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Introduction and Synthesis of Conducting Polymers

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Abstract

The conducting polymers have drawn a vital interest of researchers for quite thirty years attributable to their economical importance, superior stability, lighter weight, higher workability, resistance to corrosion and satisfactory electrical conduction. A number of the applications of polymers include: reversible batteries, electro chromic show devices, light weight reflective or lightweight sending appliances for optical info, sensors and storage for glare reduction systems and sensible windows in cars and buildings, compound lightweight emitting diodes, electrical phenomenon devices, transistors, magnetic force shielding against electro-magnetic interferences and various electronic circuits. This paper describes the overall review of Chalcogenide glass. The synthesis of Chalcogenide glass by different method is described in details. This paper also discuss the different apparatus which is used to characterized the Chalcogenide glasses for example XRD, UV-visible spectrophotometer, EDAX analysis, Photoluminescence spectroscopy, dielectric properties Field Emission Scanning Electron Microscope (FE-SEM), Differential scanning calorimetry.

Keywords: Conducting Polymer, Doping, Polyethylene, Polyaniline, Polypyrrole.

1. Introduction

Although polymeric materials have been used by mankind since prehistoric times in the form of wood, bone, skin, and fibers, the existence of macromolecules was accepted only after Hermann Staudinger developed the concept of macro-molecules during the 1920s, which got him the Nobel Prize in Chemistry in 1953 ‘‘for his discoveries in the field of macro-molecular chemistry’’ (Ye. P. et al. 2002), (R. Mülhaupt et al. 2004). The research field of conjugated (conducting) polymers came into spotlight with the preparation of Polyacetylene by Shirakawa and coworkers along with the subsequent discovery of enhancement in its conductivity after doping (H. Shirakawa, et al. 1977), (C. K. Chiang, et al.1977), (C. K. Chiang et al. 1978). Some of the most important representatives in the family of conjugated polymers in non-conducting as well as conducting forms viz., Polythiophene (PTh), Polyaniline (PANI) and Polypyrrole (PPy) were already being prepared chemically or electrochemically in the nineteenth century. The existence of Polyaniline (PANI) in four oxidation states was also recognized. A reaction scheme for the electro-oxidation of aniline at a carbon electrode was suggested by Yasui in 1935 (T. Yasui et al. 1935). It was almost a century after Letheby’s observations that Mohilner and coworkers reinvestigated the mechanism of the electro-oxidation of aniline in aqueous sulphuric acid solution at a platinum electrode and characterized Polyaniline (PANI) (D. M. Mohilner et al. 1962)**.** The first real breakthrough came in 1967, when Buvet and his group established that Polyanilines are redox active electronic conductors and PANI pellets can be used as electrodes for conductivity measurements (R. de Surville, et al., 1968, J. C. Chiang et al. 1986). Polypyrrole (PPy), on the other hand, was known as pyrrole black and was formed due to the oxidation of Pyrrole in air. PPy is an inherently conducting polymer with interesting electrical properties first discovered and reported in the early 1960s (J. C. Chiang et al. 1986). It was followed by the preparation of coherent and free standing Polypyrrole films by electrochemical polymerization by Diaz and his co-workers (B. A. Bolto et al. 1963).

