

# ORDER AND DISORDER IN CONDUCTING POLYMERS

DINESH CHANDRA TRIVEDI

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

Various methods have been described to achieve ordered molecular organisation in conducting polymers.

## INTRODUCTION

A vast majority of organic solids are electrical insulators. Due to the mobility of  $\pi$  electrons, the aromatic nucleus should show a remarkable electrical conduction but the large band gap in the macromolecular assembly makes it insulating. However, the electrical conduction in a macromolecule arises from strong intermolecular interactions to produce a delocalised electronic band structure which under certain conditions can give rise to metallic behaviour.

In 1954, it was shown that hydrocarbons like perylene form charge-transfer complexes with bromine whose resistances were of the order of 8 ohm cm [1]. The term charge-transfer complex (CT complex) implies a complex formed by interaction of two or more component molecules. In a broad sense, conducting polymers thus may also be classified as CT complexes. Conductivity in conducting polymers is intrinsically anisotropic because of the quasi one-dimensional electronic structure of these materials. Charge transport is favoured along the chain rather than between the chains. The extent of anisotropy and thus conductivity depends on the chain alignment, packing arrangement, and effective conjugation length [2]. Thus, these defect-related limitations are responsible for the amorphous nature and the not-so-high anisotropy. (The charge carrier concentration is  $10^{21}$  to  $10^{23}$  per cc as compared to  $10^{16}$  to  $10^{18}$  for semiconductors). The reason for the lower conductivity is due to the very low mobility of the charge carrier.

The mobility of the charge carrier in these materials is in the range of  $10^{-4}$  to  $10^{-5}$  cm<sup>2</sup> per volt second, whereas it is  $10^2$  to  $10^5$  cm<sup>2</sup> per volt second in semiconductors [3]. This low mobility of the charge carrier is the true hindrance in achieving high conductivity. The cause for the low mobility is the amorphous nature of the polymer. Therefore, the regularity of the polymer chain is important. Any irregularity causes interruption of periodicity of potential to give localized states in space. The localised state can be extensive in space over distances corresponding to the extent of the regular portions of the polymer chain. The degree of localization in a preferred direction depends upon the orientation of the polymer chain.

Therefore, an ordered packing will give rise to periodicity in a direction transverse to the chain and thus anisotropy in electrical conduction along with enhanced mobility of the charge carrier.

It is known that conducting polymers are not intrinsically conducting and, therefore, doping has to be carried out. The dopant introduces electrons or holes, respectively, in conduction and valence bands. In this process, the dopant itself gets ionized, and further localization of state due to kinks, folds and chain-end of polymer occurs. Thus, any contribution to localized state by doping can be avoided by choosing an ideally ordered dopant. It is likely that such a dopant will bring order in a disoriented polymer chain [4-6]. Therefore, to understand many phenomena in conducting polymers and to explore their technological applications, it is

desirable to achieve to the extent possible crystallinity in these new exciting materials.

## METHODOLOGY

It is of great interest to understand the basic process of electrochromism, which is essentially the ingress and egress of the dopant on scanning the potential between two extreme values. Our study indicates that slowly the electroactivity of such a polymer comes down in spite of keeping the upper limit of the potential at a much lower value. For example, in the polyaniline system electrochromic display is observed in the range of -0.2 to 0.4V vs SCE, whereas the degradation of polyaniline occurs around 0.8 V vs SCE. Such degradation of polyaniline can possibly be ascribed to the development of local stresses and strain due to repetitive change in geometry of the polymer [7-10].

It is believed that the cyclic sweep (potentiodynamic) method gives better quality conducting polymer film on the electrode surface because such films are comparatively free from impurities of oligomers and give cyclic voltammograms of definite features. Thus, when a film is prepared by the potentiodynamic method, the already deposited polymer experiences repetitive changes in its volume at the molecular level because of oxidation and reduction which are associated with the dopant diffusing in and out. Therefore, it is but natural to assume that such a film will have greater porosity and more of damaged polymer due to stresses than for one prepared by the potentiostatic method, and hence should have a shorter life.

Close packing required for high conductivity can be achieved by slowing down the rate of the polymerization reaction.

In general, conducting polymers synthesised by electrochemical techniques show better ordered molecular organisation because the planes of aromatic rings lie parallel to the electrode surface. Thus, the orientation occurs during electrodeposition itself. This type of behaviour has been observed in poly(paraphenylene), polypyrrole, polyindole, polythiophene and in polyaniline.

