

Polyvinyl Alcohol Conjugates: Smart Materials

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ABSTRACT

Prior to the early 1920's, chemists doubted the existence of molecules having molecular weight greater than a few thousand. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules. Staudinger proposed they were made up of macromolecules composed of 10,000 or more atoms.

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Introduction

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He formulated a polymeric structure for rubber, based on a repeating isoprene unit (referred to as a monomer). *For his contributions to chemistry, Staudinger received the 1953 Nobel Prize.* The terms polymer and monomer were derived from the Greek roots poly (many), mono (one) and meros (part). Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Polymer is a long chain molecule, which is the combination of a number of repeating units of identical structure. A special feature of most of the polymers, which distinguish them from metals, is their inability to carry electricity.

The insulating nature of the polymers is advantageous for many applications. For example, electrical wires are having the coating of insulating polymer, which is used to protect the short circuit. However during the last two decades; a new class of organic polymers with remarkable ability to conduct electrical current has been derived. This class of materials is called "synthetic metals". Some of these conductive materials are already under development for practical applications, such as rechargeable batteries, electrolytic capacitors, biosensors and chemical sensors [1]. They have tremendous potential for future scientific and technological development.

**Classification of polymers**

Polymers can be classified as natural, synthetic and conducting polymers [2]. Conducting polymers have recently emerged as a new class of electroactive materials and are useful for research and development. They have widened the possibility of modification of surface of conventional electrodes providing new and interesting properties. They may have different chemical structures, physical properties, mechanical behavior and thermal characteristics etc.

Natural polymers

Natural polymers are isolated from natural materials. These are also known as biological polymers. The examples of natural polymers are rubber, wool, cellulose, starch etc. These materials are extremely important in our daily life. [3].

Synthetic polymers

These polymers are manufactured from low cost and readily available petroleum fractions and the physical properties may be 'tailor made' for almost any desired application. The examples of synthetic polymers are polyethylene, PVC, Nylon and Terylene, conventionally known as synthetic or man-made polymeric substances. The first purely synthetic polymer was the phenol formaldehyde family of synthetic resins [4]. Synthetic polymers are man-made polymers and include most plastics, e.g. polyethylene, polypropylene, polystyrene and poly(vinyl alcohol). Most of these synthetic polymers can be tailor-made to suit desired functions. The greatest obstacles for some applications are biocompatibility and biodegradability. Poly(vinyl alcohol) finds wide use in industries such as the medical, [5] packaging [6] paper [7] and building industries[8].

Conducting polymers

In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene was accidentally prepared by Shirakawa et al. [9]. Subsequently, Heeger and MacDiarmid proposed that the polymer undergoes an increase in conductivity of magnitude by oxidative doping [10]. This quickly reverberated around the polymer and electrochemistry communities and an intensive search for other conducting polymers soon followed. Research on conducting polymers intensified soon after the discovery of poly (sulphur nitride) in 1975 which becomes superconducting at low temperatures [11]. Although, conducting polymer complexes in the form of tetracyano and tetraoxalato-platinates, the Krogman salts charge transfer complexes [12] had been known earlier. The significance lies in the rediscovery of PANI in 1977 using a Ziegler Natta type catalyst for polymerization by MacDiarmid et al [13].

Historical Background of poly(vinyl alcohol)

The first synthetic polymer (Bakelite) was not made until 1905. However, recent technical advances have allowed 'specialist' polymers, like PVA, to be manufactured. With PVA it's possible to tailor specific properties such as high strength or solubility to specific jobs. By varying the molecular structure during the manufacture process, a range of PVAs can be produced, each one subtly different from the others. Therefore different PVAs are used in a vast array of industrial, commercial and medical applications. *Poly(vinyl alcohol) (PVA) was first prepared by Herrmann and Haehnel in 1924 via the base catalyzed alcoholysis of poly(vinyl esters)* [14]. The reactions were not commercially viable due to evolution of large amounts of heat which made the reactions hazardous. In 1925, the Duo developed new and safe method for the large scale production of poly(vinyl acetate), resulting from vinyl acetate and becoming the most widely used monomer for the preparation of PVA precursor. The PVA so prepared was colloidal in form and was used in textile sizing.

