SYNTHESIS OF SOME RADIATION GRAFTED MEMBRANE FOR THE REMOVAL OF ARSENIC AND SOME HEAVY METALS FROM CONTAMINATED WATER

A Dissertation Submitted in the Partial Fulfilment for the Degree of
Master of Philosophy (M. Phil) in Chemistry

Submitted by

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PREFACE

Investigation embodied in this dissertation entitled "Synthesis of Radiation Grafted Membrane for the Removal of Arsenic and some Heavy Metals" was carried out in the Department of Chemistry, Bangladesh University of Engineering and Technology (BUET).Dhaka, Bangladesh, under the supervision of Dr. Md. Wahab Khan, Professor, Department of Chemistry, BUET, Dhaka.

The present studies are directed towards the development of novel methodologies for the synthesis of chelating functionalized radiation grafted polymeric materials for the removal of arsenic and some heavy metals.

First of all I would like to convey my heartfelt gratitude to my supervisor, Professor Dr. Wahab Khan who given me the opportunity to work in this field. I am indebted to him for the keen interest, constant encouragement, moral support and helpful guidance in carrying out this work.

I would like to convey my heartfelt gratitude to Dr. Feroza Akhtar. Director, International Affairs Division, Bangladesh Atomic Energy Commission, who introduced me to this field. I am indebted to him for the keen interest, constant encouragement, moral support and helpful guidance in carrying out this work.

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I express the gratitude to my wife Ms. Urme Binte Salam, Assistant Commissioner and Magistrate for her encouragement, immeasurable cooperation and sacrifice during the full tenure of this work.

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I am thankful to all of the Staffs of Chemistry Department, BUET for their help. Finally, I express my gratitude to the members of my family for their encouragement, sincere cooperation and sacrifice during the tenure of this work.

28·06·08·

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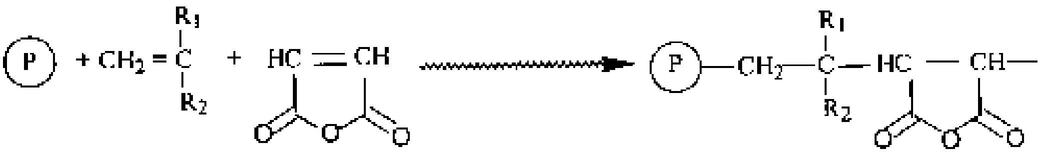
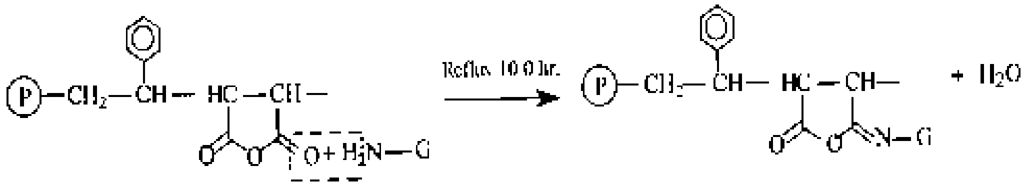
Thesis title: **Synthesis of Some Radiation Grafted Membrane for the Removal of Arsenic and Some Heavy Metals from Contaminated Water**

Abstract

In this project radiation graft copolymerization of styrene/maleic anhydride (Sty/MAn) and methyl methacrylate/ maleic anhydride (MMA/MAn) binary monomer system onto low density polyethylene (LDPE), low density polypropylene (LDPP), polyethylene pellet (PEP), polypropylene pellet (PPP), and heat pressed polyethylene (HPPE) membranes were investigated (Scheme 1). The synthesized grafted products were treated with different ammonia derivatives. In this context numerous chelating functionalized radiation-grafted polymeric materials were synthesized such as polyethylene grafted polymer of styrene/maleic anhydride (PE-g-P(Sty/MAn)) with hydrazine, phenylhydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride and *S*-Benzyl-thiouronium chloride (Scheme 2). Chelating functionalization behavior of radiation-grafted polymeric materials of synthesized polyethylene grafted polymer of PE-g-P(MMA/MAn) was also investigated. Anion exchangeable good quality polyvinyl alcohol (PVA) hydrogel was synthesized through radiation technique. The synthesized grafted and chelating functionalized products were characterized by the gravimetric method and infrared spectroscopic technique. The affinity of the treated grafted films and the hydrogel to recover arsenic and some heavy metals. such as Fe(III), Cr(III), Cu(II), Ni(II), Mn(II), Pb(II) was investigated at room temperature. It was found that the synthesized hydrogel remove 34.54% arsenic and 59.03% Fe(III) and the treated grafted membranes can remove 21.36% of Cu(II) with varying amount of other metals.



Scheme 1



Scheme 2

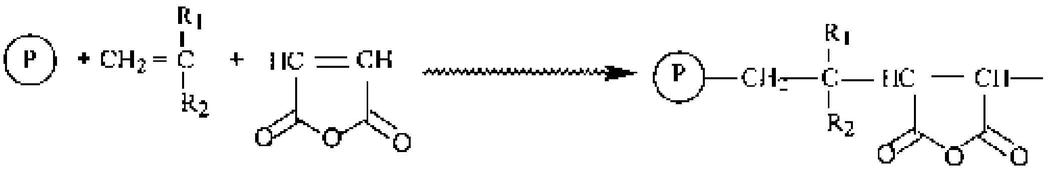
SUMMARY

Investigation incorporated in this dissertation entitled **"Synthesis of Some Radiation Grafted Membrane for the Removal of Arsenic and Some Heavy Metals from Contaminated Water"** has been presented in five sections. In section – 1 background and the importance of the radiation grafted membranes for the removal purposes are presented here. Section – 2, 3, and 4 deal with the detailed methodology and experimental procedures for the synthesis of radiation grafted membrane. Section – 5 representing the application of the synthesized radiation grafted membrane.

In section – 1, background and the importance of the radiation grafted membranes as well as the brief description of different polymerization process and with grafting process were explained. According to the literature survey numerous radiation grafted polymeric products were extensively used for the removal purposes are also presented. Here, arsenic and some heavy metals chemistry mentioned. In this section the scenario of arsenic in Bangladesh also focused and with in this context the possible remedies also touched.

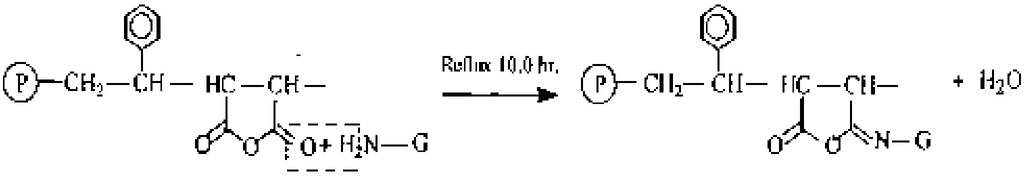
Section -2 represents the synthesis of radiation grafted membrane intermediates by using different binary monomer system on different polymeric materials as shown in the scheme1; these intermediates were used for the synthesis of our target chelating functionalized grafted product. For the syntheses of these grafted intermediates Styrene/Maleic anhydride (Sty/MAn), Methyl methacrylate/ Maleic anhydride (MMA/MAn) binary monomer systems were used onto low density polyethylene (LDPE), low density polypropylene (LDPP), polyethylene pellet (PEP), polypropylene pellet (PPP), and heat pressed polyethylene

(HPPE) used, where acetone used as the solvent. The grafting techniques were accomplished through the using of gamma radiation of ^{60}Co-gamma source.



Scheme 1

Section-3 represents the synthesis of chelating functionalized polyethylene grafted polymers with some ammonia derivatives. Here, the synthesized polyethylene grafted polymer of styrene/maleic anhydride (PE-g-P(Sty/MAn)) treated with hydrazine, phenylhydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride and *S*-Benzyl-thiouronium chloride (Scheme 2). The synthesized polyethylene grafted polymer of PE-g-P(MMAMAn)) treated with hydroxylamine hydrochloride and this grafted product do not undergo the same reaction with other ammonia derivatives also reported here.



Scheme 2

Section -4 represents the synthesis of radiation processed hydrogel. The synthesized hydrogel has anion exchangeable and cation adsorbing property. The radiation processed hydrogel was prepared by using 8.0% polyvinyl alcohol, 1.0% flour and 1.0% carrageenan. The synthesized hydrogel was used for removing the arsenic and some heavy metals from aqueous solution.

Section -5 represents the affinity of the treated grafted films and the hydrogel towards arsenic and some heavy metals. The selectivity of different chelating functionalized grafted membrane and PVA hydrogel to recover arsenic and some heavy metals , such as Fe(III), Cr(III), Cu(II), Ni(II), Mn(II), Pb(II) in aqueous solution was investigated at room temperature. It was found that the synthesized hydrogel can remove 34.54% arsenic and 59.03% Fe(III) and the treated grafted membranes can remove 21.36% of Cu(II) with varying amount of other metals.

CONTENTS

SECTION: 1

1. Background of the Present Work

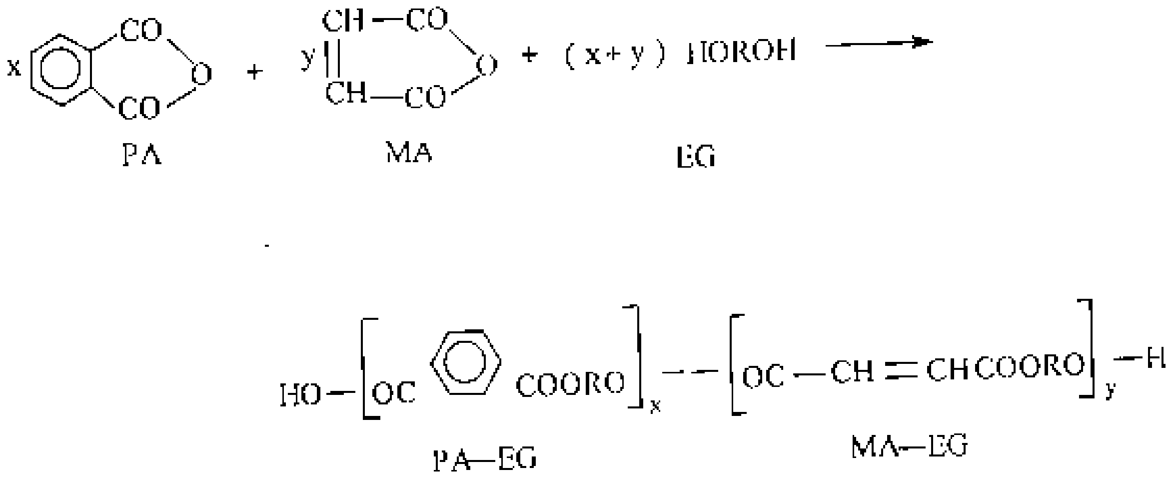
Introduction:

