



## CHAPTER I

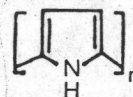
## INTRODUCTION

For electrical conduction to take place in a material, charge carriers must be present in the form of electrons, holes (the absence of an electron or electron vacancy) or ions; and for current to flow they must be able to move through the material (i.e. be mobile). Most of the low levels of conductivity measured in conventional insulating polymers are due to the motion of ions caused by the presence of impurities, and the best insulator is produced by careful purification of the polymer. High degrees of conductivity in polymer can only be obtained through the motion of free electrons or holes which are present in the structure. Unfortunately, most conventional polymers do not have any free electrons available because the chemical bonds in the structure are mainly saturated covalent ones[1].

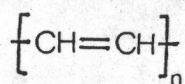
The polymers, currently being developed for electrical conduction purpose, have their molecular backbones containing conjugated double or triple bonds or delocalization of the electron in the structure such as poly(sulphur nitride)(1), polypyrrole (2), polyacetylene (3), polyphenylenes (4) etc.



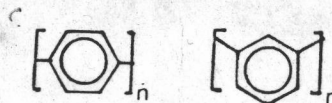
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The achievement of tailored electrical properties of polymers is pursued utilizing four distinct strategies[2-3]. The first strategy consists of seeking the modification of the intrinsic bulk properties of polymer by processing, especially by pyrolysis. In this approach, acceptable electrical properties are developed by altering the chemical composition or the structure of the initial material. The second strategy is the attainment of the desired conductivity by the incorporation of macroscopic pieces of conducting material, e.g. metal flakes, carbon-black particulates, or carbon fibers into host polymers to form conducting composites. The third strategy focuses on altering the properties of polymers at the molecular level by controlled incorporation of dopants to form charge-transfer complexes with the host polymer. This approach is referred to as molecular doping because it consists of trying to insert isolated molecular dopants, e.g. triphenylamine, arsenic pentafluoride or iodine into polymers. The fourth strategy to obtain the electroactive polymer involves the attachment of a donor species onto a polymer chain by a covalent linkage and then introduces ion-radicals onto the polymer matrix by oxidation of the bound donor species. This approach is referred to as a chemically attached system because the donors are chemically bonded to the

polymer chain. The details and a review of each strategy are reported in chapter II.

Immobilization of electroactive species onto polymer chain results in an electroactive polymer that has suitable properties for coating the electronic devices such as conducting and semiconducting electrode surfaces. This is well-known as "chemically modified electrodes (CME's)". The electroactive polymer can be used in many fields, e.g., electrocatalysis[4], electroanalysis[5-8] (as a sensor), photo-electrocatalysis[9], xerography[10-11], electrochemical display technology and information storage[12-14], photocorrosion protection[15-16], and polypeptide membranes[17].

The focus of this research is on the chemically attached technique. Previously, this technique for producing electroactive properties of polymers has been investigated by the substitution reactions of the pendant chloromethyl group in the polymer with the monofunctionalized pi-donors in aprotic polar solvent [4] which were used to remove the phase barrier by dissolving both ionic nucleophile and organic polymer reactants. However, there are disadvantages in the use of these dipolar aprotic solvents, especially in their applications on an industrial scale, as they are both expensive and difficult to recover [18-20].

Acceleration by some quaternary ammonium salts and crown

ethers had been found in the reaction of a chloromethyl group in the polymer with nucleophilic reagents in aprotic polar solvents; however, these reactions even proceed without the quaternary ammonium salt and crown ether in the aprotic polar solvents. On the other hand, over the past several years phase-transfer catalysis has been found to be useful in many organic reactions [19-20]. The phase-transfer catalysis was also applied to syntheses of polymers such as polycarbonate, polyether, polythioether, and polyester and to modifications of polymers such as poly(vinyl chloride), cross-linked poly(vinylbenzyl chloride), and poly(1-chloro-2,3-epoxypropane)[21].

Recently, the substitution reactions of the pendant chloromethyl groups in the polymers with nucleophilic reagents have been studied by using phase-transfer catalysts (PTCs) in non-polar solvents such as toluene, chlorobenzene, diglyme, and others[22]. This simple and economical method is very important for the modifications of the commercial polymers such as polymer supports, polymeric reagents, polymeric catalysts, and polymeric carriers. Also the reactions of the active alkyl halide and alkyl sulfonates with nucleophilic reagents have been studied [19-20]. Furthermore, the catalytic effect, the reactivity of alkyl halides with nucleophilic reagent, the activity of PTCs and the reactivity of haloalkyl group with nucleophilic reagents were studied from those results.

The relationship between the catalytic activity of PTCs

and the reactivity of chloromethyl group with the nucleophilic reagents in the solid-liquid two-phase reactions of poly(vinylbenzyl chloride) with potassium acetate and potassium thioacetate using quaternary salts and crown ethers as a PTC under mild condition has been studied [21]. The catalytic effect of PTCs in the substitution reaction of poly(vinylbenzyl chloride) with various nucleophilic reagents in solid-liquid and liquid-liquid two-phase systems using PTCs under mild condition was also investigated [22].

The use of PTC in the syntheses of the electroactive polymers by using the chemically attached technique has been studied [23]. In those studies, the ferrocene derivatives were chosen as a donor molecule and were coupled with chloromethylated polymers in toluene. However, the optimum reaction condition in the syntheses has not been investigated.

In this research, the optimum condition in the syntheses of the electroactive polymers is investigated by using the chemically attached technique. The polymers studied are the chloromethylated polymers, and the ferrocene derivative is used as a donor molecule. The esterification or substitution reactions of the pendant chloromethyl groups in the polymers with a donor molecule is studied under phase-transfer conditions.

The objective of this investigation was to synthesize three chloromethylated polymers. They were chloromethylated

polysulfone (POLYMER 1)(5), poly(vinylbenzyl chloride) (POLYMER 2)(6) and poly(vinylbenzyl chloride-co-2-ethoxyethyl methacrylate) (POLYMER 3)(7). These chloromethylated polymers were coupled with an electroactive species, cesium ferrocenecarboxylate (CFC)(8), by using phase-transfer catalysts (PTC) in nonpolar solvent. Polymer structure and compositions were analyzed by standard methods (e.g. IR, NMR, Viscosity, UV spectroscopy, Elemental analysis). The effect of changing reaction temperature, mole ratio of CFC/ $-\text{CH}_2\text{Cl}$  in POLYMER 1, amount of PTC, rate of stirring, type of solvents, reaction system and type of PTCs on the esterification reaction were studied in detail. Furthermore, the influence of polymer structure on the ability of substitution reaction was also investigated.

