INTRODUCTION

INTRODUCTION

There is growing need for materials having desirable chemical, mechanical and electrical properties at room temperature as well as higher temperatures and long period of time without significant loss in properties . The impact of this underscope truth have vividly directed the attention of investigators to polymeric system. New material development is aimed improving the range of service of polymers to meet practical needs.

Polymer is derived from the greek poly and meros meaning many and parts respectively. Some scientist prefer to use the word macro molecule or large molecule instead of polymer.

" According to V. A. Kargin (1), polymers now strongly occupy a prominent place in practically all branches of technology , agriculture and life. Their production is being developed vigorously. According to the forecasts of specialists the volume of production of polymeric materials will be comparable with the volume of production of metals and will considerably exceed this subsequently. The increase in production is dependent not on increase in output of individual polymers but also on continuous appearance of new modified polymer, improvement of the properties and increase in the service life of already known materials and the discovery of meal, previously unknown fields of application of polymers. All this involve a huge complex of varied scientific problems ".

" Contemporary polymer science , which is an enormous, extra ordinarily diverse, rapidly developing field of knowledge is divided in sections of organic and physical chemistry, physics and mechanics. Some of these section merge with molecular biology and medicine and the materials obtained as a result of the progress of polymer science are widely used in various branches of technology and agriculture. Despite the very varied interests and objectives, polymer science is a single field with characteristic closely interwoven special problem tasks and method of approach".

"The assortment and often also the supply of high molecular weight organic compounds in nature is limited. This refer to cellulose, proteins nature rubber and a few other substances.

Therefore extensive development of polymers was achieved only after methods had been worked out, synthesis of polymers from low molecular weight compounds (monomers) by addition polymerization or polycondensation" .

" Despite the great deal of attention given at the present time to the building of regular molecular constructions in chains of monomers efforts to produce new polymers have not lessened, one of the most important tasks in this field is the synthesis of polymers of high heat resistance, while preserving the mechanical properties (strength elasticity) of ordinary polymers. Such materials are extremely necessary in modern technology (aeroplane construction space research etc..). The majority of polymers are organic compounds, which normally have very low heat resistance. They do not withstand temperature above 150^0 - 200^0 C. Inorganic compounds have greater thermal stability but they do not possess the valuable properties of organic polymers (elasticity for example). Therefore the first step in the field of synthesis of heat resistant polymers were directed toward the preparation of linear chain polymers in which some of the " organic" atoms (H, C) were replaced by "inorganic" atoms or groups (NO_2, Cl, SO_3H etc.) thus there appeared the other hetero-organic polymers. The heat resistance of these polymers in fact proved to be 100 - 200 C higher than that corresponding polymers consisting only of carbon and hydrogen".

The inclusion of inorganic atoms for the improvement of thermal stability was not considered to be the ultimate goal of the polymer chemists and therefore several new polymeric materials containing carbon and other hetero atoms have appeared in the last one and a half decades and detailed studies regarding high temperature stability and other applications have been reported in the literature.

The field of polyester and polyaraide resin is extensively explored and they have been shown to have versatile applicability in the preparation of paints, varnishes lacquers, lubricants, insecticides, protective coating , floor tiles and extender or plasticiser.

Originating with the pioneering researches of staudinger, "polymer science" continues its onward journey unabated. The handful of monomers which contributed largely to form the very basis of polymer science and the physical and chemical aspects of it, has proliferated tremendously with the novel synthesis of many variations of vinyl and other monomer systems. At the same time, new experimental approaches and the new theoretical concepts have added and will keep on adding to the multifarious developments in the field of polymer science.

The ever increasing demand for application oriented polymeric materials has necessitated in-depth research in synthesis and characterization of new systems. At the same time, the challenging possibility that the properties of a know polymer can be adequately altered through chemical modifications has added a new dimension to the polymer world and research by now , a mammoth literature (2) has accumulated on chemical modification of polymers.

The work embodied in this thesis in concerned with the the chemical modification of very well known polymers - poly(vinyl alcohol) , poly (vinyl chloride) and poly (vinyl acetate) literature on which is indeed very large.

The major use of poly(vinyl alcohol). is as a textile size. Particularly for cotton, polyster blends poly (vinyl alcohol) is water soluble. The aqueous solution is not particularly stable especially traces of acid or base are present, still it is regarded as the most important drawback.