It has also been observed that at high electrode potentials cross linking occurs creating many sp<sup>3</sup> defects (formation of  $\sigma$  bond) which break the conjugation, and thereby limiting the path of the charge carrier. Therefore, the best electrolyte is one in which the polymerization potential can be brought down. It is practically impossible to change the thermodynamic parameters like oxidation potential of a pure monomer. But many aromatic compounds, including hydrocarbons, form CT complexes with a number of Lewis acids. These complexes are labile, and due to the delocalization of  $\pi$  electrons have lower oxidation potentials than for the monomer. Such reactions are well established (e.g. Friedel Craft reaction for the polymerization of benzene in the presence of copper salts). Even though the cupric ion has a low oxidation potential, it brings about in presence of AlCl<sub>3</sub> the polymerization of benzene to poly(paraphenylene) having a 16-20 aromatic ring. A similar strategy has also been adopted in

developing a new electrolyte based on a solid-solid mixture of  $\text{AlCl}_3$  and alkyl pyridinium halide [4]. These two solids when mixed (in 2:1 ratio), give a clear liquid of high electrical conductivity and miscible with all organic solvents in all proportions. The conductivity of this melt increases on dilution with aromatic hydrocarbons because of an increase in ionization.

Hydrocarbons form CT complexes with  $\text{AlCl}_4^-$  -  $\text{Al}_2\text{Cl}_7^-$  species present in the electrolyte. These  $\text{AlCl}_4^- / \text{Al}_2\text{Cl}_7^-$  also act as dopants for the electrodeposited polymer. Thus, the polymerization of benzene is achieved at +1.2 V, whereas with other electrochemical methods polymerisation needs more than +2.2 V. At such high potentials, the stability of the solvent used becomes questionable and hot cation-radicals generated during the polymerization reaction can abstract protons from the solvent to give a short conjugated polymer with  $\text{sp}^3$  defects.

### LANGMUIR-BLODGETT (LB) TECHNIQUE

Using LB technique, it is possible to obtain ordered architectures. Langmuir Blodgett monolayer films are formed when amphiphilic molecules in solution are deposited on water surface followed by compression. During compression, the randomly oriented molecules reorient themselves with the hydrophilic head groups on the water surface and the hydrophobic tail standing away from the water surface.

This technique has been applied to obtain thin films of conducting polymers derived from five-membered heterocyclic rings, polydiacetylene and various organic molecules [11]. However, this technique is limited to very few conducting polymer systems and the stability of such films is questionable.

### Hydrogen bonded polymers

The density of electroactive species and stability of the system are dictated by specific interactions between molecules. It should, therefore, be possible to select suitable chemical moieties and incorporate them in a conjugated system so as to force intra- and interchain order and also to some extent prevent/decrease structural defect. However, the conformational freedom in long chains can result in kinks or twists and disrupt conjugation. In many liquid crystals, the ordering is by hydrogen bond formation.

In conventional amide linkage based polymers like nylon, hydrogen bonding brings about a better organised assembly at the molecular level. Here, hydrogen bonding imparts many important qualities like mechanical strength [12]. Thus, it should be possible to realise good mechanical strengths by proper packing of conducting polymer chain using this technique.

### ROLE OF DOPANT

Dopants not only maintain charge neutrality, but also bring about a geometry relaxation in the polymer chain, and generate charge carriers.

Electrochemical synthesis is accompanied by a simultaneous intercalation of polymer with the dopant. If the dopant unit has a definite orientation (for example, elongated molecules like paratoluene sulphonic acid), then during intercalation, it can reorganise the disordered plane of the conducting polymer [13]. The ideal situation would be alternate layers of the polymer and dopant to give the ordered two-dimensional layered assembly with strong anisotropy symbolising molecular organisation. With  $\text{AlCl}_4^-$  as a dopant (here all bond lengths are between 2.122 Å to 2.130 Å and

bond angle varies from 108°.53 to 110°.70), the anisotropy in polyparaphenylene is in the ratio of 1:100 [4]. For this system the potential step technique has shown that the polymer has a layered structure.

Thus on doping, the polymer matrix reorganises to accommodate charged states formed in the gap region. Therefore, the unoriented dopant can harmfully influence the reorganisation of the polymer.

### EFFECT OF TEMPERATURE

Polypyrrole synthesised at low temperature could be stretched to twice its original length to yield anisotropic conductivity 20 times higher than that for an unstretched polypyrrole film. This type of anisotropy is completely absent for polypyrrole synthesised at room temperature [14]. Therefore, during polymerisation at room temperature cross linking occurs. This breaks the conjugation, destroys anisotropy by creating a disordered structure and thus lowers the conductivity. Though in 5-membered heterocyclic 2, 5 coupling is preferred, but the higher energy 2, 3, coupling is also possible because of the very reactive nature of the radical cation. This problem can be tackled either by an alkyl group substitution at the 3 and 4 positions or by choosing an electrolyte in which the oxidation potential can be lowered or the life time of the cation radical can be slightly increased. In other words, orientation can be achieved if the rate of polymerisation is lowered.

Alkyl substitution at the 3 and 4 positions, particularly by long alkyl chain, gives the very interesting phenomenon of order-disorder in a side chain where the folding and unfolding of the alkyl chain occur with change in temperature giving variety of colours. For example, 3-hexyl substituted thiophene can be used successfully as a thermal/pressure sensor [15].

### CONCLUSIONS

The advantage of processing these materials into well-ordered architectures may lead to smart devices such as chemical and biochemical sensors, and drug delivery systems, and will help in understanding the mechanism of charge transport in these new materials which have become the foci in material science.

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