Recently there has been substantial growth in interest in the synthesis of radiation grafted membrane, and copolymerization onto the low density polyethylene and other polymers with the different binary monomer system [1-6]. These synthesized grafted membranes then chelating functionalized, by using various functional groups containing moieties and using these chelating functionalized grafted membranes, many researchers remove some radioactive and heavy metals from the contaminated water [7]. Some researchers investigated and reported that radiation-induced grafted product of acrylic acid (AAc) onto polyethylene (PE) film rapidly adsorbed Eu, Gd, Tb, and Dy ions at high efficiency[8]. The carboxylic acid groups on the AAc-grafted PE film acted as a chelating site for the selected lanthanide ions Complex formation of lanthanide ions and the carboxylic acid group on PE film was investigated. The application of such prepared graft copolymer-lanthanide complexes in the field of fluorescence emission displays (FEDs) may be of interest[9]. Radiation graft copolymerization of binary monomer mixtures of acrylic acid (AAc) and styrene (S) onto polypropylene (PP) films by the mutual method has been investigated and the effect of different factors that may affect the grafting yield, such as inhibitor concentration (Mohr's salt), solvent composition (MeOH and H_2O), radiation dose and dose rate, was studied[10]. Direct radiation-induced grafting of acrylonitrile (AN) onto both isotactic polypropylene (IPP) and (tetrafluoroethylene-ethylene) copolymer (ET) films has been studied and the effect of grafting conditions such as inhibitor and monomer concentrations and irradiation dose on the grafting yield was investigated[11]. here the homopolymerization of acrylonitrile was reduced to a minimum using ferric chloride ($FeCl_3$), and the suitable optimum concentration of the inhibitor. The radiation-induced graft polymerization of *N*-vinyl-2-pyrrolidone onto low-density polyethylene films was conducted with γ- radiation by a simultaneous technique[12]. In this technique, the grafted copolymer was modified with cinnamonitrile or benzylidene malononitrile. The modified and grafted films were amidoximated with hydroxylamine hydrochloride in a basic medium. However, during amidoximation, the benzylidene malononitrile was cyclized to yield isoxazole ring through an addition to the nitrile group in its structure, whereas the nitrile groups of cinnamonitrile were converted into amidoxime groups. Aquatic Treatment Systems, Inc. (ATS) develops and markets enabling technologies to remove primary contaminants, which can adversely affect human health, from drinking water. The invention of the grafted polymer electrolyte membrane, relates to a method of producing a grafted polymer electrolyte membrane, and a fuel cell comprising a grafted polymer electrolyte membrane. In particular, the grafted polymer electrolyte membrane of that invention has excellent stability during use and has good adhesion when used as a solid state polymer electrolyte in a fuel cell or water electrolysis cell[13]. A chelate-forming filter which comprises a filter medium made of natural, regenerated, or synthetic fibers wherein the fiber molecules have, incorporated therein[14] and here a precursor membrane which is capable of being graft polymerized, which is pre-treated by plasma treatment in an oxidative atmosphere, a side chain polymer is then graft-polymerized to the precursor membrane; and a proton conductive functional group is introduced to the side chain polymer. In that research, the authors mentioned that the precursor membrane may be formed from any polymer or copolymer, for example, polyethylene, polypropylene, polyvinylchloride, polyvinylidenedichloride, polyvinyl fluoride (PVF), polyvinylidenedifluoride (PVDF), polytetrafluoroethylene, ethylene-tetrafluoroethylene copolymer, tetrafluoroethylene-perfluoroalkylvinylether copolymer, and tetrafluoroethylene-hexafluoropropylene copolymer. The side chain polymer may be any hydrocarbon polymer which contains a proton conductive functional group or which may be modified to provide a proton conductive functional group. The side chain polymer may be, for example, poly(chloroalkyl styrene), poly(α-methyl styrene), poly(α-fluorostyrene), poly(p-chloromethyl styrene), polystyrene, polyacrylic acid, polymethacrylic acid, poly (vinyl alkyl sulfonic acid), and copolymers there of. Sulfonic acid group was preferred as the proton conductive functional group. The removal of cesium-134 and cobalt-60 with radiation-grafted copolymers from their liquid wastes and the introduction of new characteristics to some synthetic polymers were achieved through the Y-radiation-induced graft copolymerization of an acrylamide/vinyl acetate comonomer onto polypropylene films for the preparation of synthetic membranes[15]. The possibility of practical uses for these membranes in the removal of cesium-134 and cobalt-60 from their liquid wastes was also reported. Use of radiation grafted PVC-acrylamide membranes in radioactive waste treatment studied by using the acrylamide monomer (AAm) was grafted onto poly(vinyl chloride) (PVC) films using Y-radiation to produce high performance functional membranes which can be employed as ion-exchangers. The preparation and characterization of the synthetic membranes was also reported in that research[16].

It is known that, of inorganic form, arsenite [As (III)] is the most abundant species that exists in natural water in Bangladesh[17]. Thus the removal of arsenic from drinking water has become a topic and challenge of the people in order to protect their lives. Apart from this arsenic contamination, metals are also the most important trace level constituents of natural water[18]. Many heavy metals are harmful as well and the level of drinking water standards is deteriorated due to the presence of these metals[19]. In recent years, a great deal of interest has been observed in relation to the applicability of chelating agents for removal or separation of metal ions from contaminated water[19, 20, 21].

Concept of Copolymerization

A polymer whose chain molecules are composed of more than one kind of repeating chemical units is commonly called a copolymer. A simple case of a step growth copolymer is the linear unsaturated polyester formed by inter molecular condensation of a mixture of phthalic acid (anhydride) (PA) and maleic acid (anhydride) (MA) with a given diol, say ethylene glycol (EG) resulting in what may be termed as a copolyester with at least two distinctly identifiable repeating units in the chain molecules:

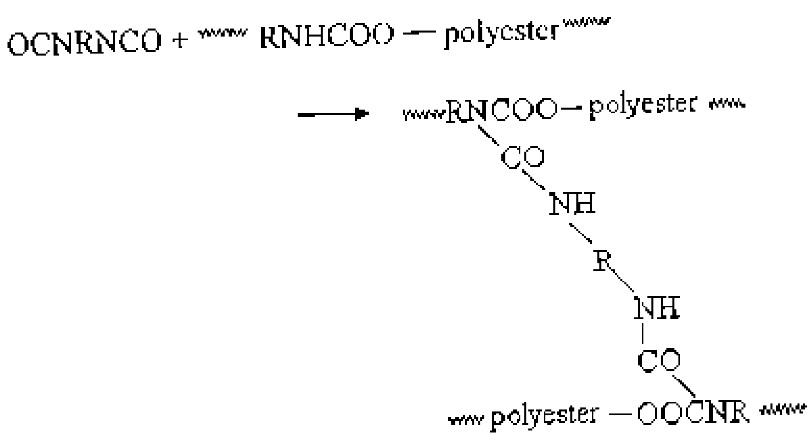


Above equation, showing the formation of copolyester by a polycondensation process clearly identifies two types of repeating chemical units, (PA-EG) and (MA-EG), though in a very oversimplified manner[22]. In the actual copolymer the two types of distinguishable chemical units would normally appear at random along the chain, and the overall composition would depend on the relative values of x and y. Similarly ,one can prepare step-growth copolymers with different interunit chemical linkages by proper selection of combinations of different bifunctional monomeric species bearing. $-OH, -COOH; -NH_2, -NCO$ or other functional groups, and using two, three or all the functional species simultaneously or in a phased manner in the presence or absence of a related polyfunctional and monofunctional species during the synthesis. However, polycondensation leading to formation of copolymers from this kind of complicated mixtures of monomeric species is of little or rare practical importance of relevance. More relevant step-growth copolymerization systems involve formation of copolymer structures with a specific interunit linkage such as amide (– CONH), ester (– COO –), urethane (– NHCOO –), etc; following the approach as in Eq.(4.1).It may or different kinds of interunit linkages, such as low molecular weight linear or branched polymers and selected bifunctional monomeric species examples of this kind of step growth copolymers are found in the making of polyester urethanes or polyether urethanes using low molecular weight performed linear polyesters or polyether with hydroxyl end groups and allowing them to further react with each other through diisocyanates leading to chain extension and producing useful elastomeric products commonly known as

$$n\mathrm{HO\text{-}polyester{-}OH} + n\mathrm{OCNRNCO} \longrightarrow [\mathrm{polyester{-}OOCNHRNHCOOO}]_n$$

(polyesterurethane)

polyurethane rubbers, which may be vulcanized or cross-linked when heated with excess diisocyanates in a mould, e.g.,



An altogether different kind of copolymer is obtained by polymerization of two or more vinyl and related monomers, all taken together in a reaction vessel. The copolymer molecules contain segments of all the monomers used in their structure, usually in a calculable proportion depending on many factors depending on the feed monomer composition, the chain growth mechanism and the inherent reactivities of the monomers with a given chain carrying species[22].

The number of reactions to be necessarily considered to describe the copolymerization of more than one monomer increases geometrically with increase in the number of participating monomers, giving increasingly varied and complicated structure of the copolymer molecules at the same time. A case of binary copolymerization involving the two monomers M_1 and M_2 may be simply represented as:

$$nM_1 + mM_2 \longrightarrow \sim\sim (nM_1)_n — (nM_2)_m —$$

monomer mixture

copolymer

The structure of the vinyl copolymer shown in above Eq. is far too simplified, however; the two monomer units appear in the copolymer structure in a random sequence in general.

Binary Copolymerization of Vinyl Monomers by Free Radical Mechanism

Analysis of the System and the Reactions Involved

In a free radical copolymerization, the number of chain free radicals to be considered is given by the number of monomers present and the reactivity of a chain radical is particularly determined by the free radical bearing terminal monomer unit and the size and chemical nature of those preceding the radical bearing terminal unit in the chain considered to be of little consequence in this context.

In a binary copolymerization, therefore, to different chain radicals can be identified and each radical being capable of adding both the monomers, though not usually or necessarily with equal or comparable ease, the system is characterized by four simultaneously occurring propagation reactions. With two different kinds of chain radicals, and considering termination taking place only bimolecularly, the process is associated with three different chain terminations reactions along with the possibility of several chain transfer reactions. Chain initiation takes place by reaction of primary radicals (derived from decomposition of the radical initiator used) with either of the monomers present with almost equal ease and efficiency in general or else, in the absence of an initiator, by thermal or photo activation of either monomer with different relative ease depending on the chemical nature of the monomer used.

Structure and Reactivity of Monomers and Radicals

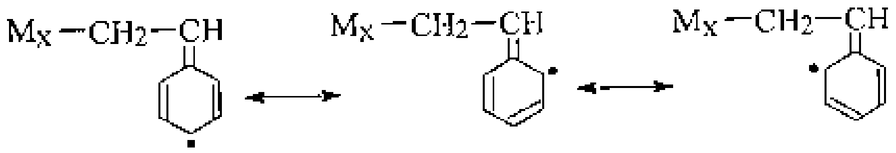
Nature and number of substituents and the site of the substituents in case the unsaturated (olefinic) monomers bears more than one substituent on the unsaturation have decisive roles to play in determining the reactivity or stability of a specific monomer and the corresponding radical. The substituents influence or modify reactivity or stability by three basic approaches: (i) by activating or deactivating the // bond and thus rendering the monomer less stable and hence more reacting or vice versa, (ii) by imparting enhance or reduced stability to the derived radical depending on better or limited prospects of or resonance, and (iii) by providing different degrees of steric hindrance at the reaction site.

A relative order of reactivities of a series of monomers (M_2) is conveniently obtained by comparing the reciprocal monomer reactivity ratio. The order of monomer reactivities is roughly parallel for all radicals, with some exceptions the general order of enhancement of reactivity of a monomer by a substituent toward radical attack is as follows [22]:

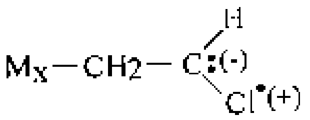
$—C_6H_5, —CH{=}CH_2 > —COR, —CN > —COOH, —COOR > —Cl > —OCOR > —OR$

Resonance Stabilization

The relative order of monomer reactivities toward radical generally corresponds to the stabilization of the radical formed on addition of the monomer .The more reactive monomer generally yields radical of higher stability through resonance. A second substituent on the same carbon atom usually leads to an additive effect on the monomer reactivity or on the resonance stabilization of the corresponding radical. Among the vinyl monomers styrene is the most and vinyl space acetate is the least reactive ,while styrene radical is the least and vinyl acetate radical the most reactive .The styrene radical owes a high order of stability due to the high order of stability due to the possible existence of three quinonoid resonance structures[22], and as



a consequence, the radical stability corresponds to a resonance energy of nearly 20 kcal/mol. In comparison, substituents having no unsaturation in conjugation with the ethylenic or vinylic double bond, such as — Cl or — OR, produced radicals of resonance energy as low as 1 - 4 kcal/mol, as because only polar or nonbonded forms contribute to resonance[23].



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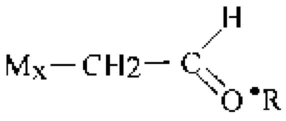


The substituents also tend to stabilize the monomer, but the degree of stabilization is much smaller for the monomer than for the radical. The resonance stabilization due to conjugation amounts to only about 3 kcal/mol for styrene and butadiene as against a resonance stabilization to the tune about 20 kcal/mol for the corresponding radicals.

Technical Significance of Copolymerization

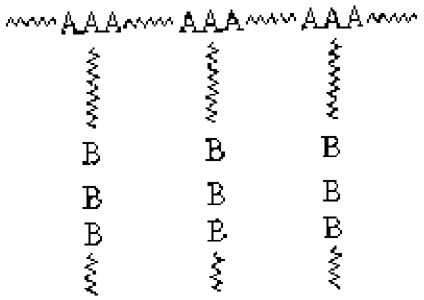
The modification of a polymer by introducing a second monomer during the polymerization process has long been used to alter its physical properties and sometimes to achieve improved processing characteristics. Incorporation of a second monomer structure as repeating units in the polymer. i.e., the copolymer molecules reduces overall molecular symmetry leading to lowering (or loss) of degree of crystallinity and of softening temperature[22]. Copolymerization is therefore considered as a case of internal plasticization the modification of poly (vinyl chloride), (PVC) by taking small proportions of vinyl acetate (VA) monomer with vinyl chloride (VC) during polymerization to make more flexible and soluble resins of easier process ability is well known. Similarly, straight polybutadiene has many technical disadvantages arising from it poor take and difficult process ability. But copolymerization of butadiene with styrene, acrylonitrile and other monomers has lead to many technically important resinous and rubbery products. There is practically unlimited scope for variation in polymer structure and polymer properties through copolymerization. In fact, the number of technically important copolymers far surpasses that of important homopolymer. Besides the synthesis of copolymers having random or alternate sequences of monomeric units which have so far being considered and discussed. it is also possible to recognized and synthesized copolymers having to other different kinds of sequences, and there commonly known as block and graft copolymers.