In 1931 proposed the preparation of PVA fiber. This was a novel idea, which was only put into practice seven years later [14] who prepared acetalized PVA fiber which closely resembled viscose rayon and cotton fibers. At that time PVA fibers were regarded as a possible replacement for cellulose in some applications. However, due to the high cost associated with their production PVA fibers have not yet reached their full potential.

General properties and applications of PVA

Polymer application is indisputably related to polymer structure. Typically PVA is a polyhydroxyl polymer capable of undergoing both intra and intermolecular hydrogen bonding. The small size and the strong hydrogen bond interactions of the hydroxyl groups force the polymer chains into a crystal lattice resulting in PVA being partially crystalline. Consequently PVA has excellent mechanical and thermal properties; excellent oxygen barrier properties, oil, grease and organic solvent resistance, low moisture permeability, high heat resistance and UV and IR radiation stability. In addition to these it is biodegradable and non-toxic. Likewise fibers derived from PVA have similar properties along with high tensile and compressive strengths, high tensile modulus and high abrasion resistance. As a result of these unparalleled properties of PVA has found usage as adhesives [15], colloids in emulsion polymerization [16], binders in the paper industry, films [17], membranes[18], as drug delivery systems in medicines, cancer cell-killing embolic material [19] and in textile and paper sizing [14].

Modification of PVA

Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties with high tensile strength and flexibility.

Why the need for modified PVA ?

PVA is a sought-after polymer because of its excellent properties which include biocompatibility, oil, grease and solvent resistance, low moisture permeation, oxygen barrier properties, and non-toxicity. In the medical industry, PVA is insolubilized by crosslinking. The hydrogels produced are used in the preparation of contact lenses and materials for drug delivery [20]. PVA fibers for application in the clothing and construction industries are crosslinked [21] prior to use. Anionic groups are attached onto PVA in order to prepare temperature and pH sensitive hydrogels [22], soft tissue replacement hydrogels [23], water-alcohol separation membranes [24], and high strength transparent films [25]. In the paper industry PVA is added as a polymeric additive where it imparts oil, oxygen and moisture resistance properties [26]. In order to enhance the interactions between PVA and cellulosic fibers, the chemical modification of PVA by attachment of ionic groups is desirable. Attachment of cationic groups enhances the interaction between the anionic cellulosic fibers and the PVA [27]. The ionic bonds formed are stronger than hydrogen bonds, and a combination of the two types of bonds yields better fiber-fiber interactions.

Types of modification

The hydroxyl functionality of PVA undergoes all the reactions typical of secondary alcohols. Modification can thus be brought about by two techniques:

Copolymerization of the vinyl ester and second monomer with the required functionality, followed by hydrolysis [28].

Post polymerization modification, whereby PVA is first prepared and then Modified [29].

Stereoregularity of PVA

Polymer configuration and conformation describe its geometric structure. Configuration refers to the order that is determined by chemical bonds which cannot be altered unless chemical bonds are broken, while conformation refers to the order arising from the rotation of molecules about the single bonds. Configuration of polymer chains is described by the stereoregularity.

Stereoregularity refers to the arrangement of adjacent repeating units in a polymer chain. Three distinct features are often associated with the stereoregularity of monosubstituted vinyl polymers (monomer type $\text{CH}_2=\text{CH}_x$): isotactic, syndiotactic and atactic. When a polymer is isotactic (*Fig. 1*) all the substituents are on the same side of the polymer chain. In the case of a syndiotactic polymer, the polymer chain is composed of alternating substituent groups. In an atactic polymer there is random arrangement of the substituents on either side of the polymer chain (*Figure-1*).