Similarly PVC is most widely used domestic plastic of the day but nevertheless , its thermal & light instability still is regarded as its drawback. And poly (vinyl acetate) is also widely used in adhesives, both of the emulsion type and of the hot-melt type. But this polymer is atactic and hence amorphous , sticky and undergoes several cold flow at only slightly elevated temperatures. Low molecular weight polymer are brittle but become gumlike. It is very sensitive to heat & light and that is its drawback.

Keeping in view the more important attempts to modify poly (vinyl alcohol), poly (vinyl chloride) and poly (vinyl acetate), which will be highlighted in the following pages -. This research is also concerned with the synthesis and characterization of a novel ion-exchange resins.

In order to appreciate the significance of the research thus achieved, it is necessary to keep abreast of the most significant development in the field. Accordingly this thesis summarises some important aspects of chemical modification of polymer in general.

SOME GENERAL ASPECTS OF THE CHEMICAL MODIFICATION OF POLYMERS

The physico-chemical properties of a polymer can be modified by suitable chemical modifications with conventional reactions such as elimination, addition, cyclization, substitution and the typical reaction characteristic of the functional groups of the organic compounds. In most cases, the modified polymers are characterized by many improved properties which make them in this context and are now discussed briefly in the subsequent paragraphs.

Reactivity of Functional Groups of Polymers

The functional groups present in a polymer will determine the mode of reaction by which the polymer can be modified. When a polymer contains functional groups, it undergoes the typical reactions for organic compounds such as esterification, saponification, etherification, condensation etc. Due to the changes in solubility and consequently the morphology of the polymer, these chemical transformations are not expected to proceed with a quantitative yield so that the resultant polymer usually contains both the transformed and untransformed groups.

However, the organic reactions of the high polymers usually depend largely on the functionality of the groups and the location of reaction sites in the polymers.

Monofunctional Chemical Reactions

This type involves the modification of the polymer involving the modification of one functional group or atom. Monofunctional polymeric reactions proceed generally through the same mechanism as that for similar low molecular weight compounds. The acetylation of poly (vinyl alcohol) with acetic anhydride, the acidolysis of poly (N-vinyl-ter-butylmethane) with hydrobromic acid , the methylation of poly (acrylic acid) with diazomethane, the reduction of poly(methyl methacrylate) are some of the examples belonging to this category. (3-5)

Polyfunctional Chemical Reactions

Complexity will arise when more than one functional groups present in the polymer undergo chemical transformations due to the possibility of various types of reactions. In this case, the relative position of the reactive groups plays an important role in the final degree of conversion and the chemical transformation is influenced by the following spatial arrangements of the monomeric units in the polymer :

(I) Head to tail arrangement,
(ii) Head to head arrangement,
(iii) Microtacticity of the polymer.

Functional group interactions sometimes offer the new routes for the synthesis of some compounds which are generally not obtained by direct synthetic procedure. Teyssie et.al . (6) for example , reported the Friedel-Craft condensation of poly (vinyl chloride) with aromatic hydrocarbons to yield styrene units and 1,4-methyleneindline rings.

Site of Reactions

Sometimes statistical transformation of the groups may occur independently along a polymer chain in the reactions discussed above. The liable site present in the polymer which is particularly sensitive to a radical attack is also important. Besides these, the reactivity of the end groups and side groups present in the macromolecular chain is of considerable importance for this type of reactivity of macromolecules.

CHEMICAL MODIFICATION OF VINYL POLYMERS THROUGH DIFFERENT TYPES OF REACTIONS

Some important chemical reactions are frequently used for the chemical modification of vinyl polymers. A brief discussion on these follows below.

(i) Chloromethylation

Many reports are available (7-13) which include the modification of vinyl polymers through chloromethylation reaction. Chloromethyl ether is a good solvent (14) for vinyl aromatics and rapidly swells crosslinked copolymers which, in turn, is used for chloromethylation. Sometimes, the rate is increased by the use of catalysts such as $AlCl_3$ or $ZnCl_2$ (15). Introduction of the base polymer due to the presence of liable chlorine atom which can further undergo different types of reactions such as amination (7-13), phosphorylation (16) etc.