Block and Graft Copolymers

The probability of finding long sequences of one monomer in an ordinary random copolymer is very remote except in the trivial case where one monomer is present in a large excess. Methods of synthesis of polymer containing such long sequences of specific monomer units are of great interest, since they often lead to polymers with properties widely different from those of the two homopolymers or the corresponding random copolymers or their blends. Polymers with long sequences of two monomers can have two distinctive arrangements of change: (i) "Block copolymers" — where the sequences follow one another along the polymer chain axis:

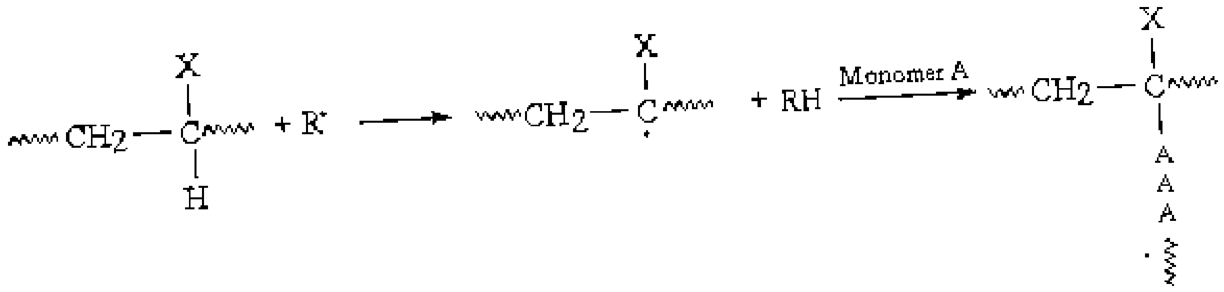
∿∿∿AAABBB∿∿∿BBBAAA ∿∿∿AAABBB∿∿∿

(ii) "Graft copolymer" — where long or short sequences of one monomer appear as grafted or pendent change linked to a "backbone" of long sequences of another monomer:



The ultimate aim in preparing a graft or block copolymer is to obtain the desired copolymer free from homopolymers as per as practicable. Although the copolymer structure resulting from the graft and block copolymerization processes are quite different, the former being a chain-branching process and the later a chain extension process, both may be considered as a chain modification process differing only in direction. They are usually prepared by polymerizing a second monomer in presence of the preformed polymer of a different kind of monomer and the process generally depends on the presence of labile sites particularly sensitive to radical attacks at different points along the chain axis or chain ends of the reactant macromolecules. Reactive groups, according to their presence as end groups or as side groups along the chain may also lead to formation of block or graft copolymers by appropriate design of the overall process polymer-polymer reaction through selected functional groups present or incorporate on them may also lead to block or graft copolymer structure. Studies of block copolymer are very much limited in comparison with those of graft copolymers because formation of block copolymers solely depends on the presence of reactive groups or labile atoms at chain ends of linear polymers. The physical properties of high polymers containing blocks of two or more repeat units two, three or many blocks in a chain have not been studied and examined extensively, even though modification of polymers to block copolymer structures is being used commercially. A commercial product commonly known as "thermoplastic elastomer" is a triblock copolymer containing a middle block of polybutadienes of polyisoprene linked in a linear fashion to two end blocks of polystyrene and is prepared by anionic polymerization. Formation of polyurethane rubbers by chain extensions of different polyesters or polyethers as depicted by previously mentioned also involves an approach to block copolymerization.

Graft copolymerization usually involves polymerization of a monomer onto a different polymer backbone; the various reactions associated with polymerization process can be utilized for the synthesis of graft copolymers. Most graft copolymers are formed by free radical polymerization, and often the major activation involves chain transfer. The reaction shown involves generation of a radical site on the performed polymer by a chain transfer mechanism and then growth of a new polymer structure from that new radical site:



(Graft Copolymer)

Techniques of polymerizations:

For laboratory and industrial purposes, polymerization is practiced by a variety of approaches and techniques that requires different design considerations with respect to recipe of polymerization physical conditions for the process and process equipment. Generally, polymerizations are studied and practiced by four different techniques:

1. Bulk or Mass Polymerization
2. Solution Polymerization
3. Suspension Polymerization and
4. Emulsion polymerization

Of the four techniques, the last two are essentially heterogeneous polymerization systems containing a large proportion of a non-solvent, usually water acting as a dispersion medium for the immiscible liquid monomer. Bulk and solution polymerization may be either homogenous all the way, or homogenous to begin with, but becoming heterogenous with progress of polymerization due to the polymer formed being insoluble in its monomer (for bulk polymerization) or in the solvent used to dilute the monomer (for solution polymerization). Polymerization of monomers used in the gaseous phase to begin with also usually end up in a heterogenous system. Most condensation polymerizations are conveniently done by employing or solution techniques.

1. Bulk or Mass Polymerization

Polymerization in bulk, i.e., of undiluted monomer is apparently the most obvious is not the most simple method or technique of polymer synthesis. In terms of polymerization recipe, this obviously provide the most simple system, requiring the use of a very low concentration of an initiator as the only addi8tive of monomer and that again decomposes and reaches almost a vanishing concentration at the end of the polymerization process. For uncatalyzed vinyl polymerization (using no catalyst or initiator) done thermally photochemically or otherwise, the polymer produced would be most pure, free from any (additive) contaminants except probably traces of unreacted monomer.

Vinyl polymerizations are highly exothermic. Again, to obtain polymer at convenient rates, temperature in the range 80-200^{0}C is needed. For dissipation of the heat liberated with progress of polymerization, continuous stirring of the monomer-polymer mixture is essential. But the stirring process and heat dissipation becomes progressively difficult with conversion due to the gain in the medium viscosity due to solubilization or precipitation of the polymer in the monomer, more so in the high conversion zones. The auto acceleration of gel effect often makes the problem more acute. If left uncontrolled, excessive rise of temperature at local points known as "hot spots" may lead to discolouration, thermal degradation, branching development of chain unsaturation or even crosslinking, thus giving rise to irreproducible and often inferior product quality. Because of these problems and disadvantages, bulk polymerization techniques finds rather limited use in commercial production of vinyl polymers, e.g., in the production of poly(methyl methacrylate) as acrylic castings (sheets), and in the making of certain grades of polystyrene , poly(vinyl chloride) and (low density) polyethylenes. The heat dissipation problem in such a cases is kept to a minimum and within tolerable limits by two approaches: (i) by carrying out the polymerization to low conversions as in high pressure polymerization of ethylene using narrow but long tubular reactor at temperatures far higher than the melting temperature of the polymer; and (ii) by accomplishing the polymerization in stages – first up to about 20-30% conversion in a stirred reactor at 80-100°C and subsequently allowing the monomer-polymer syrup(viscous mass) poured in an appropriate assembly to polymerize to (near) completion at progressively higher temperatures in stages (e.g., preparations of acrylic castings from methyl methacrylate monomer) or allowing the monomer-polymer syrup, called the prepolymer to flow under gravity aided by some positive pressure down a vertical tower reactor with appropriate design of heat transfer or heat dissipation and having a temperature gradient with increasing temperature zones downward for the reaction mixture till it reaches at the stage of near complete conversion (manufacture of polystyrene from styrene monomer).

2. Solution Polymerization

Solution polymerization, i.e., polymerization of a monomer in presence of a diluent miscible in all proportions with the monomer and usually with the ability to dissolve polymer is conceived as a means to overcome much of the problems and disadvantages of the bulk method. The solvent reduces the viscosity gain with conversion, allows more efficient agitation or stirring of the medium, thus effecting better heat transfer and heat dissipation and minimization or avoidance of local overheating or heat accumulation. Although the solution technique allows much better control of the process, it has its own demerits. The solution method often requires handling of flammable or hazardous solvents and removal or recovery of the solvent to isolate the polymer after polymerization is over. Chain transfer to solvent may also pose a problem and purity of the polymer may suffer due to retention of last traces of solvent in the isolated product. Solution polymerization, is however advantageous if the polymer formed is to be applied in solution by brushing or spraying as in the case of making or coating (lacquer) grade poly(methyl methacrylate) resins from methyl methacrylate and related monomers. In certain cases the solvents generally used may not be able to dissolve the polymer being formed and so the system becomes heterogenous in character with polymer formation (polymerization of acrylonitrile in water or in some common organic solvents).

3. Suspension Polymerization:

This is a case of heterogenous polymerization right from the beginning. This technique is design to combine advantages of both the bulk and solution techniques, and it is one of the extensively employed techniques in the mass production of vinyl and related polymers. This technique primarily involves breaking down or dispersion of the liquid monomer into separate tiny droplets in a large continuous mass of a non solvent commonly referred to as the dispersion or suspension medium, by efficient agitation. Water is invariably used as the suspension medium for all water insoluble monomers because of many advantages that go with it, viz., ready availability at low cost, non-toxic nature, ease of storage and handling without the necessity of recovery, etc. Moreover the boiling temperature of water is a convenient upper limit for radical vinyl polymerization and in aqueous suspension system the rise in temperature in any location due to exothermic nature of polymerization cannot go beyond the boiling temperature of the medium.

The size of the monomer droplets usually range between 0.1-5mm in diameter. Continuous agitation is allowed to prevent coalescence of the droplets. Low concentrations of suitable water soluble polymers such as carboxymethyl cellulose (CMC), or methyl cellulose, poly (vinyl alcohol) (PVA), gelatine, etc., are used to raise the medium viscosity and they play the role of suspension stabilizers particularly in the intermediate stages of conversion when the tendency of the suspended droplets to collects together becomes high as the polymer beads become strictly. The water soluble polymeric stabilizer form a thin layer on the monomer-polymer droplets and stabilization is affected due to repulsion between like charges thus gathered on different droplets. Finally divided suspended clay practical such as kaolin or china clay in small amounts is sometimes used to interfere mechanically with the agglomeration of breads. In suspension polymerization oil-soluble initiators such as organic peroxides, hydroperoxides or azocompounds are used and thus, each tiny droplet behaves as a miniature bulk polymerization system. At the end of the process, polymers appear in the form of tiny beads or pairs and hence, the process is also known as bead or pearl polymerization. The polymer are filtered, washed profusely with water to remove the water soluble stabilizer as far as practicable, and dried. They, however, usually retain traces of stabilizers besides the residual initiators as contaminant.

4. Emulsion Polymerization:

(a) **Description of the system** The use of water as a medium of polymerization by the solution and suspension technique described and discussed above. A special feature about water is that it provides us with a medium characterized by zero chain transfer constant [27]. Another polymerization techniques in which water is used as the medium, is the "emulsion polymerization". Polymers from water-insoluble monomers are usually obtained at faster rates in the aqueous medium by the emulsion technique water soluble initiators. For efficient making of an emulsion, it is necessary to agitate the monomers-water mixturing process of a measured does of an emulsifying agent, i.e.. soap or a detergent. To minimize fluctuations in surfaces tension of the emulsion as polymerization progresses, small proportion of a surface tension regulator (usually a long chain fatty alcohol such as cetyl alcohol) is used. Small volume of a selected buffer solution is added to minimize or eliminates variation of pH of the system due to hydrolysis or other reactions. a chain length regulator and or chain transfer agent of high transfer constant, such as dodecyl mercaptan is obtain used in low concentration to permit optimum control of polymer chain length. A selected inhibitor, none as a short-stop may be added in small amounts late in to the system in order to stop the reaction at a desired extent of polymerization.

A low concentration of a water-soluble polymer such as carboxymethyl cellulose (CMC), poly (vinyl alcohol) (PVA), gelatine, dextrin, etc., is normally used in the emulsion polymerization system not to control the polymerization processes with respect to rate or degree of polymerization but with the purpose of obtaining stable emulsion and to prevent emulsion break-down with progress of polymerization, this ingredients is commonly called a protective colloid or (emulsion) stabilizer.