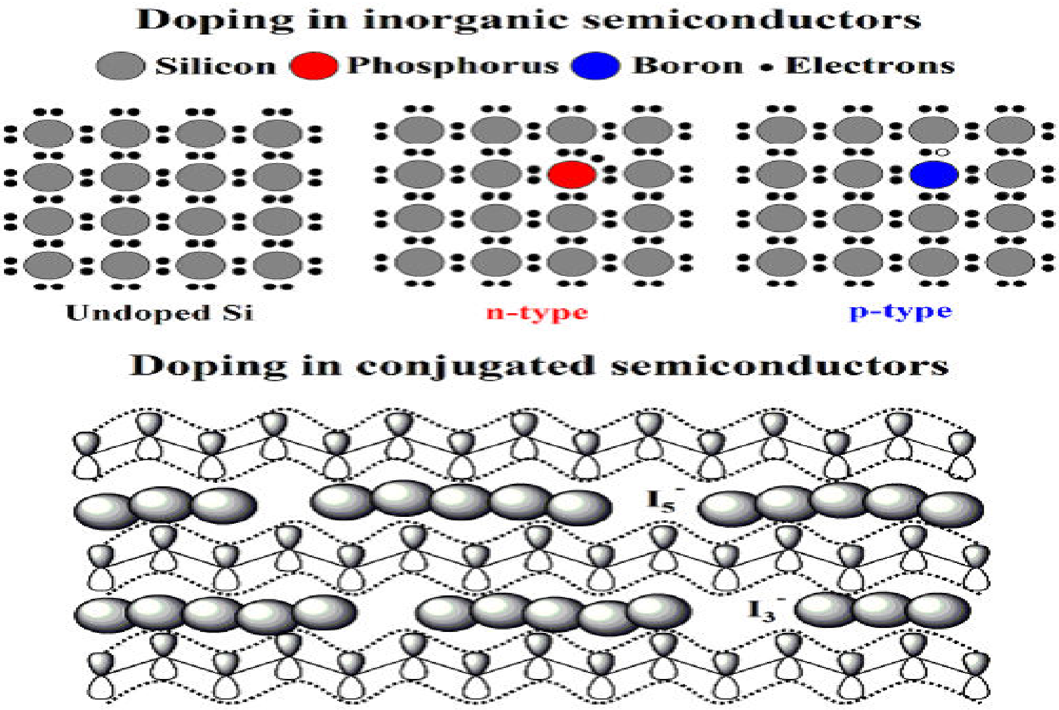


Fig.1 Schematic illustration indicating the difference between the doping mechanisms in inorganic semiconductors and conjugated polymers.

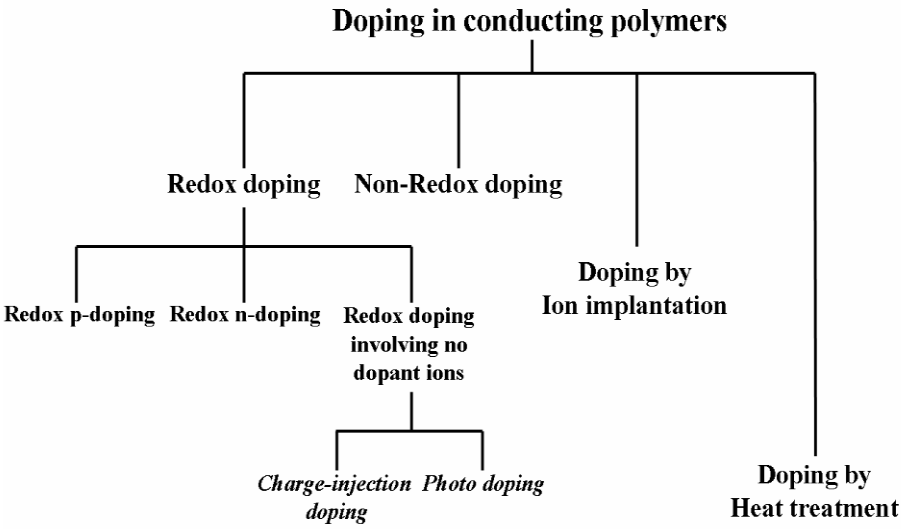


Fig.2 Different methods for doping in conducting polymers.

The conducting polymers have drawn a vital interest of researchers for quite thirty years attributable to their economical importance, superior stability, lighter weight, higher workability, resistance to corrosion and satisfactory electrical conduction. A number of the applications of polymers include: reversible batteries, electro chromic show devices, light weight reflective or lightweight sending appliances for optical info, sensors and storage for glare reduction systems and sensible windows in cars and buildings, compound lightweight emitting diodes, electrical phenomenon devices, transistors, magnetic force shielding against electro-magnetic interferences and various electronic circuits. This paper describes the overall review of Chalcogenide glass. The synthesis of Chalcogenide glass by different method is described in details. This paper also discuss the different apparatus which is used to characterized the Chalcogenide glasses for example XRD, UV-visible spectrophotometer, EDAX analysis, Photoluminescence spectroscopy, dielectric properties Field Emission Scanning Electron Microscope (FE-SEM), Differential scanning calorimetry.

