

## Polymer science

# Conducting rubber bounces back

Paul Calvert

THE conventional picture of conducting polymers, as typified by polyacetylene ( $-\text{CH}=\text{CH}-$ )<sub>n</sub>, is that they are black, rigid, conjugated (having alternating single and double bonds) and insoluble. Their properties have a closer resemblance to coal than to polyethylene. M. Thakur of AT&T Bell Laboratories now makes the surprising claim (*Macromolecules* **21**, 661–664; 1988) that conjugation is not necessary for a polymer to be conducting, and that natural rubber (*cis*-polyisoprene) becomes conducting when treated with iodine. This raises the disconcerting possibility that the rest of us may have been overlooking the obvious.

The *trans* form of polyacetylene has a conductivity of about  $10^{-5}$  siemens (S)  $\text{cm}^{-1}$ , which makes it a semiconductor. The polymer is black and shiny because the conjugation, the extended sequence of alternating double and single bonds, reduces the energy gap between the fixed, valence-electron states and the free, conduction states: visible light is absorbed by electrons jumping from the valence band into the conduction band. Reduction of the polymer with alkali metals puts electrons into the conduction band and makes the polymer more conducting. Similarly, reaction of the polymer with an oxidizing agent, such as iodine, forms a charge-transfer complex. This removes a valence electron, leaving a hole in the valence band which can also travel through the polymer and conduct. Normal iodine-doped polyacetylene can reach conductivities above  $100 \text{ S cm}^{-1}$ .

At first it was thought that the conduction arises from electrons or holes travelling along chains, and then leaping the gaps at the ends. It later became clear that conductivity is dominated by carriers jumping from chain to chain, because the paths along the chains are normally blocked by irregularities. This was proved last year by the formation of polyacetylene with very high conductivities, in which the polymer chains have been fully straightened (Basescu, N. *et al.* *Nature* **327**, 403–405; 1987 and my accompanying News and Views article on page 371 of that issue).

Conjugation was nonetheless thought to be necessary because the electrons have to be delocalized over a large distance to produce a small energy gap between the valence and conduction bands. This extended orbital structure also locks the chain into a rigid conformation such that it cannot melt or dissolve. Polyisoprene ( $-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-\text{CH}_2-$ ) has an isolated double bond with no conjugation. Every chemist knows that rubber is

attacked by bromine at the double bond, and that rubber bungs in iodine bottles go black. Thakur measured conductivities, after iodine doping, of  $10^{-2}$ – $10^{-1} \text{ S cm}^{-1}$ , 10 orders of magnitude above normal rubber. He believes that the iodine forms a charge-transfer complex and has some infrared evidence to support this.

There are two worrying aspects of this work. First, it makes us all look stupid. There have been studies of various composites of polyacetylene and rubber, but apparently no-one noticed doping and conductivity in the rubber component. Second, the effect is seen with *cis*- and *trans*-polyisoprene (natural rubber and gutta-percha, respectively), and also with poly-2,3-dimethylbutadiene ( $-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-$ ) but not, however, with poly-1,4-*cis*-butadiene ( $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ ). Thakur suggests that this is because of the methyl

( $\text{CH}_3$ ) groups increasing the electron density in the double bonds, but this effect is not normally large.

Polyphenylacetylene attracted attention as a conducting polymer some years ago, but it was shown that the effect arises from ionic conductivity by  $\text{I}^-$  and not electronic conduction (Cukor, P. *et al.* *Makromolek. Chem.* **182**, 165–171; 1981). Thakur checked this possibility by long-term direct-current measurement where ions would be expected to become depleted so that the conductivity drops off. No drop-off with time was seen. Polyphenylene-sulphide becomes conducting when doped with arsenic pentafluoride, because of a chemical reaction that forms a new, dopable polymer (Frommer, J.E. *et al.* *Am. chem. Soc. Symp.* **242**, 447–453; 1985). Thakur's spectroscopic studies show no evidence of such a structural rearrangement. Thus one's prejudice says that there must be a catch, but this report by Thakur is a carefully constructed piece of work with no obvious loopholes. If it does stand up, we shall have a lot of rethinking to do. □

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## Particle accelerators

# The light that never was

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As physics has progressed, the secrets of 'elementary' particles and their interactions have successively become more difficult to unlock, and are tied up in smaller and smaller objects—from atoms to nuclei and now to quarks. The Heisenberg uncertainty principle requires that smaller distances can only be probed by higher and higher energies and has led to the building of immense particle accelerators, for instance at CERN and in the US national laboratories. Probing smaller objects also means that more particles per unit area are required to give a reasonable interaction rate, and the need for a high centre-of-mass energy leads to concentrating on head-on colliding-beams systems. H. Hora proposes elsewhere in this issue (*Nature* **333**, 337–338; 1988) an unconventional accelerator based on intense laser beams that can raise particle energies to  $10^{12}$  electron-volts (1 TeV) without being unmanageably large. It shares, however, many difficulties of other accelerator designs using nonlinear effects.

Over the past half century, the designers of particle accelerators have a proud record of doubling the particle energy every few years. This progress has been possible only by continual innovation, and since about 1980 there has been a concerted effort to find the successor to the conventional radiofrequency linear

accelerator. For a while, the combination of lasers to generate exceedingly high fields, and ionized plasmas to provide a resonant medium with a longitudinal electric field, seemed to promise a compact design for new machines. But plasmas are bedevilled with instabilities which could ruin the beam quality of an accelerator. Not surprisingly we now have, in Hora's proposal, an imaginative attempt to design a laser-based accelerator without a plasma.

Hora postulates a phase-modulated light wave, in which a nonlinear (or ponderomotive) force is somewhat enhanced and electrons initially in the laser beam are expelled with a velocity rather greater than their initial oscillation velocity. The fact that the required light wave fails to satisfy Maxwell's equations of electromagnetism is not the main objection to the application of this scheme. Rather, the device is analogous to electrostatic accelerators such as the van der Graaf, and it is not clear how stages can be cascaded together to achieve the desired particle energies.

Having to live within the rigours of Maxwell's equations is a long-standing problem in attempts to use lasers to accelerate charged particles. In a vacuum, the electric field of an electromagnetic wave is transverse and does not provide