In principal and practice, and as a physical system, emulsion polymerization is distinctly different from suspension polymerization. It is associated with almost all the advantages of suspension polymerization and moreover, using selected efficient redox initiator systems emulsion polymerization is conveniently accomplished at ambient or slightly elevated temperatures giving very high rates and degrees of polymerization at the same time. The rate and the degree of polymerization in the emulsion system can be varied in a large measure independently of each other. The emulsion technique is extensively employed for the polymerization of dienes, such as isoprene and butadiene, and vinyl compounds such as vinyl chloride, vinyl acetate, styrene, various acrylates and methacrylates and for making various copolymers of these and other related monomers.

(b) Principle and Theory The surfactant on the emulsifier plays an important role. When soap or detergent is taken in an aqueous system in excess of a low critical concentration, micellar or layer aggregates consisting of 50,100 or even more soap or detergent molecules are formed. They may be lamellar micelles or spherical micelles with their polar ends (heads) facing water remaining in the outer surface and the long hydrophobic hydrocarbon tails meeting at the central or interior part of the micelle [22, 23]. The diameter or thickness of the initial micelles approximates twice the length of the soap or detergent molecules (40-80 A) When water insoluble monomer is present, part of it gets "solubilized" and finds room with in the micelles, presumably among the hydrophobic tails of the soap or detergent molecules forming the micellar aggregates. The solubilization leads to some swelling of the initial micelles. A major part of the monomer taken, however, remains initially in microscopic droplets. The micelles offer a far greater total surface area then the droplets, even though the total volume of the micelles is sigficantly lower then that of the monomer droplets .A schematic representation of micelles with or without solubilized monomer, surfactant molecules or ions in aqueous solution and monomer droplets is given in fig.

Experiments clearly demonstrate that polymer is not formed in the monomer droplets. This leaves the aqueous phase and the micelles as the locus of polymerization in the emulsion system. Aqueous polymerization can be readily effected without the use of an emulsifier and without having excess monomer as droplets (i.e., using the monomer within its solubility limit in water), though at much lower rates. But this alone is far insufficient to account for the bulk of the polymer formed in a typical emulsion system. In presence of a surfactant, then polymerization rate increases with surfactant concentration.

Polymerization begins in the aqueous phase as that is where the initiators occur and react or decompose in to radicals. The primary radicals immediately pick up monomers dissolved in water to bring about chain initiation. With very low concentration of monomer in the aqueous phase, chain growth at relatively low rates proceeds till the radicals enter micelles which are present abundantly in the system. It is also not altogether unlikely that the primary radicals would find straight entry into the micelles being attracted by their high monomer reserve. Within the micelles, polymerization or chain growth takes place much rapidly in view of high monomer concentration due to accumulation of solubilized monomer there. As polymer is formed, due to monomer depletion in the micelles, more monomer is transferred to the micelles from the reservoirs of monomer droplets. The former expands at the expense of latter. Soon after a low conversion stage (a few percent) in the emulsion system, the low surface tension of the initial emulsion rises quite sharply evidently as a consequence of a fall in surfactant concentration in the aqueous phase of the emulsion leading to breakdown or disruption of the micelles and consequent insatability of the monomer droplets. Micelles give way to numerous polymer particles which at the stage average to not more than 200-400 A° diameters. Nearly all of the surfactant used gets adsorbed on the surfaces of the polymer particles. A redistribution of surfactant in favour of polymer particles makes the monomer droplets unstable at the stage. If agitation is discontinued, the monomer droplets cluster together into a continuous phase with zero polymer content. Monomer is now feed to the growing polymer particles by diffusion through the aqueous medium. As polymerization proceeds further, the polymer particles swell and grow in size even though they remain sensibly constant in their number. The rate of polymerization is practically constant over most part till about 60-80% conversion, excepting the initial zone up to several percent. From the stage of monomer droplets completely disappear, the rate follows a fast decreasing trend with further conversion. In the final analysis, the emulsified polymer particles grow to a size in the range of 500-1500 Å in diameter which is much larger than the micelles initially formed but much smaller than the initially formed monomer droplets (<10000 Å). After polymerization to optimum conversion, appropriate dose of a short – stop of inhibitor is added to stop further conversion. The polymer is isolated by breaking the emulsion using salt or acid, coagulating, filtering, washing and drying.

(c) **Polymerization** Under general conditions employed in emulsion polymerization, radicals are generated from the aqueous initiator at rates of the order of 10^{13} per cubic centimeter per second. The number of polymer particles amount to about 10^{14} per cubic centimeter. If all the radicals generated eventually enter polymer particles, the rate of radical entry in a particle will average out to about one every 10 seconds. The equilibrium radical concentration in the aqueous medium $[R^{\cdot}]_{aq}$ has been shown to be about 10^{8} radicals per cubic centimeter. Judging against the radicals being generated at a rate of 10^{13} per cubic centimeter per second, the average life time[24] of $[R^{\cdot}]_{aq}$ till its entry into a polymer particle comes out to only about 10^{-5} s. Rate of radical termination aqueous $(R_t)_{aq}$, expressed as $(R_t)_{aq} = 2k_t[R^{\cdot}]^2_{aq}$, calculated using literature value of the termination rate constant k_t , comes out to be of the order of 10^{8} radicals per cubic centimeter per second which is less than the rate of radical generation by many orders of magnitude.

Apart from this radiation grafted polymeric membrane synthesis regard, we can focus our attention also to arsenic and heavy metals chemistry. Arsenic is naturally occurring element. Its atomic number is 33, atomic weight is 74.92. Chemically, arsenic is always present as compounds with oxygen, chlorine, sulphur, carbon and hydrogen on one hand and with lead, gold and iron on the other. Organic arsenic is generally fewer toxic than inorganic arsenic [25, 26, 27]. Arsenic in element form is insoluble in water. It is soluble in oxidize form. Inorganic arsenic has been recognized as a human poison since a long times. Oral intake of arsenic has proved to be deadly on many occasions. But it had been used to treat skin ailments, worms and syphilis in the past. A century ago, incidences of skin cancer were observed due to use of arsenic medicine It is still used in cattle fodder to enhance physical growth.

Arsenic contamination is a global problem now. It virtually appears on all continents. It occurs as a result of geological processes and actives by man which include agriculture, manufacturing, mining, smelting etc. Contamination from food and beverage is also extensive.

Arsenic in Bangladesh

In Bangladesh, high arsenic concentrations are suspected to exist so far in 53 districts out of the total 64 and people of 34 districts have been found to be suffering from various affections caused by arsenic pollution. The physiographic regions vulnerable to arsenic contamination are Ganges floodplain, the Atrai flood plain, the tidal regions, the coastal plain and the Meghna floodplain[26]. The high probability zone, moderate probability and low probability areas of contamination together cover almost 60% of the total country area.

Source of Contamination

The Bangladesh arsenic contamination is possibly the largest mass poisoning case in the world now. The 'Green Revolution' has been identified theoretical to be the recent cause of the problem which has involved large-scale unplanned withdrawal of ground-water, gradually denuding the arsenic deposited under the fertile delta of Bangladesh millions of years ago by the rivers from the Himalayas or some other source. The arsenic affected areas of West Bengal are lying on sediment of Younger Deltaic Deposition (YDD) which extends east-ward towards Bangladesh covering the approximate area of the aforesaid 41 districts which lie mostly in the Atrai, Meghna and Genetics flood plains and the tidal regions.

Investigation

The Dhaka Community Hospital (DCH) and the School of environmental Studies (SOES), Jadavpur University, Calcutta, India scientists and support personnel conducted a number of surveys, collecting water samples from 1 lac tube-wells covering 64 Districts including the 53 district suspected to be arsenic contaminated. The samples were then laboratory -tested and the results of 53 districts show concentration of arsenic in ground-water to be above the maximum permissible limit, which is 0.05mg/l[26]. So far, the collected from 53 districts contained arsenic above 0.05mg/l. While comparing the West Bengal arsenic scenario with the available data of Bangladesh, it appears that Bangladesh's arsenic contamination disaster may be more severe and jeopardizing in nature and extent. An updated status report on West Bengal situation shows that 8 districts, 58 blocks and 830 villages are affected, the total area and population of these districts being 38,000km^2 and 38 million respectively. On the other hand, the area and population of the affected regions of Bangladesh are 87,000km^2 and 65 million respectively.

Toxicity manners

Toxicity for arsenic in human body is manifested in three manners:

(a) Arsenic in urine (for recent exposure)

(b) Arsenic in blood (for instant exposure)

(c) Arsenic in skin, hair and fingernails (for chronic exposure)

Health Effects for Arsenic

1. Large doses for arsenic can produce human deaths.

2. Lower level impact in many different body tissues or systems: results in 'systemic' effects.

3. Oral intake has greater harmful effects than dermal or inhalation exposure.

4. Following effects may be observed when arsenic is taken orally:

a) Skin abnormalities (dark/light spots on skin, on palms and soles) may progress to skin cancer.

b) Increase cancer risk, especially in liver, bladder, kidney and lung

c) Irritation of digestive tract, leading to pain, nausea, vomiting, diarrhoea

d) Decreased production of red and white bloods cells

e) Abnormal heart function

f) Blood vessel damage

g) Liver and/ or Kidney damage

h) Fetus damage during pregnancy etc.

Toxicity of Arsenic

1) Arsenic and certain arsenic compounds are known carcinogens.

2) Amounts of arsenic intake required to cause harmful effect depends on the chemical and physical form of arsenic.

3) Inorganic from of arsenic is more toxic than organic forms.

4) Water-soluble forms are more toxic.

5) Human is most sensitive to arsenic than animals

6) Studies in human bodies indicate a considerable variation among individuals

   a) Some human bodies can ingest over 150μg/kg/ day without apparent ill-effects (1000-1500 μg/kg/day for adults)

   b) Sensitive individuals affected at 20μg/kg/day (1000-1500 μg/kg/day for adults)

7) Doses of 600 - 700 μg/kg/day (around 50,000 μg/kg/day for adults; 3,000 μg/kg/day for infants) have caused death in some cases.

8. Maximum Concentration of Arsenic in Drinking Water:

The US Environmental Protection Agency (USEPA) has Maximum Concentration Level (MCL) of arsenic set as 20 μg/L.

Many scientists view this is above the threshold or reasonable risk to human health and there is a consideration to lower this to-10 μg/L, which is equal to the WHO, approved limit.

Symptoms of arsenicosis

The symptoms of arsenic toxicity may take 8 - 14 years to be manifested in a person's body after the patient starts drinking arsenic contaminated water. This period differs from patient to patient, depending on the quantity/volume of arsenic ingested, nutritional status of the person, immunity level of the individual and the total time -period of arsenic ingestion. The apparent symptoms of arsenicosis may be said to have manifested themselves as **melanosis** and **keratosis** [28,29] mainly.

Melanosis: Change of complexions towards blackishness/duskiness. The limbs are first affected, then the rest of the body which shows gradual complexion change which is 'diffuse melanosis'. When the body is marked by black white spots, it is known as 'spotted melanosis'.

Keratosis: - The palms of the hands and foot-soles become hardened by onslaught of Keratosis. It is not painful or ichy in the beginning, but in later stage. may start rotting and develop gangrenous ulcers. This is called pre-cancerous stage which may cause skin cancer, such as squamous cell carcinoma and basal cell carcinoma. The hardening of the palms and foot-soles is called diffuse Keratosis. Warlike seeds are seen growing on this keratosis of palms and soles. Such tumors may also occur otherwise, which is known as spotted keratosis.

Due to arsenic toxicity, limbs may be affected by ulcer or gangrene, which in some cases have to be amputated. The study reveals that females are more susceptible to toxic effects of chronic arsenic exposure and as such their pregnancy outcome are likely to be adversely affected[30].Moreover, general weakness, burning sensation, hot feeling, chronic cough etc. may be evident in such patients.