Doping of conjugated polymers either by oxidation or by reduction in which the number of electrons in the polymeric backbone gets changed is generally referred to as redox doping (M. G. Kanatzidis, 1990) [Fig.1 and 2]. The charge neutrality of the conducting polymer is maintained by the incorporation of the counter ions.

Redox doping can be further subdivided into three main classes: *p* type doping, *n* type doping and doping involving no doping ions viz., photo-doping and charge injection doping (A. F. Diaz, 1981, H. J. Ahonen, et al., 2000). Both chemical and electrochemical redox doping techniques can be employed to dope conjugated polymers either by removal of electrons from the polymer back-bone chain (*p*-doping) or by the addition of electrons (*n*-doping) to the chain. In chemical doping the polymer is exposed to an oxidizing agent such as iodine vapors or a reducing agents viz., alkali metal vapours, whereas in electrochemical doping process a polymer coated, working electrode is suspended in an electrolyte solution in which the polymer is insoluble, along with separate counter and reference electrodes.

Photo-doping is a process where conducting polymers can be doped without the insertion of cations or anions simply by irradiating the polymer with photons of energy higher than the band gap of the conducting polymer. This leads to the promotion of electrons to higher energy levels in the band gap. Charge injection doping is another type of redox doping that can also be used to doped an Undoped conducting polymer (J. H. Burroughes et al.1988), (J. H. Burroughes et al. 1990). In this method, thin film of conducting polymer is deposited over a metallic sheet separated by a high dielectric strength insulator. The non-redox doping of conducting polymer is a process of doping conducting polymers in which the number of electrons associated with the polymer chain is kept constant. In fact it is the energy level in the conducting polymer that gets rearranged in the non-redox doping process (A. G. MacDiarmid, 2001). The best example of non-redox doping is the conversion of emeraldine base form of Polyaniline to protonated emeraldine base (poly-semiquinone radical cation) when treated with protic acids. It has been observed that the conductivity of Polyaniline is increased by approximately 10 orders of magnitude by non-redox doping. Ion implantation and heat treatment methods have also been used to dope conducting polymers; however, it has rarely been used for doping conducting polymers.

2. Ionization process in Conducting Polymers

Ionization in conducting polymer is due to doping. The introduction of charge during the doping process leads to a structural distortion of a polymeric structure in the region of the charge, giving an energetically favorable conformation. These structural distortions are intrinsic to the development of ionization states called polarons and bipolarons.

2.1 Common Structural Features of Conducting Polymers

The common structural features of these polymers include.

(1) Conjugated system along the polymer backbone.

(2) Generally planar structure

(3)Intra-chain conductivity $\rho_{\|}$ is much larger, than the inter–chain conductivity ($\rho_{\perp}$).

The anisotropy ratio is $\rho_{\perp}/\rho_{\|}$a parameter used to estimate the one-dimensionality of a particular system. In view of their large anisotropy ratio, these systems are also called quasi-one-dimensional systems. Baughman et al. in 1982 have observed the different factors in relation to structure that lead to enhance the electrical conductivities in the conducting polymers. It has been observed that polymers which have the most homogeneous chain structures appear to be the best conductors. Heterogeneity, on the other hand, can yield carrier localization on the chain unit, which provides the lowest potential for holes (or electrons in the case of donor doping). Bredas et al. have shown that there exists a link between the homogeneous character of the polymer backbone and the width of the highest occupied π-band. The width of the π-bands can be correlated to the degree of delocalization of the π-systems along the polymer backbone and also to the mobility of the carriers in these bands. It was shown that as the ionization potential deceases and the width of the highest occupied π band increases, the band gap decrease thus creating a better conductor. These results show why polymer research is primarily centered on π-bonded unsaturated systems since these materials have low ionization potentials and large electron affinities. The π electrons will be removed or added easily to these systems and the small effect is observed on the σ-bonds those are necessary to hold the basic backbone of polymer intact.