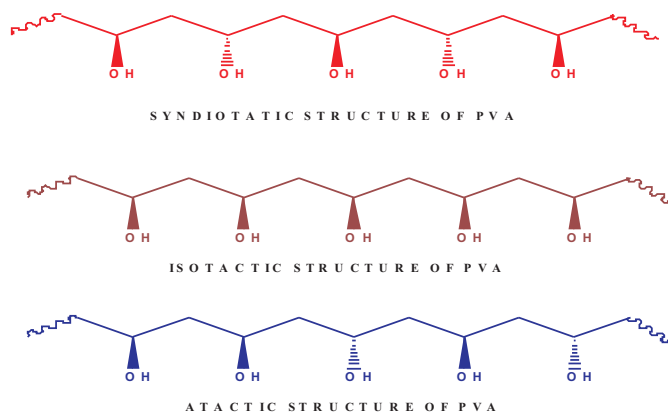


Figure-1: Isotactic, syndiotactic and atactic sequences of fully hydrolyzed PVA.

Depending on the number of repeating units under consideration, tacticity can be further classified in terms of diads, triads, tetrads, pentads etc where by two, three, four and five repeating units are considered While dealing with diad sequences, the pairs of adjacent repeating units can

either be isotactic (meso,) or syndiotactic (racemo,) to one another as shown in *Figure-*



Figure- 2: PVA diad sequences.

For triad sequences, three adjacent repeat units are under consideration and they can be described as being isotactic (*mm*), heterotactic (*mr*) or syndiotactic (*rr*) to one another as shown in figure-3.

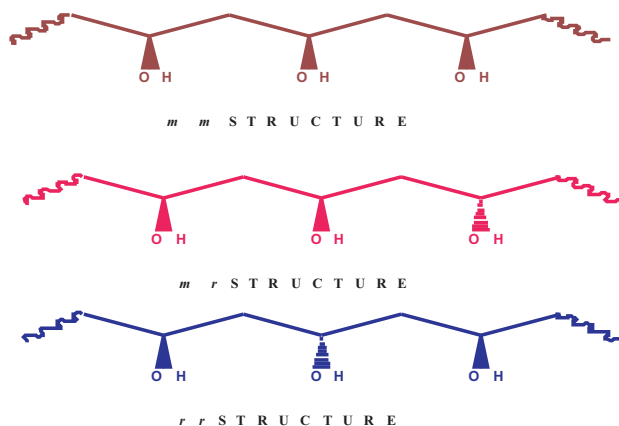


Figure-3: PVA triad sequences for fully hydrolyzed PVA.

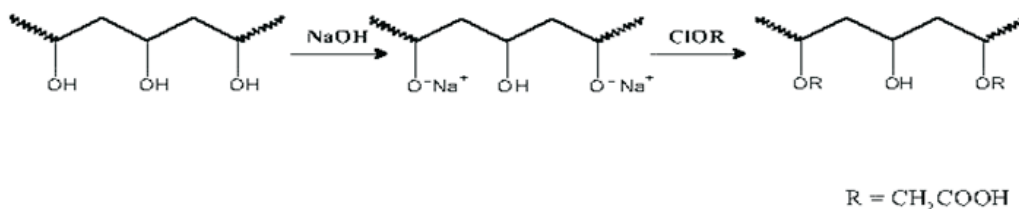
Tetrad sequences are given as *mmm*, *mmr*, *rmr*, *mrm*, *rrm* and *rrr*. The same general rules for the assignment of stereosequences are observed for higher tacticities i.e. pentad, heptad, etc. Generally the FRP propagation mechanism follows Bernoullian statistics [30]. This means that the stereoregularity of the growing chain is not affected by the ultimate or penultimate monomer to be added to the polymer chain. Stereoregularity can be determined by nuclear magnetic resonance via integration of the relevant signals or be calculated using the probability parameters P_m and P_r [31].