Social problems associated with Arsenicosis

A number of social problems arise out of arsenic poisoning of human beings such as:

a) Mistaking the skin disorder for leprosy or some other contagious disease and the resultant quarantining;

b) The affected are being avoided or discouraged to appear in the public;

c) The affected are being avoided or discouraged to appear in the public;

d) The affected children are being debarred from attending schools, the adults discouraged to attend offices, go shopping, visit medical professionals in the hospital etc.

e) With advancement of the disease, patients are rendered incapable of laboring/selling labor and hence victimized by poverty;

f) Affected young women being compelled to stay unmarried;

g) Diseased married women being sent back to their parents with children;

h) Affection of one in jeopardizing the lives of both members of a couple;

How to Ascertain Arsenic Contamination in Human body

From the symptoms, if someone is suspected to have arsenicosis, then his source of drinking water must be found and water sample tested. If it is found to contain arsenic in greater than acceptable limit (the limit being 0.05mg/l), then drinking that (tube-well) water has to be stopped forthwith. Unfortunately, we don't have facilities in available ways for testing such problems. The DCH has an arrangement of having suspected tube-well water samples tested for presence at the SOES laboratory at Jadavpur West Bengal in India. This test is carried out at Jadavpur according to AAS method Bangladesh Atomic Energy Commission and BCSIR laboratories also carry out water tests following AAS method. Anyone can contact either source or any of their associates or the local health department officials at any place. People may also get in touch with the DPHE officials in this regard. At present the DPHE has facilities to carry out such tests in its Rajshahi, Comilla. Mymensingh and Khulna laboratories following 'spectrophotometer' method. NGO and other agencies have limited facilities for such tests in kit method. It should be kept in mind that the tube-well pumping water, which is considered safe, might not remain so if it is within the arsenic contamination zone. So, such tube-wells should be tested every six months or so such contamination.

Treatment for Arsenic Poisoning

At any early stage of apparent contamination through drinking water,

a) Drinking water from contaminated source must be stopped forth-with

b) Taking nutritious, especially foods rich in Vitamin A, B, C and E will cure the apparent contamination[29].

c) Advanced level of toxicity is difficult cure but medical consultations are a must in all cases.

It also needs to be remembered that arsenic toxicity is not contagious or hereditary manifestations. We should not avoid such patients and offer -all co-operation so that their rehabilitation becomes an easier (through time-consuming in many cases) process.

How to Combat Arsenic Contamination

Change of habits is the chief tool of combating arsenic toxicity. Only decades back, it was customary in our rural areas to collect drinking water in the afternoon, allow it to settle throughout the night and use it for drinking the next day. But due to the increase in the number of tube-wells and tube-well water being easily available round the clock to everyone, our people became gradually used to drinking tube-well water straight from the pump. Moreover, we like to pump out the water deposit in the tube first before drinking the fresh (!) water, which is cooler in summer and less cool in winter. All these changed habits only compel us to drink water that is richer in arsenic and all other mineral contents.

Due to awareness of hygiene, our people got accustomed to drinking tube-well water, to avoid diarrhea disease mainly. But some tube-wells have fallen in the grip of arsenic toxicity lately and as a result, we are faced with a great threat to our public health to day.

Now is our time to get back to our old habit of drinking surface water first toward off arsenic poisoning. Then we have to –

1. Test all tube-wells for arsenic pollution and use only the arsenic free tube-well water for drinking and cooking
2. Use dug-well or pond water, in case all tube-wells are found to be polluted;
3. Use pond water after treating it, when there is no alternative;
4. Use river water after treatment when none of the above is available;
5. If arsenic poisoned water must be taken, then we collect the water and allow it to deposit sediments before using it. This water has to contain iron in that case. After allowing the water-filled pitcher to settle for 12 to 24 hours, three-fourths of the water from the upper part of the pot has to be poured slowly into another clean container. This water had better be filtered with the help of a 4-5 layered clean gauzy material which should reduced its arsenic contents by at least 70%. The water then may be filtered further before drinking.
6. Alum treatment: An alum nugget (not powdered) may be dipped for a second in the pitcher full of iron and arsenic polluted water to ease its arsenic deposition process. Later, this water has to be treated as per method mentioned in (5) before using.

Why treat water? It must be remembered that oxygen in atmosphere reduces the arsenic content in water. The sediment-rich water left must be poured carefully into a dung-heap to neutralize its arsenic toxicity.

It should be reiterated here that groundwater is being exploited recklessly in Bangladesh as it has been in the neighboring Indian state of West Bengal. In Bangladesh, large-scale irrigation started with deep tube-wells in the later part of the '60s. Although the country has huge wetlands, flooded in the river basins, ox-bow lakes and high rainfall, groundwater is considered the major source of water in many districts and its use is increasing every-day. To combat this situation, we need urgent watershed management and awareness campaigns at the grassroots level. Villagers must be made aware of the hazards of drinking arsenic – contaminated water and cooking with it and informed that the diseases are not contagious. Safe tube-wells must be marked properly and villagers urged to drink their water only. All such tube-well should be checked once every three months. Deep tube-wells are also to be checked at regular intervals. People should be encouraged to drink safe water and eat nutritious foods both toward off and get cured of sweet water are among the highest in the world. Moreover, annual rainfall is also more than 2000mm. The arsenic calamity of Bangladesh can be curbed if withdrawal of groundwater is restricted, surface water properly utilized and rainwater harvested. We need a suitable 'Watershed Management' most urgently.

Abutting India, Myanmar, and the Bay of Bengal, Bangladesh is a small country in the South Asian region with an area of 147,570 square kilometers. Geographically it is situated between 20°34' and 26°38' north latitude and 88°01' to 92°41' east longitude[30]. Numerous rivers and their tributaries transect the nation, largely a flat delta. A large number of other water bodies such as lakes, canals, and streams are also scattered around the country. The climate of Bangladesh is sub-tropical monsoon with a maximum average temperature of

34°C in summer and a minimum of 11°C in winter. The country receives heavy rainfall during the rainy season; the average annual rainfall varies from 1,194 mm to 3,454 mm.

Despite possessing a small geographical area, Bangladesh has a relatively large population of 134 million people. Poverty is rampant, and the Gross Domestic Product per capita averages around US $360. Most of the people do not have access to basic needs like food, education, adequate housing, and health services. The United Nations Human Development Program (UNDP) Human Development Index positions Bangladesh at 139 in the world[31].

Even though Bangladesh is famous, from ancient times, for its abundance of water from various sources, one of the major problems that the country has been suffering for decades is the scarcity of safe drinking water. Prior to independence in 1971, surface waters from ponds, lakes, and rivers, and to a lesser degree, groundwater from dug wells, were the traditional sources of drinking water for the people of Bangladesh. In coastal areas, rainwater for drinking has also been used on a limited scale for a long time. Despite the abundance of surface water, there has always been the question of quality. The surface water sources are being misused as a sink for highly polluting wastewaters from domestic as well as industrial sources. Pollution loads far exceeding dispersion capacities cause severe degradation of water quality. This microbiologically unsafe surface water, with its bacteriological and fecal contamination, extracted a heavy toll on human lives. Every year, hundreds of thousands of people, particularly children, died of cholera, diarrhea, dysentery, typhoid, and other water-borne diseases.

Arsenic in Drinking Water in Bangladesh and Related Problems

DPHE in 1993 detected arsenic in groundwater at Barogharia of Chapai Nawabganj district (the western part of Bangladesh) following reports of extensive contamination of groundwater by arsenic in West Bengal, India. As per the latest statistics, out of 64 districts groundwater of 59 districts in Bangladesh contains arsenic. And out of these 59 districts worst affected parts of Bangladesh are the southern and the northeastern districts[32] (DPHE/BGS, 1999). The access to safe drinking water in Bangladesh has declined by 17 percent in last three years due to the presence of arsenic in groundwater. Arsenic is a cumulative substance, which slowly passes out of the body through the urine, hair, fingernails/toe nails, and skin. It takes around 8-14 years after starting to drink arsenic contaminated water for symptoms to appear. This period depends on the amount of arsenic ingested, the length of exposure and immunity level of the person. Symptoms of the initial stage of the disease are skin pigmentation, eye infections, trachea and cancer. Although arsenicosis, the disease caused by arsenic contamination, is not an infectious, contagious or hereditary, it creates social problems for the victims and their families.

Treatment of Arsenic Contaminated Water

There are several methods available for removal of arsenic from contaminated water, both at the community and household level. These options are needed to make use of the huge number of tube wells likely to be declared abandoned for producing water with high levels of arsenic concentration. The most commonly used methods of treatment of high-arsenic water are by addition of coagulants such as alum and potassium permanganate. Table 1 shows a comparison of the main technologies for arsenic removal.

These methods are basically for use in large conventional treatment plants, but some of them can be reduced in scale and conveniently be applied at the household level. During the last few years, many small-scale arsenic removal technologies have been developed, field-tested, and used under arsenicosis prevention and mitigation research programs in Bangladesh and India.

Advantages and disadvantages:

The failure of concerted efforts to provide community water supplies for all is what led to the massive growth in private hand pump tubewells as a source of drinking water in the first place. The fact that rural people have grown used to drinking tube well water is one of the principal reasons to consider arsenic removal from tube well water as a suitable option for water supply. However, it is also said that community-level arsenic removal is preferable to household-level options. The question of viability of household arsenic removal units is associated with persuading millions of households to use those units and ensuring that they are used correctly, and is negatively juxtaposed with the advantages of centralized operation and maintenance. The household arsenic treatment method is regarded as an alternative for the transitional period until a "permanent" solution is found. Yet, considering the financial constraints of large-scale arsenic removal plant, in many arsenic affected areas, household arsenic removal units may be the only option in the absence of an alternative safe source of water supply.

Table 1: Technologies for Arsenic Removal[[illegible],31]

Technologies		Advantages	Disadvantages
<u>Oxidation and Precipitation:</u> Atmospheric oxygen, hypochlorite, or permanganate is added to the water to oxidize arsenite to arsenate and thereby facilitate its removal.	Air Oxidation	Relatively simple and low-cost process.	Relatively slow process (air oxidation).
	Chemical Oxidation	Chemical oxidation is a rapid process. Oxidizes other impurities and kills microbes.	It removes only a part of the arsenic
<u>Coagulation/ Co-precipitation:</u> Coagulants form flocks that bind arsenic and are then filtered out.[35]	Alum Coagulation Iron Coagulation	Relatively low capital cost Relatively simple operation Common chemicals available	Produces toxic sludge Low removal of arsenic. Pre-oxidation is required. Removal efficiencies may be inadequate to meet strict standards

Technologies		**Advantages**	**Disadvantages**
Sorption Techniques: Arsenic is adsorbed onto surface of media[35].	Activated Alumina Iron Coated Sand Ion Exchange Resin Other Sorbents	Relatively well known and commercially available. Well-defined technique Plenty of possibilities and scope of development.	Produces arsenic-rich liquid and solid waste. Replacement/ regeneration is required High-tech operation and maintenance. Relatively high cost
Membrane Techniques: Selectively permeable membranes remove arsenic by filtration.	Nanofiltration Reverse Osmosis Electrodialysis	Well-defined and high removal efficiency. Toxic solid wastes produced. Capable of removal of other contaminants	High capital and running costs . High-tech operation and maintenance Arsenic-rich rejected water is produced

Sources: This table is a modified reproduction of the table comparing different arsenic removal processes given by Dr. M. Feroze Ahmed in "Treatment of Arsenic Contaminated Water" (a theme paper presented during the International Workshop on Arsenic Mitigation in Bangladesh, Dhaka, January 14-16, 2002) Information is also collected from Elizabeth. Jones, *Arsenic 2000: An Overview of the Arsenic Issue in Bangladesh*, Draft Final Report (Dhaka: Water Aid Bangladesh, December 2000).

Arsenic Removal Technologies

Technologies for removal of arsenic from drinking water already exist as incidences of arsenic contamination in groundwater have already been reported from various parts of the world. The removal technology usually relies on its very strong adsorption to iron and aluminum oxides, and if sufficient of these are added, the arsenic concentration can be reduced to a level as low as the standard set for Bangladesh. Several technologies are currently being promoted for application in Bangladesh. They claim to be effective in removing arsenic from tube well water. These are all new and in development stage. The effectiveness, viability and sustainability of the technologies under field conditions in Bangladesh are yet to be ascertained before their adoption and scale-up thereof. Some of the technologies so far tried both in laboratory and at field level are discussed below.

Auto-attenuation, which needs collection of groundwater from the wells and allowing it stand for a specific period of time, was tried in Rajshahi and Meherpur. Groundwater having high concentration of dissolved iron is readily oxidized and forms ferric precipitates. The auto-oxidation of Fe^{2+} to Fe^{2+} generates favorable substrate with surface reactive sites for the adsorption of uncharged As (III) as well as anionic As (V) species. The test result showed that it needs further modifications for high-arsenic groundwater.

The three-bucket system (known as Sono Filter) was developed in 2001 with composite iron matrix (CIM) as the active arsenic removal component. It retains all the excellent features of a 3-Kolshi system with stability and long life use. The Sono arsenic filter was invented in 2006 by Abul Hussam.