2.2 Bulk and Nanopolymer

Polymer nanocomposites (PNC's) include a chemical compound or polymer having nanoparticles or nanofillers spread within the chemical compound matrix. These is also of various form (e.g. platelets, fibres, spheroids), however a minimum of one dimension should be within the range of 1–50 nm. These PNC's belong to the class of multi-phase systems (MPS, viz. blends, composites, and foams) that consume nearly ninety fifth of plastics production. These systems need controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and also the combination ways for all MPS, together with PNC, are similar. Chemical compound nanoscience is that the study and application of nanoscience to polymer-nanoparticle matrices, wherever nanoparticles are those with a minimum of one dimension of but a hundred nm. The transition from small to nanoparticles is result in amendment in its physical still as chemical properties. Two of the main factors during this are the rise within the quantitative relation of the extent to volume, and also the size of the particle. The rise in surface area-to-volume quantitative relation, that will increase because the particles get smaller, results in the increasing dominance of the behavior of atoms on the extent of particle over that of these interior of the particle. This affects the properties of the particles once they are reacting with alternative particles. Owing to the upper extent of the nanoparticles, the interaction with the opposite particles inside the mixture is a lot of and this will increase the strength, heat resistance, etc. and plenty of factors do amendment for the mixture. The example of a nanopolymer is Si nanospheres that show quite totally different characteristics; their size is 40–100 nm and that they are a lot of tougher than Si, their hardness being between that of sapphire and diamond.

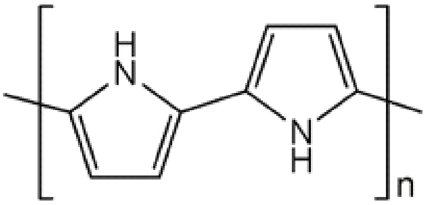
2.3 Metal-Insulator transition in doped conducting polymers

Metal-Insulator (M-I) transition is one of the most interesting physical aspects of conducting polymers. When the mean free path becomes less than the inter-atomic spacing due to increase in disorder in a metallic system, coherent metallic transport is not possible (Heeger, 2002). When the disorder is sufficiently large, the metal exhibits a transition from the metallic to insulating behavior. As a result of this transition which is also known as the Anderson transition all the states in a conductor become localized and it converts into a Fermi glass with a continuous density of localized states occupied according to Fermi statistics. Although there is no energy gap in a Fermi glass but due to the spatially localized energy states a Fermi glass behaves as an insulator (P. W. Anderson, 1958). It has been found that electrical conductivity of a material near the critical regime of Anderson transition obeys power law temperature dependence (W. L. McMillan, 1981). This type of M-I transition has been observed for different conducting polymers viz., Polyacetyle, Polyaniline, Polypyrrole and Poly(p-phenylene vinylene) etc. and is particularly interesting because the critical behavior has been observed over a relatively wide temperature range. In conducting polymers, the critical regime is easily tunable by varying the extent of disorder by means of doping or by applying external pressure and/or magnetic fields.

In the metallic regime, the zero temperature physical phenomenon remains finite, and σ (T) remains constant as T approaches zero (R. Menon, et al., 1998). Though disorder is mostly recognized to play a very important role within the physics of metallic polymers, the effective length scale of the disorder and also the nature of the M-I transition.

In this thesis, we've taken two preferred host conducting polymers like Polyaniline (PANI) and Polypyrrole (PPy), which are synthesized in laboratory within the kind conducting chemical compound composites.

Polypyrrole (PPy) could be a sort of organic chemical compound fashioned by chemical change of Pyrrole. It’s conjointly referred to as conducting polymers. The honor in Chemistry was awarded in 2000 for work on conductive polymers together with Polypyrrole.



Most commonly PPy is prepared by oxidation of pyrrole, which can be achieved using ferric chloride in methanol:

$$n\ C_4H_4NH + 2\ FeCl_3 \rightarrow (C_4H_2NH)_n + 2\ FeCl_2 + 2\ HCl$$

Polymerization is thought to occur via the formation of the pi-radical cation $C_4H_4NH^+$. This electrophile attacks the C-2 carbon of an un-oxidized molecule of pyrrole to give a dimeric cation $(C_4H_4NH)_2]^{++}$. The process repeats itself many times. Conductive forms of PPy are prepared by oxidation (p-doping) of the polymer:

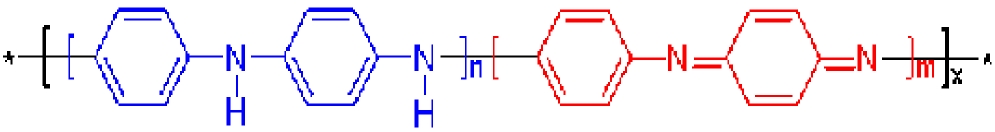
$$(C_4H_2NH)_n + x\ FeCl_3 \rightarrow (C_4H_2NH)_n Cl_x + x\ FeCl_2$$

The polymerisation and p-doping also can be affected electrochemically. The ensuing semiconductive polymers square measure in the buff off of the anode. Polypyrrole is additionally being investigated in temperature cell technology to extend the catalyst dispersion within the carbon support layers and to sensitize cathode electro-catalysts, because it has been inferred that the metal electro-catalysts (Pt, Co etc.) once coordinated with the atomic number 7 within the Pyrrole monomers show increased chemical element reduction activity.

Polypyrrole (together with alternative conjugated polymers like Polyaniline, Poly (ethylene dioxythiophene) etc. has been actively studied as a cloth for artificial muscles, a technology that might supply various blessings over ancient motor causative parts. Polypyrrole was accustomed coat oxide and reverse section oxide to yield a cloth capable of ion exchange and exhibiting hydrophobic interactions. Polypyrrole was utilized in the microwave fabrication of multi-walled carbon nanotubes (CNTs), a replacement methodology that permits getting CNTs in an exceedingly matter of seconds. The Chemical and Engineering News in 2013 gives that Chinese analysis has made a waterproof polymer sponge coated with a skinny layer of Polypyrrole that absorbs 20 times its weight in oil and is reusable.

Polyaniline (PANI) could be a conducting chemical compound of the semi-flexible rod chemical compound family. Though the compound itself was discovered over one hundred fifty years ago, solely since the first years of 1990 decades, has Polyaniline captured the extraordinary attention of the scientific community. This interest is attributable to the discovery of high electrical conduction. Amongst the family of conducting polymers and organic semiconductors, Polyaniline has several engaging process properties. As a result of its made chemistry, Polyaniline is one among the foremost studied conducting polymers of the past fifty years.

Polymerized from the cheap phenylamine compound, Polyaniline is found in one among three perfect chemical reaction states:



2.4 Polyaniline (PANI)

In the above figure, x equals 0.5 the degree of chemical action (DP). Leucoemeraldine with n=1, m=0 is that the totally reduced state. Pernigraniline is that the totally oxidised state (n=0, m=1) with imine links rather than alkane series links. Studies have shown that the majority varieties of Polyaniline square measure one in all the 3 states or physical mixtures of those parts. The emeraldine (n=m=0.5) type of polyaniline, typically said as emeraldine base (EB), is neutral, if doped (protonated) it's known as emeraldine salt (ES), with the imine nitrogen's protonated by the acid. Protonation helps to delocalize the otherwise unfree diiminoquinone-diaminobenzene state. Emeraldine base is considered the foremost helpful type of Polyaniline attributable to its high stability at temperature and also the proven fact that, upon doping with acid, the ensuing emeraldine salt type of Polyaniline is extremely electrically conducting. Leucoemeraldine and permigraniline square measure poor conductors, even once doped with the acid.

The colour modification related to Polyaniline in numerous reaction states will be utilized in sensors and electrochromic devices. though color is helpful, the most effective technique for creating a Polyaniline sensing element is arguably to require advantage of the dramatic changes in electrical conduction between the various reaction states or doping levels (D. M. de Leeuw, et al. 1997) J.

Treatment of emeraldine with acids will increase the electrical conduction by 10 orders of magnitude (H. Burroughes, et al. 1988). Undoped Polyaniline contains a conduction of 6.28×10^{-9} S/m, whereas conductivities of 4.60×10^{-5} S/m will be achieved by doping to four percent of HBr. A similar material will be ready by reaction of leucoemeraldine. Polyaniline is nobler than copper and slightly less noble than silver that is that the basis for its broad use in computer circuit board producing and in corrosion protection.