(ii) Amination

Amination of chloromethylated vinyl polymers leads to the preparation of anion-exchange resins - weak base resins having primary, secondary and tertiary amino groups will obtained using ammonia or primary or secondary amine as the amination agent (7,9,11,13). The reaction with tertiary amines yields strong base resins having quaternary ammonium groups. (8,10,11,13).

(iii) Phosphorylation

Phosphorylation reaction of vinyl polymers has been carried out in presence of PCl_3 using Friedel-Craft catalyst anhydrous

$AlCl_3$. Alkaline hydrolysis of the phosphorylated product at 60^0 - 70^0 C followed by the treatment with 1-2N HCl gives phosphonic acid groups (17,18) whereas hydrolysis under mild conditions (19) also yields phosphonic acid groups. The hydrolyzed products can be used as phosphorylated cation-exchange resins.

(iv) Sulfonation

Sulfonation is one of the most important methods by which the vinyl polymers have been widely modified. Sulfonation can be carried out either by treating the polymer with a suitable sulfonating agent directly or by using a suitable solvent. The common sulfonating agents are concentrated $H_2SO_4.SO_3$ or chlorosulfonic acid and the suitable solvents for sulfonation are 1,2-dichloroethane, carbon disulfide and other halogenated solvents. Jones reported (20) that generally, introduction of sulfonic acid group in a benzene ring will occur in 1 : 1 ratio.

Sulfonation of polymers results in the incorporation of either strong cation-exchange sulfonic acid ionogenic groups or non-ionogenic sulfone groups (20). The latter results in the cross linking of two polymer chains and is usually obtained during the direct sulfonation of the polymer matrix by concentrated $H_2SO_4.SO_3$ (in absence of solvent).

(v) Dehydrohalogenation

Depending upon the conditions used, various products may be obtained by dehydrohalogenation of halogenated vinyl polymers and then grafting suitable compounds onto it. For example, Jain et al (21). reported the grafting of methylmethacrylate onto dehydrochlorinated PVC. The grafted polymer exhibits considerable improvement of the different properties of the unmodified PVC. Kennedy et al (22). also reported the improvement of thermal stabilities of grafted and alkylated PVC-based polymers.

(vi) Addition Reaction

These comprise reactions including the addition of thiols (23-25) to unsaturated polymers and hydrogenation of unsaturated polymers under suitable conditions of temperature and pressure in presence of suitable catalysts (26-29).

(vii) Nitration

It is an example of a reaction in which the polymer dissolves with increasing substitution . The nitration and reduction vinyl aromatic polymers offer several ways to the preparation of electron-exchange resins (30).

PRESENT STATUS OF RESEARCH ON CHEMICAL MODIFICATION OF POLY (VINYL ALCOHOL), POLY (VINYL CHLORIDE), POLY (VINYL ACETATE)

Poly(vinyl alcohol), poly(vinyl chloride), poly(vinyl acetate) are the cheapest and most important polymers and has got wide technological as well as common domestic applications. But their inferior thermal stability, mechanical and dielectric properties,lack of crystallinity and very little electrical conductivity have limited its applicability. Further, a recent report by Biswas and Pakirisamy (31) on synthetic ion-exchange resin focused the rather meager literature available on PVC-based ion-exchange resins. With a view to improving these properties, a substantial amount of work has been carried out in this interesting field of chemical modification of above polymers. This section intends to highlight the salient aspects of the chemical modification of vinyl polymers with special reference to PVC.

COMMON METHODS FOR MODIFICATION

Modification can be broadly classification into the following ways.