Nikolaidis et al. suggested a simple filter, which is a tube filled with sand and iron fillings (zero-valent iron) and is designed to fit in a well outlet[36]. It can be an effective low–cost tool. $BaSO_4$ is to be added if not present in water. In the presence of $BaSO_4$, iron oxidizes and reacts with arsenic to form arsenopyrite that precipitates out and remains trapped in the filter. Laboratory experiments show 97% removal for initial arsenic concentration of 45 to 8600 μg/l.

Joshi and Chowdhury developed a home arsenic removal unit using iron-coated sand[37]. The unit was able to produce 600 – 700 l of water at a flow rate of 6 l/h maintaining an arsenic concentration of 0.01 mg/l for an initial arsenic concentration of 1.0 mg/l.

Parknikar describes two types of metal-microbiological interactions[38] that can be used for arsenic removal: i) microbial oxidation of As (III) to As (V) and its subsequent precipitation and ii) bio-accumulation of arsenic by microbial biomass. The oxidation method can be operated in an immobilized reactor reservoir. A cheap source of organic substrate like sugarcane juice can be added along with iron fillings[37]. Iron fillings promote development of iron – oxidizing bacteria that oxidize iron at a rate 50 - 103 times faster than chemical oxidation of iron. Arsenic is then adsorbed on the ferric iron. Treated overflow of water typically contain arsenic < 0.05 mg/l for initial concentration up to 4.0 mg/l.

Lehimans et al. conducted pilot studies to adopt biological filtration for removal of As(III), the oxidation state where arsenic is the most delicate to treat.[39] In addition, complete iron removal was achieved. They mentioned that this filtration allows simultaneous elimination of As (III) and iron. SORAS is a simple method that uses irradiation of water with sunlight in PET or other UV transparent bottles to reduce arsenic level from drinking water[40]. Swiss Federal Institute of Environmental Science and Technology, Switzerland and Swiss Agency develop the process for Development and Cooperation (SDC), Bangladesh. The method is based on photochemical oxidation of As (III) followed by precipitation or filtration of As (V) adsorbed on Fe (III) oxides. Field tests in Bangladesh show removal efficiency between 45-78% with an average of 67%. Concerning the Bangladesh guideline value of 50 μg/l, SORAS can treat raw water having an arsenic concentration below 100 – 150 μg/l.

Khair found Bijaypur clay from Mymensingh and processed cellulosic materials like delignified jute, bleached sawdust and pulped newspaper to be capable of adsorbing both As (III) and As(V) in solutions acidified with vinegar or hydrochloric acid[41]. Iron (III) hydroxide–coated newspaper pulp in lab scale adsorption filters coagulated arsenic. The material showed potential for use min small-scale home treatment units. Workable exposure length, flow rate and extractant volume demonstrated arsenic removal at least or even below 0.050 mg/l. The sludge was regenerated by sodium hydroxide elution.

Laterite has been tested as an adsorbent and proved to be a promising low– cost remedial technique to safeguard drinking water[42]. Laterite is vesicular clayey residuum occurring abundantly in the tropical regions. Adsorption experiments showed that the removal efficiency varied between 50 and 90% for 5 g of added laterite per 100 ml water under an equilibrium period of 20 minutes[42]. Modification of laterite by treating with 0.01 M HNO_3 increased the adsorption capacity of laterite due to an increased specific surface area [42].

Chatterjee et al. patented a filter and tablet system to remove arsenic from water[43]. The tablet contains Fe^{3+} salts, an oxidizing agent and activated charcoal. The filter was made by using fly ash, clay, charcoal etc. The system is made up of two jars. For 20 liter of water, using one tablet. 95 – 100% removal of arsenic was achieved.

Adsorbing Colloid Flotation (ACF) with ferric hydroxide as the coprecipitant, anionic surfactant sodium dodecyl sulfate (SDS) as the collector and nitrogen micro-bubbles has been shown to be effective in removing arsenic from low concentration of arsenic aqueous solution. When pH is in the range of 4 – 5, 99.5% arsenic removal efficiency can be achieved.

The Bucket Treatment Unit was developed by DPHE-Danida and is being under the Arsenic Mitigation Pilot .Project. This project was launched in Lakshpur and Chaumuhini Pourashavas in the coastal region of Bangladesh. The system can treat any kind of tubewell water, regardless of the arsenic concentration, and to an arsenic level below Bangladesh's standard of 0.05 mg/l.

BCSIR has developed a low cost arsenic filter[41]. The technology consists of adding a floc forming composition to the arsenic contaminated water followed by stirring and settling. The chemicals are composed of iron oxide, alum, activated charcoal and calcium carbonate, which are to be mixed in definite proportions, homogenized and micronized. After settling the water is passed through a filter bed composed of sand and some iron bearing minerals of definite particle size range, which are to be activated by suitable chemical and heat treatment. The dose of the floc forming composition depends on the extent of arsenic contamination. Water containing upto 2.7 ppm arsenic could be purified below safe limit set by WHO.

Project Earth Industries, USA, developed an arsenic removal unit which is used with a hand pump tube-well. The Unit was tested at Sonargaon, Naraynganj, where groundwater arsenic concentration is very high. The principal component of the Arsenic Removal Unit consists of an adsorption media. The removal mechanism involves adsorption of arsenic onto the media surface as tubewell water flows through it. Along with arsenic a number of other anions and cations (including iron) also get adsorbed on it.

Shin Nihon co. Ltd. of Japan developed a households arsenic removal unit, which is a cylindrical container made of plastic and fitted with a tap close to the bottom for outflow. The container is filled with READ-F adsorbent resin. The inlet of the tap is fitted with a screen to block the entry of the resin into the tap. The adsorbent is always kept under water to retain its effectiveness. This is an effective system in removing arsenic from drinking water containing a low level of iron.

Coolmart Water Purifier, Korea, developed another purification unit, which consists of a series of beds containing activated carbon, silver-activated carbon, bio-mineral sand, zeolite and silica sand through which water passes. A laboratory tests of the system shows that around 25 litres of water containing 300 ppb of arsenic and 0.1mg/l of iron could be treated by the purifier satisfying the Bangladesh drinking water standard for arsenic.

Allergy Environmental Research and Skin Care Institute (AARSCI), Integrated Quality and Environmental Management (IQM) etc. have developed simple cost effective filters. AARSCI used indigenous materials such as coconut coir, coconut shells and husk, along with small amount of alum to prepare the filter bed. IQM prepared the filtering bed using the clay pots, sunlight, air, iron. sand or ferrous salts and alum. Another filter developed by US Company called Arsen: X filter. which has been tested successfully in the Sadar thana of Kishoreganj. This filter not only removed arsenic, but also reduced other contaminants including fluoride and lead and it can be safely land-filled or recycled as non hazardous material. 100 percent removal of arsenic from water is accompanied by a unique bonding of arsenic into molecular structure of the filter and therefore, it does not disassociate.

Tetrahedron has developed a filter medium based on anionic resin. The filter has already been tested successfully. They claimed that the bed can easily be regenerated using Sodium Chloride solution, which is available in our country and the filter can be used for ten years.

To save millions of people from arsenic poisoning it is important to detect the arsenic concentration in groundwater and also to provide a suitable, user friendly and cost effective arsenic removal process for the rural people of Bangladesh. Unfortunately, the very first step towards prevention and arsenic testing is in great chaos. The instruments are expensive and require skilled person to operate. There is no licensing authority to supervise the testing procedure in Bangladesh. At present, very few laboratories can provide reliable result. On the other hand removal technologies so far tried for the rural people have potential but not tested thoroughly for adoption. Most of the rural people are illiterate. They developed the habit of drinking hand tube wells water during the last 30 years. So any change in their behavioral needs more friendly approach and technology.

Ratan et al. (1997) reports possible hazards associated with metals of surface water bodies of Bangladesh due to anthropogenic activities. Surface water samples from Rajrampur of north-western Chapai Nawabganj (one of the worst arsenic affected areas). The surface water investigated by Peuraniemi, V., Institute of Geosciences and Astronomy. Oulu, Finland (1999) that reports that the largest lake at Rajrampur is surrounded by agricultural land contain by far the highest level of arsenic, likely derived from agriculture. They also reported elevated concentrations of As, Cr. Cu, Ni, Pb and Zinc in soil samples (Islam, et al., 2000).

The average composition of nonfiltered water samples:

Heavy Metals	**Standard*µg/l**	**Rajarampur µg/l**	**Shamta µg/l**
As (Arsenic)	4	97,05	15,36
Cr (Chromium)	0,7	1,41	5,65
Cu (Copper)	3	7,71	18,3
Ni (Nickel)	0,3	4	6
Zn (Zinc)	3	8,03	16,56
Pb (Lead)	3	8,03	16,56

*Standard – typical values taken from Wedepohl (1969-79) for surface water

Chromium in surface water exceeds the worldwide average value; the pH value of soil is around 8, at which chromium is not supposed to be mobile and available in surface water. Chromium occurs with ultrabasic rocks at the very early stage of magma crystallisation. Catchment areas of Ganges delta do not show any source. Nickel in these surface water exceeds the average world-wide value several fold (Islam et al, 2000).

Safiullah (1998) also reports concentration of arsenic (0.035 mg/l) in surface water of Kumar River at Faridpur. On December 21, 1997 the daily The Independent reports that the quality of country's surface water has markedly deteriorated is a matter of great concern, but the nature and extent of the fall in quality was not precisely known.

Human activities can alter natural relationship of surface and ground water:

a) After the construction of Farakha barrage and during dry period (Dec-April) ground water table in Bangladesh drop to such extent that surface water bodies disappear as they drain into the falling ground water table.

b) During monsoon water table is very high, bringing the ground water table close to land surface resulting the near surface and surface water can pick up agrochemical as contaminants.

c) Irrigation has potential to hasten leaching of applied and natural chemicals.

d) Over-pumping of water, wells can cause "cone depression". If the cone depression is large, it can change the slope of the ground water table – contaminated water can flow down slope along the cone of depression.

Deterministic and statistical models of transport in soils, atmosphere, surface and ground waters developed by Center researchers continue to improve. These models range 'in scale from origin and movement of groundwater and assessment of long-term degradation of these waters to regional scale atmospheric models used to calculate transport of air pollutants from source areas within large geographic areas. These models have also been coupled with hydrologic models of runoff to quantify patterns of erosion and input of nutrients and other chemicals to lakes and rivers. Center for Ecological Health Research, university of California reports (1996):

A new method for probabilistically quantifying the origins and ages of ground waters arriving at discharge points (e.g., wetlands, wells) was developed that also rigorously accounts for the physical process involved in pollutant transfer between different geologic materials. Results indicate that the currently observed deterioration in groundwater quality in a typical alluvial groundwater basin is due to land use practices in the 1940's and 1950's and that the deterioration may continue for many decades, thereby eventually impacting any wetlands and streams that are sustained by groundwater discharge.

Pollution through agrochemicals

Several studies have shown that heavy metals are present in the parts per million (mg/kg) ranges, and occasionally as high as parts per thousand, in fertilizers produced from recycled industrial by-products (US EPA, 1997).

Banned Pesticides in Industrial countries but allowed for export:

- arsenic trioxide
- 2,3,4,5-Bis(2-butylene)tetrahydro-2- furaldehyde [Repellent-11]
- bromoxynil butyrate
- cadmium compounds
- calcium arsenate
- carbofuran (granular only)
- copper arsenate
- endrin
- lead arsenate

Arsenic is an elemental metal used in insecticides, herbicides, and manufacturing processes (Coffel, 1989). Arsenic is used extensively in insecticides as calcium arsenate to boll-weevil in cotton fields, and in herbicides and plant desiccants as lead arsenate to control codling moth, plum curculio, cabbage worm, potato bug, tobacco horn worm, and other pests that attack fruits and vegetables. Many thousands of As (+3) and As (+5) compounds with carbon-arsenic bonds have been synthesised and tested for their effectiveness against various agricultural pests. Methyl arsenic and dimethyl arsenic or salts are extensively used for weed control. Phenyl arsenic acid, cacodylic acid, methane arsenic acid and Lewisite (CH_3-CH = $CHAsCl_2$) as a chemical warfare agent, are some of the well-known and widely used arsenicals (Moore and Ramawiorthe, 1984). The toxicity of arsenic compounds is different from those of heavy metals. For arsenic the toxicity to the rat declines with arsenite > arsenate > methyl arsenate = dimethyl arsenate. The toxic dose increases by about fifty between arsenite and methyl acid salts. The toxic effects appear to be caused by binding to sulphydryl lipid groups by trivalent arsenic, and pentavalent arsenic appears to be reduced to the trivalent form (Harrison. 1990). Green Plaster produced in India is very likely to enter Bangladesh as "no name" pesticides. "Heavy metals" are a non-scientific term used to refer to metals, which are in the third period or so (and higher) of the periodic table.