4. Synthesis of Polymers and their Polymer Composites

Electrochemical polymerization (ECP) is performed in a single-compartment cell containing electrochemical bath which includes a monomer and a supporting electrolyte dissolved in appropriate solvent. It also includes three different electrode such as working electrode (cathode), reference electrode and counter electrode (anode). Film deposited on the counter electrode (anode). Usually ECP is carried out either Potentiostatically (i.e. constant voltage condition) or Galvanostatically (i.e. constant current condition) by using a suitable power supply. Potentiostatic conditions are recommended to obtain thin films while galvanostatic conditions are recommended to obtain thick films (R. Menon, et al., 1998).

Chemical polymerization is that the process within which comparatively tiny molecules, referred to as monomers, mix with chemicals to supply a really giant catenulate or network molecule. The compound molecules could also be all alike, or they will represent two, three, or a lot of totally different compounds. Sometimes a minimum of one hundred compound molecules should be combined to form a product that has sure distinctive physical properties like physical property, high durability, or the flexibility to make fibers that differentiate polymers from substances composed of smaller and easier molecules; usually, several thousands of compound are incorporated in an exceedingly single molecule of a compound. The formation of stable valence chemical bonds between the monomers sets chemical change aside from different processes, like crystallization, within which giant numbers of molecules combination underneath the influence of poor intermolecular forces.

5. Conclusion

The chalcogenide glasses are the low-phonon-energy substances and are typically clear from visible to the infrared. Doping chalcogenide glasses by the rare-earth components has displayed the varied applications of active optical devices. Due to their giant nonlinearities, the chalcogenide glasses are promising materials for all optical switching (AOS) applications. Doping chalcogenide glasses with rare-earth components has allowed the likelihood of victimization these glasses for active applications like amplifiers and lasers. There are various useful applications within the medical, civil and military areas as the chalcogenide glass fibers transmit within the IR. The Chalcogenide fibers are well-suited for chemical-sensor applications i.e., fiber-optic chemical detector systems for the quantitative remote detection and identification further as detection chemicals in the mixtures.

References

1. Anderson, P. W. (1958), *Phys. Rev.*, 109, 1492–1505.
2. Ahonen, H. J. et al., (2000), *Macromolecules*, 33, 6787–6793.
3. Burroughes, J. H. et al., (1988), *Nature*, 335, 137-14.
4. Burroughes, J. H. et al., (1990), *Nature*, 347, 539-541.
5. Bolto, B. A. et al. (1963), *Aust. J. Chem.*, 16, 1090–1103.
6. Chiang, C. K. et al., (1977), *Phys. Rev. Lett.,* 39, 1098–1101.

7. Chiang, C. K. et al., (1978), *J. Chem. Phys*., 69, 5098-5104.
8. Chiang, C. K. et al., (1978), *J. Am. Chem. Soc*., 100 1013–1015.
9. Chiang, J. C. and MacDiarmid, A. G. (1986), *Synth. Met*., 13, 193-205.
10. de Surville, R. et al., (1968), *Electrochim Acta*, 13, 1451-1458.
11. de Leeuw, D. M. et al., (1997), *Synth. Met*., 87, 53-59.
12. Diaz, A. F. (1981), *Chemica Scripta*, 17, 145–148.
13. Heeger, A. J. (2002), *Physica Scripta*, 102, 30-35.
14. Kanatzidis, M. G. (1990), *Chem. Eng. News*, 68, 36-54.
15. MacDiarmid, A. G. (2001), *Synth. Me*t., 125 11-22.
16. Mamunya, Y. P. et al., (2002), *Eur. Polym. J*., 38, 1887-1897.
17. Mülhaupt, R. (2004), *Angew. Chem. Int. Ed*., 43, 1054–1063.
18. McMillan, W. L. (1981), *Phys. Rev. B*, 24, 2739–2743.
19. Menon R., et al., (1998), 2nd ed., Skotheim, Inc. New York, 27.
20. Mohilner, D. M. et al., (1962), *J. Electrochem. Soc*, 84, 3618.
21. Shirakawa, H. et al., (1977), *J. Chem. Soc. Chem. Commun*., 13, 578-580.
22. Yasui, T. (1935), *Bull. Chem. Soc. Japan*, 10, 305-311.
23. Ziemelis, et al., (1991), K. E. *Phys. Rev. Lett*., 66, 2231-2234.