Reactions of the hydroxyl group

PVA can undergo esterification and etherification reactions with monomers of the appropriate functionality to yield both anionic and cationic PVA.

Etherification

Williamson's ether synthesis has been used in the preparation of anionic and cationic PVA, cellulose [32] and starch [33]. It is a two steps process: the first step involves the alkalization of the hydroxyl group with a strong base such as sodium hydroxide and in the second step the reaction of that alkoxide with an alkyl halide to yield the ether. PVA has been functionalized by etherification with a functional alkyl halide. *Scheme-4* summarizes the steps involved in Williamson's etherification of PVA [34].

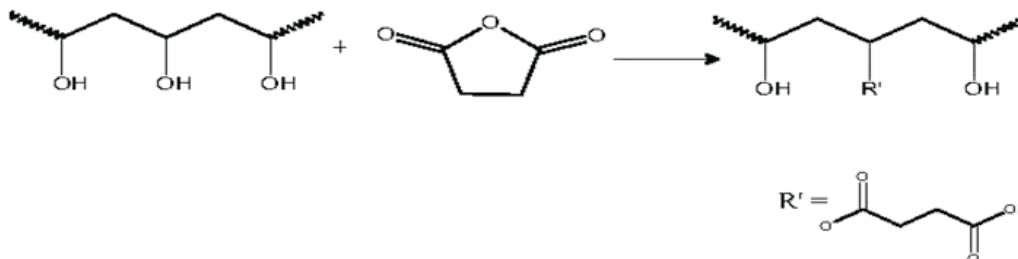


Scheme-4 : Williamson's etherification of PVA

Anionic or cationic PVA can be synthesized by using anionic or cationic alkyl halides. Haacket al. [33] prepared cationic starch electrolytes via Williamson's ether synthesis using 3-chloro-2-hydroxypropyltrimethyl ammonium chloride and 2,3-epoxypropyltrimethyl ammonium chloride as the etherifying agents.

Esterification

PVA can also be modified by esterification with carboxylic acids or anhydrides. Gimenez et al. [34] synthesized anionic PVA by reacting PVA with phthalic anhydride and succinic anhydride. The esterification reaction is illustrated in Scheme-5



Scheme -5 : Esterification reaction of PVA with succinic anhydride

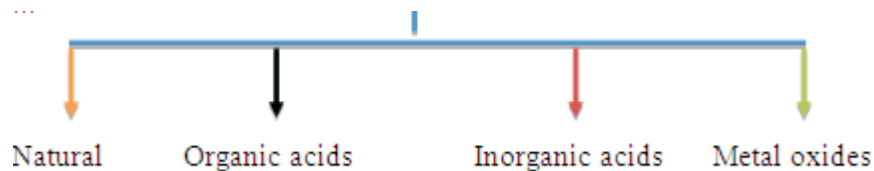
Doping in PVA polymers

Doping of polymeric semiconductors is different from that in inorganic or traditional semiconductors. Doping of conducting polymers involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled chains and fibrils. The dopant concentrations may be as high as 50%. Also incorporation of the dopant molecules in the quasi one-dimensional polymer systems considerably disturbs the chain order leading to reorganization of the polymer. Doping of the polymer leads to the formation of conjugation defects, viz. solitons, polarons or bipolarons in the polymer chain [35].

Classification of doping agents

Doping agents or dopants are either strong reducing agents or strong oxidizing agents. They may be neutral molecules or inorganic salts, which can easily form ions. Thus, dopants may be classified as,

Dopants



Application of PVA conjugates as a conducting polymers

Academic, governmental and industrial laboratories throughout the world are involved in the basic research and assessment of possible applications of conducting polymers that makes the conducting polymers an interdisciplinary area in nature [36]. These conducting organic molecular electronic materials have attracted much attention largely because of their many projected applications as shown in Fig.-6. There are two main groups of applications. The first group utilizes their conductivity as main property. The second group utilizes the electroactivity. An extensive research has to be done to bring many of the applications in a reality. The stability and possibility both need to be substantially improved if they are to be used commercially. Conducting polymers are becoming of increasing importance for a variety of applications, but still more research is needed to a certain their use in sensors, electronic devices, electroluminescence, molecular electronics as catalysts supports, low conducting coating for high voltage transmission cable and for anodic protection of steel against corrosion. A temperature sensor for the applicable component

is also important commercially [37]. Antistatic coating also plays a vital role in the case of micro films, slide plate in audio cassettes and in photographic film developing [38].