General Information of Heavy Metals

Heavy metals are elements having atomic weights between 63.546 and 200.590 (Kennish, 1992), and a specific gravity greater than 4.0 (Connell et al., 1984). Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony (Kennish, 1992).

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low (Kennish, 1992). The colloidal and particulate metal may be found in: 1) hydroxides, oxides, silicates, or sulfides; or 2) adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system (Connell et al., 1984).

The behavior of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. Sediment composed of fine sand and silt will generally have higher levels of adsorbed metal than will quartz, feldspar, and detrital carbonate-rich sediment. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter (Connell et al., 1984).

The water chemistry of the system controls the rate of adsorption and desorption of metals to and from sediment. Adsorption removes the metal from the water column and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. Metals may be desorbed from the sediment if the water experience increases in salinity, decreases in redox potential, or decreases in pH.

1. *Salinity increase:* Elevated salt concentrations create increased competition between cations and metals for binding sites. Often, metals will be driven off into the overlying water. (Estuaries are prone to this phenomenon because of fluctuating river flow inputs.)
2. *Redox Potential decrease:* A decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water.
3. *pH decrease:* A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column (Connell et al., 1984).

Health Effects

Ingestion of metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), barium (Ba), and chromium (Cr), may pose great risks to human health. Trace metals such as lead and cadmium will interfere with essential nutrients of similar appearance, such as calcium (Ca^{2+}) and zinc (Zn^{2+}).

- *Lead:* Because of size and charge similarities, lead can substitute for calcium and included in bone. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension[45].

- *Cadmium* Cadmium may interfere with the metallothionein's ability to regulate zinc and copper concentrations in the body. Metallothionein is a protein that binds to excess essential metals to render them unavailable when cadmium induces metallothionein activity: it binds to copper and zinc, disrupting the homeostasis levels (Kennish, 1992). Cadmium is used in industrial manufacturer and is a byproduct of the metallurgy of zinc.

- *Mercury:* Mercury poses a great risk to humans, especially in the form of methyl mercury. When mercury enters water it is often transformed by microorganisms into the toxic methyl mercury form. Symptoms of acute poisoning are pharyngitis, gasteroenteritis, vomiting, nephritis, hepatitus, and circulatory collapse. Chronic poisoning is usually a result of industrial exposure or a diet consisting of contaminated fish (mercury is the only metal that will bioaccumulate). Chronic poisoning may cause liver damage, neural damage, and teratogenesis (USEPA, 1987)

- *Arsenic*: Arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water. Ingestion causes vomiting, diarrhea, and cardiac abnormalities (Viessman and Hammer, 1985).

- *Chromium.* The presence of abundant chromium anions in the water is generally a result of industrial waste. The chronic adverse health effects are respiratory and dermatology (Viessman and Hammer, 1985).

Environmental Effects

Aquatic organisms may be adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system (see "Environmental Fate/Mode of Transport"). Slightly elevated metal levels in natural waters may cause the following sub lethal effects in aquatic organisms: 1) histological or morphological change in tissues; 2) changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation, 3) change in biochemistry, such as enzyme activity and blood chemistry, 4) change in behavior; 5) and changes in reproduction (Connell et al., 1984).

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacean can excrete essential metals, such as copper, zinc, and iron that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success (Connell et al., 1984).

Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake (Connell et al., 1984). Thus, bivalves tend to suffer from metal accumulation in polluted environments. In estuarine systems, bivalves often serve as biomonitor organisms in areas of suspected pollution (Kennish, 1992). Shell fishing waters are closed if metal levels make shellfish unfit for human consumption.

In comparison to freshwater fish and invertebrates, aquatic plants are equally or less sensitive to cadmium, copper, lead, mercury, nickel, and zinc. Thus, the water resource should be managed for the protection of fish and invertebrates, in order to ensure aquatic plant survivability (USEPA, 1987). Metal uptake rates will vary according to the organism and the metal in question. Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992). With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms (Kennish, 1992).

Metals may enter the systems of aquatic organisms via three main pathways

1. Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the blood stream.
2. Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream.
3. Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water (Connell et al., 1984).

Irrigation Effects

Irrigation water may transport dissolved heavy metals to agricultural fields. Although most heavy metal do not pose a threat to humans through crop consumption, cadmium may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant (De Voogt et al., 1980).

Most irrigation systems are designed to allow for up to 30 percent of the water applied to not be absorbed and to leave the field as return flow. Return flow either joins the groundwater or runs off the field surface (tailwater). Sometimes tailwater must be rerouted into streams because of downstream water rights or a necessity to maintain stream flow. However, usually the tailwater is collected and stored until it can be reused or delivered to another field (USEPA 1993a).

Tailwater is often stored in small lakes or reservoirs, where heavy metals can accumulate as return flow is pumped in and out. These metals can adversely impact aquatic communities. An extreme example of this is the Kesterson Reservoir in the San Joaquin Valley, California, which received subsurface agricultural drainwater containing high levels of selenium and salts that had been leached from the soil during irrigation. Studies in the Kesterson Reservoir revealed elevated levels of selenium in water, sediments, terrestrial and aquatic vegetation, and aquatic insects. The elevated levels of selenium were cited as relating to the low reproductive success, high mortality, and developmental abnormalities in embryos and chicks of nesting aquatic birds (Schuler et al. 1990).

Sources:

1. *Nonpoint sources:*

Natural: Chemical and physical weathering of igneous and metamorphic rocks and soils often release heavy metals into the sediment and into the air. Other contributions include the decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates, and oceanic spray (Kennish, 1992).

Anthropogenic: Surface runoff from mining operations usually has a low pH and contains high levels of metals such as iron, manganese, zinc, copper, nickel and cobalt. The combustion of fossil fuels pollutes the atmosphere with metal particulates that eventually settle to the land surface. Urban storm water runoff often contains metals from roadways and atmospheric fallout (Connell et al., 1984). Currently, anthropogenic inputs of metals exceed natural inputs.

2. *Point sources:* Domestic wastewater effluent contains metals from metabolic wastes, corrosion of water pipes, and consumer products. Industrial effluents and waste sludges may substantially contribute to metal loading (Connell et al., 1984).

Environmental Fate/Mode of Transport:

Transport in water: Water can transport metals that are bound to sediment particles. The primary route for sediment-metal transport is overland flow

Water also transports dissolved metals. Although dissolved metals are primarily transported in overland flow, some underground transport is possible. Metals that are introduced to the unsaturated zone and the saturated zone will most likely not be transported a long distance. Dissolved metals that are carried below the land surface will readily sorbs to soil particles or lithic material in the unsaturated zone and the saturated zone.

Transport in air. Metals introduced into the atmosphere may be carried to the land surface by precipitation and dry fallout. Additionally, because metals readily sorb to many sediment types, wind-borne sediment is a potential route for metal transport.

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to humans and to the environment.

Heavy metals are of real concern in the aquatic environment. Small amounts of metals are necessary for growth, but at elevated levels can become toxic. In my field of oceanography and physiology (study of algae) metal chemistry is a hot research item. Locally, we have trouble with copper leaching from the anti-fouling paint on the Navy ships and precipitating out into the sediments. From the sediments the copper will continue to come out into the water and become a constant source of copper. Many studies have been done on marsh plants because they take heavy metals up into their cells and therefore can "cleanse" the water. However, unless the plants are harvested, the metals may return to the water as the plants decompose after death. So you can see that even when sources of pollution are identified and stopped, the pollutants can continue to cycle in the system. In addition, pollution can cause a shift in the kinds of micro algae that can be supported in a system, and since these algae are the basis of the food chain, the kinds of algae can determine the kinds of animals that can live there. Therefore, a non-toxic level of a metal contaminate can alter the basis of the food chain and therefore alter the types of fish and other animals that can be supported in an ecosystem.

Heavy metals in soils near the nickel smelter chemistry, spatial variation, and impacts on plant diversity

Air pollution induced changes were observed both in plant communities and in soil chemistry in forest ecosystems near the nickel-copper smelter in the Kola Peninsula, Russia. All measured forest plant community parameters describing their floristic composition and structure were affected by pollution. Heavy metals were significantly concentrated in organic horizons of forest soils. The concentrations of ammonium acetate-extractable nickel and copper in organic horizons near the smelter were approximately two orders of magnitude higher than the background levels in the region. Based on pH values, air pollution has not resulted in a detectable topsoil acidification near the smelter. However, concentrations of extractable magnesium, potassium and nitrogen in organic horizons tended to be lower towards the smelter. The spatial variability of data obtained results in necessity of the two complementary, macroscopic and microscopic, approaches to ecosystem investigation. The macroscopic approach better revealed the influence of pollution. The ordination of the major species diversity indexes was highly related to soil properties, suggesting that the content of heavy metals and nutrients is the best soil related predictor of species diversity in polluted areas. Besides direct input of pollutants from the atmosphere, soil contamination and nutritional disturbance contribute significantly to the observed vegetation damage in sub arctic forest ecosystems.

SECTION: 2

2. Present Work: Synthesis of Radiation grafted Membrane Intermediates by Using Different Binary Monomer System onto Different Polymeric Materials.

2.1 Rationale:

Recently there has been substantial growth in interest in the use of radiation induced graft copolymerization of functionalized monomer onto polymer membranes for chelating sorbent materials [20-22]. Graft copolymers involving maleic anhydride moieties have been the subject of considerable interest, because these anhydride groups have reactive carbonyl groups which are subjected to numerous reactions. In this respect radiation induced graft copolymerization of styrene/maleic anhydride (Sty/MAn) and methyl methacrylate/ maleic anhydride (MMA/MAn) binary monomer onto the different polymeric materials are: low-density polyethylene (LDPE) film, polyethylene pellet (PEP), polypropylene pellet (PPP), low-density polypropylene (LDPP) and heat pressed polyethylene (HPPE) sheet were studied. Varieties of functional groups are possible to introduce into the graft copolymer and the possibilities of their practical uses in selectivity of some toxic metal ions are more popular day by day. It has been recognized that the ionizing radiation is a very suitable tool for the preparation of grafted polymeric materials, especially for different vital application [46-49]. This process has versatile advantages[50-53], for example: easy process control, simultaneous crosslinking of the polymer to grafted polymeric materials formation and sterility of the product with high degree of assurance level, no necessity to add any initiators, no waste, and the technology is environment friendly since it leaves no residue or pollutant in the environment etc [46-47]. The necessary requirement to produce a usable grafted polymeric material is the formation of cross-links between different polymer chains, resulting in a three-dimensional network structure [48, 50]. This requirement is achieved by the irradiation of the different polymeric materials in acetone solution of binary monomer systems: Sty/MAn and MMA/MAn through gamma rays.

2.2 Results and Discussion:

2.2a. Grafted Polymeric Product of PE-g-P(Sty/MAn)

Here we demonstrate an approach where radiation grafted membrane of low-density polyethylene with binary monomer of styrene and maleic anhydride through radiation technique. In this purpose Co-60 γ-rays were used for the completion of the grafting reaction. By this technique a good grafting was achieved and this was 288% at 15kGy dose with LDPE and the binary monomer system was Sty/MAn. In the glass ampoule LDPE was taken and then the solution of acetone with binary monomers poured in that ampoule, and finally the prepared sample solution was exposed in the Co-60 γ-rays. In this case we have found homopolymer of styrene also, and this homopolymer was removed from the grafted product by washing through the solvent acetone.

Here, the change of grafting percentage with radiation dose is investigated, and the grafting percentage of low-density polyethylene film with binary monomer of styrene and maleic anhydride increases with increasing the dose. With the increase of radiation dose, the concentration of the free radicals increases, that is the *G* value for each radical increases, therefore the site of monomer addition in the polyethylene was increased, so the resulting grafting increased.

2.2b. Grafted Polymeric Product of PE-g-P (MMA/MAn)

Here we demonstrate an approach where radiation grafted membrane of low-density polyethylene with binary monomer of methyl methacrylate and maleic anhydride through radiation technique. For the completion of the grafting reaction same techniques were applied as 2.2a. For this technique also, a good grafting was achieved and this was 253% at the same dose with LDPE and the binary monomer system was MMA/MAn. In the glass ampoule LDPE was taken and then the solution of acetone with binary monomer poured in that ampoule, and finally the prepared sample solution was exposed in the Co-60 γ-rays. After completion of the radiation-exposing period. the grafted film was removed and washed thoroughly by acetone to extract the residual monomers and the homo polymer of methyl methacrylate, which were accumulated in the grafted films. For finding more accurate grafting result the films were then further immersed in acetone for 48 hr and then removed from acetone, dried and then weighed finally for calculating the degree of grafting value in percentage. The completion of the removal of homopolymer was ascertained through the unchanged weight determination for calculating the accurate grafting result.