Radiochemical Grafting of Different Components

Many attempts have been made to improve the different properties of PVC by radiation - induced grafting of different components onto it. Radiochemical grafting of acrylic acid containing Mohr's salt (32) enhances the melting properties and moisture regain of the unmodified PVC whereas radiation - induced nucleophilic substitution of PVC and NaN_3 in dimethyl formamide with acrylic acid (33) shows better absorbability for Cu-ion of the base polymer, although grafting efficiency is suppressed in the former case in presence of metal ion in the order :

$$Cu^{2+} < Fe^{2+} < Fe^{3+}$$

Substituted and unsubstituted acrylic esters such as neopentylglycol diacrylate and neopentylglycol dimethacrylate, when treated with PVC radiochemical, crosslinked products (34) with excellent oil aging resistance, better insulating capacity for wires and cables are obtained . γ-irradiation of PVC films swollen in acrylic acid-1,2-dichloroethane mixtures yields acrylic acid vinyl chloride graft copolymer (35) with a quasimolecular dispersion of the carboxylic acid chain in the PVC matrix. The grafted polymer shows good swelling property in water at elevated temperature at high grafting ratio in comparison to the swelling ability of methacrylic acid - vinyl chloride graft copolymer. The reduced swelling ability of the latter is related to the higher hygroscopic character of the methacrylic chains (35).

Radiation induced grafting of vinyl ether derivatives, e.g., ethyl vinyl ether (36), butyl vinyl ether (37,38), 2-N-carbazolylethyl vinyl ether (36), butyl vinyl ether (37,38), 2-N-carbazolylethyl vinyl ether (38) has been reported by several workers. Grafting of butyl vinyl ether has been performed at different temperatures of butyl vinyl ether has been performed at different temperatures using γ-irradiation in 50% solution of the either in benzene but it has been reported (37) that maximum grafting occurs at the glass transition temperature region and the rate of grafting decreases with increase in rate of diffusion of H_2O molecules (a chain transferring agent) to active centers of grafting (37,38). Grafting efficiency of 2-N-carbazolylethyl vinyl ether in dichloromethane using $AgSbF_6$ onto PVC reportedly (39) increases with decreasing temperature as well as with increasing liable allylic chlorine concentration in the polymer which may be due to the partial dehydrochlorination.

Grafting by Copolymerizing Different Components with Vinyl Chloride

Different properties of PVC have been reportedly improved by copolymerizing different monomers such as vinyl acetate, acrylonitrile, methyl methacrylate, ethylene-propylene and styrene-polystyrene with vinyl chloride. Grafting of styrene has been performed (40) in dimethyl formamide by Friedel-Craft mechanism using $TiCl_3$ as catalyst - the overall activation energy of grafting is 71.2 KJ/mole. Acrylonitrile has been grafted electrochemical onto PVC (41) by immersing it in acrylonitrile resulting 34% weight gain of the grafted has been reported with no thermal shrinkage (42). Grafting of acrylamide is influenced (43) by squaric acid and its metal ions using $AgClO_4$ as catalyst - the resultant grafted polymer is more flexible and consists of longer chain of PTHF grafted from displaced Cl-atom along the PVC chain. Polystyrene has been grafted onto PVC by Friedel-Craft mechanism at 0^0 - 20^0C in presence of $AlCl_3$ which enhances the impact strength, flux strength and heat resistance of the grafted copolymer than the homopolymers or their mechanical mixtures. Grafting of bitumens onto PVC (50) by Friedel-Craft reaction confirms improved ageing and segregation resistance of unmodified PVC. An aqueous solution of PVC on heating with an amide derivative (e.g. $HSCH_2$-CH_2-CONH-Bu) is presence of a quaternary ammonium salt [e.g. $(C_{10}H_{21})_3$ NMe^+Cl^-] followed (51) by the treatment with an epoxy resin (Epon 826) yields a polymer having better flame retardance and flexibility .

Crosslinking of PVC using Different Components :

Apart from the methods discussed earlier , improvement of different properties of PVC may be achieved by cross linking it using different components in various ways. Blending of 6-(dibutylamino)-5-triazine-2-4-dithiol with PVC (52) for 30 minutes at 180^{0}C using carbon black as filler, yields a crosslinked product with improved heat distortion temperature and zero strength but peroxide initiated (dicumyl peroxide) crosslinking of PVC with triallyl cyanoaurate and diallyl phthalate (53) yields products having young's modulii 618 and 330 kg/cm^2 at 98^0 C respectively and also improves markedly the physicochemical properties of PVC. Vinyl acetate-vinyl γ-irradiation. On dispersing PVC in n-hexane in presence of Et$_3$Al, 6-caprolactone has been grafted (44) onto PVC, the tensile strength of the modified polymer is 2.36 kg/cm^2, weight loss at 170^{0}C for 3 hrs being 0.34%. The physicochemical properties of grafted ethylene-vinyl acetate-vinyl chloride copolymer are claimed (45) to be superior to those for a mechanical mixture of PVC and ethylene-vinyl acetate copolymer whereas grafting of ethylene-vinyl acetate onto vinyl chloride in presence of an oil solution polymerization initiator (46) reportedly enhanced the elongation strength , oil resistance and brittleness temperature of the unmodified PVC. Tensile strength, modulus and elongation have also been improved by grafting alkyl(meth) acrylate (e.g., Bu-acrylate) (47) onto PVC. Vinyl chloride-polyurethane graft copolymer (48) has been prepared by radical polymerization of vinyl chloride in thermoplastic polyurethane sol - the resultant product exhibits higher tensile strength, abrasion resistance and hydrolysis resistance than unmodified PVC.