The cost of such polymers must also be substantially lowered. However, one must consider that although conventional polymers were synthesized and studied in laboratories around the world, they did not become widespread until years of research and development had been done. In a way, conducting polymers are at the center stage of development as their insulating brothers were some 50 years ago. Regardless of the practical applications that are eventually developed for them, they will certainly challenge researchers in the years to come with new and unexpected phenomena [39].

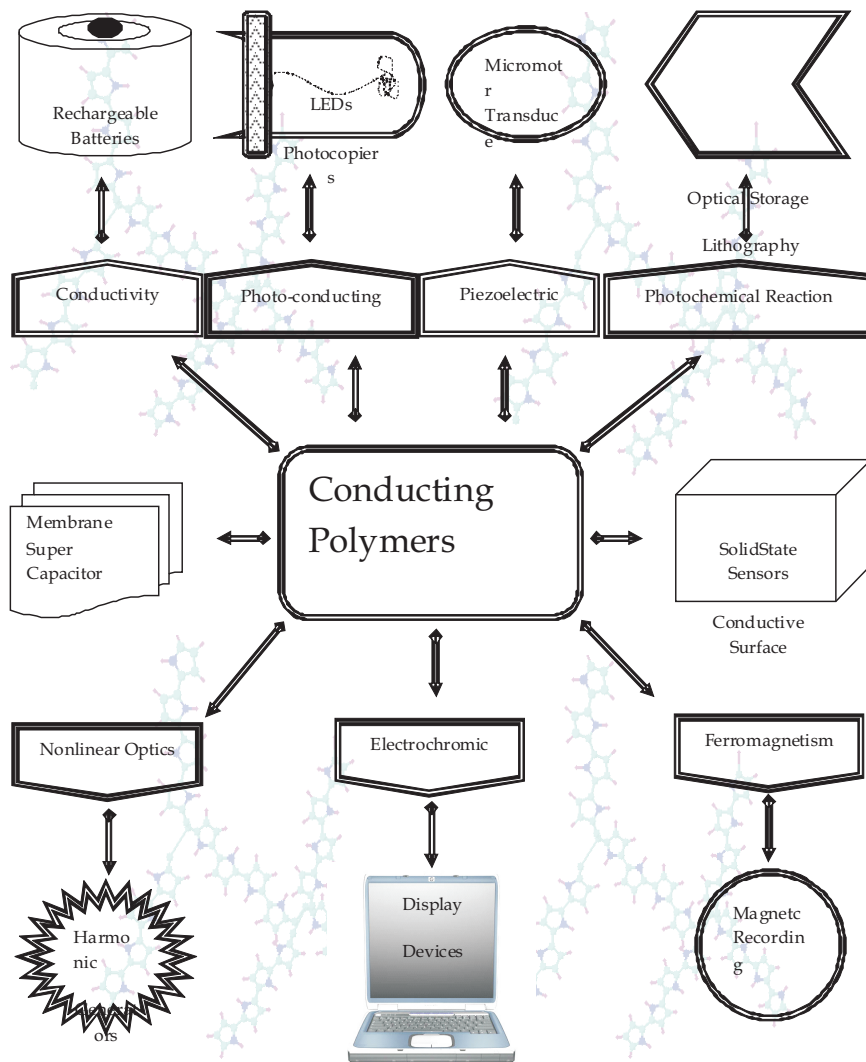


Fig.-6 : Applications of conducting polymers

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