released on dedoping the polymer by application of a small electric potential. In practice many chemical and medical problems will have to be solved before experiments can begin *in vivo*. Recently biocompatible implants (pacemaker) using polypyrrole doped with heparin have also been demonstrated. Structures similar to muscle fibres have been proposed by researchers in Italy and Japan. They are based on the property that a conducting polymer in a fibre form undergoes dimensional changes as a result of electrochemical doping and undoping. Work results from expansion and contraction along the fibre's length. A bilayer (3×1 cm) formed by an electroactive material (polypyrrole) and an adherent, non-conducting and flexible polymeric film works like a muscle. More possible applications include conductive paints, toners for reprographics and printing, and components for aircraft where the combination of light weight, mechanical strength and moderately high conductivity are required.

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