Grafting by Direct Nucleophilic Substitution

There are few reports on grafting of different components onto PVC by direct nucleophilic substitution of Cl-atom. Substitution has been achieved (49) by suspending PVC in water or other solvents and then treating it with Na-thiolate, lauryl thiolate or diethyl thiocarbamate. The grafting efficiency has been increased (upto 33%) by introducing an ether linkage at the position or adding the solvent. Grafting of polytetrahydrofuran (PTHF) onto PVC was also performed using THF as solvent chloride graft copolymer, on irradiation with 10 Mard electron beam with tris (2-ethylhexyl) trimellitate, affords a crosslinked product which shows no discoloration on heating at 100^{0}C for 48hrs. The melt flow properties of the conductive PVC-carbon black graft composite (54) are reportedly improved by using fatty acid chlorides whereas organosilane and titanate coupling agents have little effect on the melt flow. Vinyl chloride may be crosslinked using hydrogensiloxane (55) as crosslinking agent in the presence of Pt-catalyst to improve the heat degradation resistance of the base polymer - use of methylhydrogensiloxane exhibits deformation 4.1% at 120^0 C compared with 10.6% for an uncrosslinked PVC (55).

Modification of PVC by other Ways

There are several other methods by which modification of PVC can be achieved . A charge-transfer complex (56) having good heat and light stabilities is obtained by immersing PVC in $ACNMe_2$ solution containing tetracyanoquinodimethane followed by drying the product in vacuum for 2 hrs at 100^0C . The graft PVC-poly (amido amine) copolymer adsorbs heparin (57) thus providing potentially nonthrombogenic surface. ESCA characterization (57) of the graft copolymer reveals that the amount of heparin adsorbed is relatively independent on the length of the grafted chain.

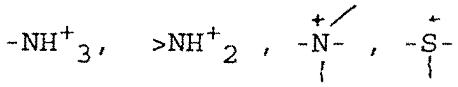
SYNTHETIC ION-EXCHANGE RESINS FROM CHEMICALLY MODIFIED POLYMERS

One of the most important uses of chemically modified polymers is their applications as synthetic ion-exchange resins.

For practical purposes, because of wide structural variations possible, the organic ion-exchangers are more potential than the natural ion-exchangers such as ion-exchange coals, mineral ion-exchangers etc. The organic ion-exchangers are macroreticular, three-dimensional crosslinked network of hydrocarbon chains having ionogenic groups

$$-COO^- \; , \; -SO^-_3 \; , \; -PO^{2-}_3$$

as cation exchanging groups, and



$$-NH^+_3 , \; >NH^+_2 \; , \; -\underset{|}{\overset{+\diagup}{N}}- \; , \; -\underset{|}{\overset{+}{S}}-$$

as anion exchanging groups. All these ion-exchangers have a hydrophobic part (i.e., the hydrocarbon part) and a hydrophilic part (i.e., the incorporated ionogenic groups) which are responsible for the ion-exchanging capacity of the resins. A schematic diagram of an ion-exchange resin is given in the Figure 1.

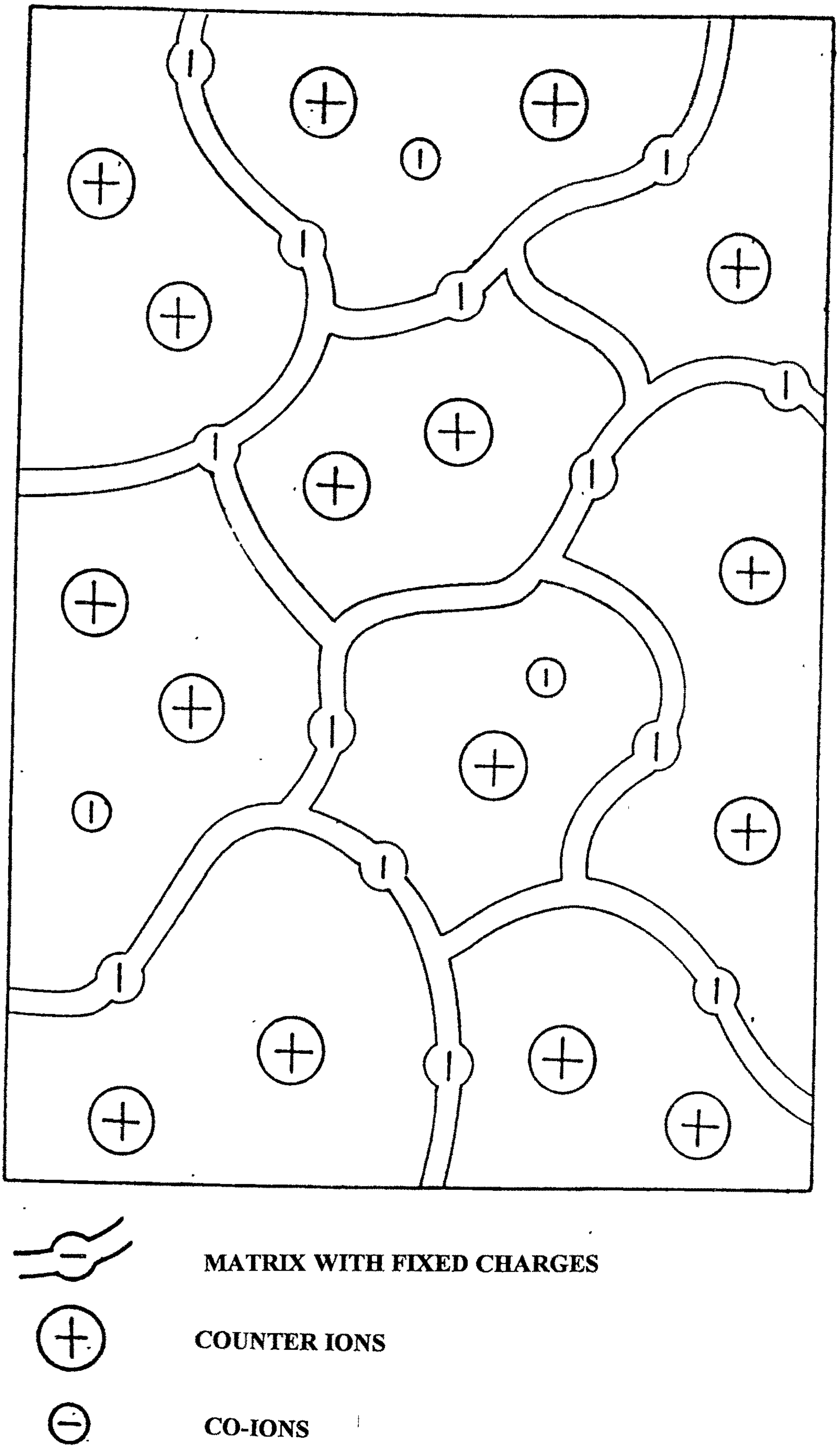


Fig. 1. Schematic Diagram of an Ion-Exchange Resin.

Organic ion-exchangers based on styrene, S-DVB copolymers have been most exhaustively studied. In comparison, little attempts appear to have been made for the development of ion-exchangers through chemical modification of polymers, they are simplest (structurally) and the most widely used polymers. A recent review on synthetic ion-exchange resins by Biswas and Pakirisamy (31) focused the rather meager literature available on PVC-based resins. Dima et al. (58-62) reported the synthesis and properties of polyene sulfonic acid cation-exchange resins obtained by the sulfonation of PVC using chlorosulfonic acid in 1,2-dichloroethane solvent having sulfonic and carboxylic exchange capacities of 2 - 4.3 meq/g and 0.3-1.5 meq/g respectively . The resins synthesized from suspension-polymerized PVC show greater sulfonic and carboxylic exchange capacities than those obtained from and emulsion-polymerized PVC (59). Sulfonation of dehydrohalogenated PVC gives bifunctional cation-exchange resins containing - SO_3H and -COOH groups (63-64). The amount of -SO_3H groups present in the resin is independent of the temperature but the amount of -COOH groups increases with increase in temperature. Arylation of PVC with benzene at 0^0C followed by sulfonation with chlorosulfonic acid in 1,2-dichloroethane at 20^0C and 90^0C gives cation-exchange resins. (65) A brown cation-exchange resin (66) may be obtained by heating PVC with 3-aminopyridine in water at 100^0 -110^0C, which with an aqueous solution (pH - 7) containing 100 mg/l gold (as $HAuCl_4$) for 1hr yields an aqueous solution containing 2.1 mg/l gold. A spherical high-strength anion-exchanger (67) has been obtained by amination of polyvinylbenzyl chloride with 5 -

70% solution of polyamines in water. Nishimure and Nizutani (68) reported a PVC-based cation-exchange resin membrane having a high concentration of ionogenic groups. Indusekhar et al. (69) also reported a cation-exchange membrane from PVC and other vinyl monomers. The membrane may be prepared by mixing and dispersing PVC, dioctyl phthalate and cyclohexanone and then adding it to a mixture obtained by heating styrene, divinylbenzene and benzoyl peroxide for 15 minutes at $60^0 - 90^0C$. The resultant dispersion was heated at $60^0 - 90^0C$ for 2 - 5 hrs. and was spread over a glass plate to prepare a film. The film was sulfonated with concentrated H_2SO_4 (98%) to give a cation-exchange membrane having high ionic selectivity greater than 0.92 in 0.1 - 0.2N KCl solution and electrical resistance 2 ohm cm^2. Radiation induced graft copolymerization of 2-acrylamido-2-methyl-propanesulfonic acid onto PVC (70) in water-acetone system may also give also rise to a sulfonated cation-exchange resin having maximum adsorptive activity to metal ions (mainly Li ion) in the 2 : 3 water : acetone ratio.

AIM AND OBJECT OF THE PRESENT WORK

The survey of the available literature on chemical modification of polymers [poly (vinyl alcohol), poly (vinyl chloride) and poly (vinyl acetate)] reveals that considerable scope exists for further modification of these polymers with a view to developing modified systems with properties superior to the polymers which were of interest from the point of view of study included are physico-chemical and ion-exchange properties. Thermal property and electrical properties are included in last chapters.

The literature survey revealed that the -OH , Cl and $-CH_3$ groups displacement method has been successfully used for introducing various groups in polymer systems. However, it appears that no systematic attempt has so far been made to study the effect of introducing aromatic phenolic groups or other groups in polymeric systems and to evaluate any modification in the above mentioned properties. Accordingly , the first objective of this work was to introduce (i) anthranilic acid (ii) gallic acid (iii) p-hydroxybenzaldehyde or p-hydroxybenzoic acid (iv) pyrogallol (v) 8-hydroxyquinoline (vi) salicylic acid (vii) hydroquinone and (viii) β-resorcylic acid moieties. Appropriate reaction conditions leading to optimum yield's were developed and the structures of the modified polymers were analysed through elemental and spectroscopic analyses.

The second novel aspect of this research was the synthesis of ion exchange resins from modified polymers. Numerous chelating polymers which have been studied so far, are mostly based on polystyrene and polystyrene - divinyl benzene resins and no information is available concerning the ion-exchange resins made from modified polymers [except poly(vinyl chloride)] .

The last objectives were to study the influence of such chemicals modification on the following properties of the modified polymers. such as, total capacity , moisture retention ability , density , void volume fraction, rate of exchanger , pH titration behaviour , apparent pK_a, pK_b and isoionic point values, oxidation resistance, the effect of equilibration at different temperatures on the capacity of the resin and swelling behaviour in various solvents. They were further characterised by thermal analysis and electrical properties which were included in last chapters.

The results obtained are discussed in the following pages.