2.2c. Grafted Polymeric Product of PEP-g-P(Sty/MAn)

Here we demonstrate an approach where radiation grafted membrane of polyethylene pellet with binary monomer of styrene and maleic anhydride through radiation technique. In this purpose Co-60 γ-rays were used for the completion of the grafting reaction. By this technique a satisfactory grafting result was not achieved compared to the LDPE film and the value was only 3.1% where as for LDPE it was 288% at the same dose, with LDPE and the binary monomer system was Sty/MAn. Due to the high molecular and grafting density in PEP, the grafting percentage of PEP with binary monomer of Sty/MAn systems decreased compared to the LDPE film. It shows the radiation dose 15 or 20 kGy is not enough for the formation of large number of free radical to form the grafted product like that of LDPE system. Therefore, we may conclude by saying that in the exposed low dose only a lower extent of PEP free radical is formed, that's why the grafting was poor compared to others. In the glass ampoule PEP was taken and then the solution of acetone with binary monomers poured in that ampoule, and finally the prepared sample solution was exposed in the Co-60 γ-rays.

2.2d. Grafted Polymeric Product of PEP-g-P (MMA/MAn)

Similarly the radiation grafted membrane of polyethylene pellet with binary monomer of methyl methacrylate and maleic anhydride obtained through radiation technique. Here also a satisfactory grafting was not achieved compare to the LDPE film and the value was only 2.9% where as for LDPE it was 288% at the same dose with LDPE and the binary monomer system was Sty/MAn. Same cause was involved in the case of low grafting result.

2.2e. Grafted Polymeric Product of PPP-g-P(Sty/MAn)

According to the same way radiation grafted membrane of polypropylene pellet with binary monomer of styrene and maleic anhydride obtained through radiation technique. The grafting percentage was only 2.0%. Due to the high molecular density, crosslinking density and small surface area in PPP, the grafting percentage of PPP with binary monomer of Sty/MAn system decreased compare to the LDPE film. That is the applied radiation dose 15 or 20 kGy is not enough for the formation of a greater extent of free radical, to form the grafting product like that of LDPE system.

2.2f. Grafted Polymeric Product of PPP-g-P(MMA/MAn)

The grafting result was only 1.80% for the radiation grafted membrane of polypropylene pellet with binary monomer of methyl methacrylate and maleic anhydride through radiation technique. The cause of poor grafting result was mentioned before.

2.2g. Grafted Polymeric Product of LDPP-g-P(Sty/MAn)

The grafting result was only 10.00% for the grafted membrane of low-density polypropylene with binary monomer of styrene and maleic anhydride through radiation technique. The cause of poor grafting result was mentioned before.

2.2h. Grafted Polymeric Product of LDPP-g-P(MMA/MAn)

The grafting result was only 6.80% for the radiation grafted membrane of low-density polypropylene with binary monomer of methyl methacrylate and maleic anhydride through radiation technique. The cause of poor grafting result was mentioned before.

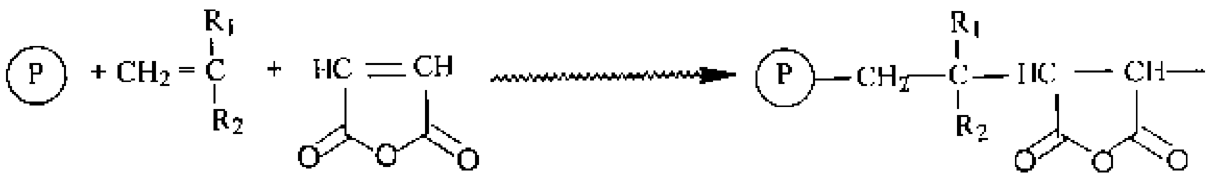
2.2i. Grafted Polymeric Product of HPPE-g-P(Sty/MAn)

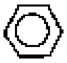
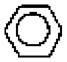
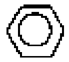
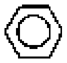
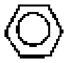
The grafting result was only 1.80% for the radiation grafted membrane of heat pressed polyethylene (HPPE) sheet with binary monomer of styrene and maleic anhydride through radiation technique. The poor grafting results explained before.

2.2j. Grafted Polymeric Product of HPPE-g-P(MMA/MAn)

The grafting result was only 1.68% for the radiation grafted membrane of heat pressed polyethylene (HPPE) sheet with binary monomer of methyl methacrylate and maleic anhydride through radiation technique. The grafting result explained before.

All of the grafting reactions are shown in the **Scheme 1**.



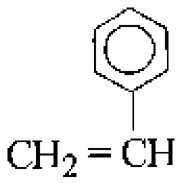
where R₁	R₂	P	Intermediate
	H	LDPE	2.2a
$COOCH_3$	CH_3	LDPE	2.2b
	H	PEP	2.2c
$COOCH_3$	CH_3	PEP	2.2d
	H	PPP	2.2e
$COOCH_3$	CH_3	PPP	2.2f
	H	LDPP	2.2g
$COOCH_3$	CH_3	LDPP	2.2h
	H	HPPE	2.2i
$COOCH_3$	CH_3	HPPE	2.2j

Scheme 1

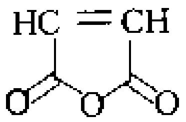
2.2.1. Starting Materials:

The starting materials for this grafted polymerization step were styrene (Sty), maleic anhydride (MAn), methyl methacrylate (MMA) and different polymeric materials, e.g., low-density polyethylene (LDPE) film, polyethylene pellet (PEP), polypropylene pellet (PPP), low-density polypropylene (LDPP) and heat pressed polyethylene (HPPE) sheet were studied.

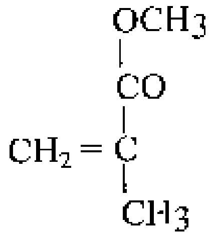
The structures of those materials are shown below:



Sty



MAn



MMA

The grafted product was characterized by the gravimetric method and spectroscopic technique. The infrared spectroscopic report was different with the grafted product of low-density polyethylene (LDPE) film and other polymeric materials with Sty/MAn binary monomer, and the weight of the grafted product remarkably increased from the polyethylene film as well as the other polymeric materials polyethylene pellet (PEP), polypropylene pellet (PPP), low-density polypropylene (LDPP) and heat pressed polyethylene (HPPE) sheet.

2.3. Characterization of the Products:

2.3a. Characterization of the Grafted Polymeric Product PE-g-P(Sty/MAn)

Firstly, the radiation grafted membrane of low-density polyethylene (LDPE) film with Sty/MAn binary monomer was characterized gravimetrically. The LDPE film was weighed before the radiation grafting reaction and after the completion of the grafting reaction followed by removing the homopolymer and monomers, the weight of the product was again taken. Then, the degree of grafting percentage was calculated according to following relation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

Where, W_o and W_g represent the weights of initial and grafted films, respectively.

Secondly, the grafted product of low-density polyethylene (LDPE) film with Sty/MAn binary monomer was well characterized by the Fourier-Transformed Infrared Spectroscopic (FTIR) data. Infrared spectroscopic data of LDPE and grafted product were taken for comparison and the spectra of these two reports were completely different. The infrared spectra of grafted product PE-g-P (Sty/ MAn) showed C = O group of antisymmetric and symmetric stretching vibration in the range of 1857.3 and 1707.8 cm^{-1} respectively and this C = O group comes from the maleic anhydride moieties. On the other hand the frequency number at 1603 cm^{-1} showed, due to the presence of aromatic C = C in the benzene ring, which comes from the styrene portion of the grafted product. The characteristic band for $-CH_2-$ group of LDPE at 2858.3 cm^{-1}. The characteristic band at 1857.3, 1707.8 and 1630.7 cm^{-1} for the infrared spectrum of low density polyethylene were absent, that's the evidence for the formation of grafting reaction of LDPE film with copolymer unit, MAn-Sty. That is the infrared spectra analysis confirms the formation of graft polymer.

2.3b. Characterization of the Grafted Polymeric Product PE-g-P(MMA/MAn)

The synthesized radiation grafted product was characterized gravimetrically. The LDPE film weighed before the radiation grafting reaction and after the completion of the grafting reaction followed by removing the homopolymer and monomers again the weight of the product taken. Then, the degree of grafting percentage was calculated according to the same relation.

The infrared spectra of grafted product PE-g-P (MMA/MAn) showed C = O group of antisymmetric and symmetric stretching vibration in the range of 1857.3 and 1708.8 cm^{-1} respectively and this C = O group comes from the maleic anhydride moieties. Another C = O group absorption frequency observed at 1789.8 cm^{-1} for the MMA moieties. The characteristic band for $-CH_2-$ group of LDPE at 2848.3 cm^{-1}. The characteristic bands at 2995.2 and 2918.1 cm^{-1} due to the $-OCH_3$ and $-CH_3$ group respectively in MMA portion. The characteristic bands at 1857.3, 1789.8, 1708.8, 2995.2 and 2918 cm^{-1} for the infrared spectrum of low density polyethylene were absent, that's the evidence for the formation of grafting reaction of LDPE film with copolymer unit, MMA-Sty. That is the infrared spectra analysis confirms the formation of graft polymer.

2.3c. Characterization of the Grafted Polymeric Product PEP-g-P(Sty/MAn)

This radiation grafted product was characterized gravimetrically. The PEP weighed before the radiation grafting reaction and after the completion of the grafting reaction followed by removing the homopolymer and monomers again the weight of the product taken. Then, the degree of grafting percentage was calculated according to the previously mentioned relation.

The grafted product of polyethylene pellet with Sty/MAn binary monomer was characterized by the gravimetric method only. Infrared spectroscopic data of PEP grafted product was not recordable because PEP can not permit the infrared radiation. That's the increase of weight after the exposing of gamma radiation is an evidence for the formation of grafting reaction of PEP with copolymer unit, MAn-Sty.

2.3d. Grafted Polymeric Product of PEP-g-P(MMA/MAn) Characterization

This synthesized radiation grafted product was characterized gravimetrically. Infrared technique was not applied due to the same mentioned reason.

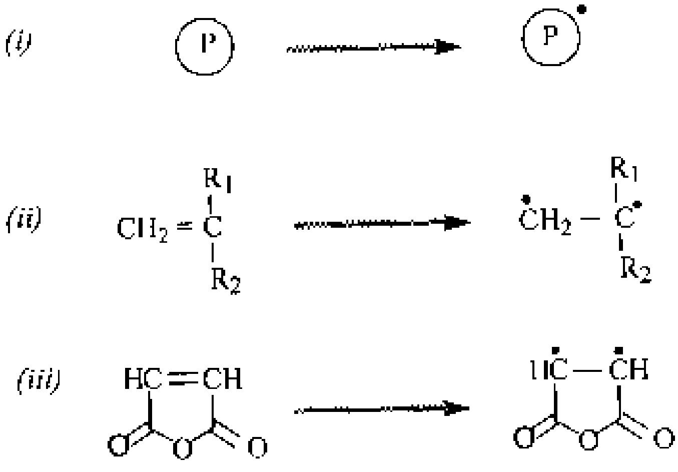
Similar explanation is applicable for the characterization of grafted product of 2.2e, 2.2f, 2.2g, 2.2h, 2.2i and 2.2j.

2.4. Mechanism:

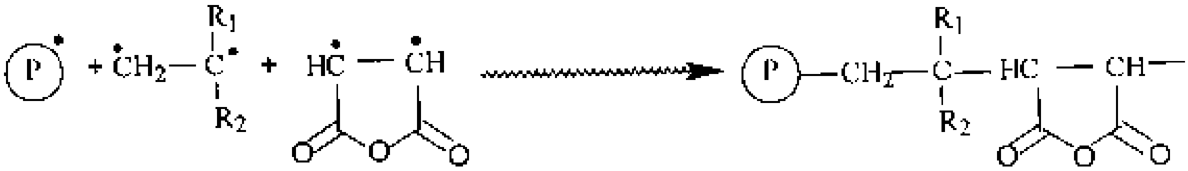
A tentative mechanism for the formation of the synthesized radiation grafted membrane of low-density polyethylene (LDPE) film with Sty/MAn binary monomer is illustrated in the **Scheme 1.1**

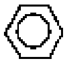
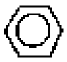
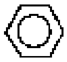
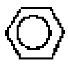
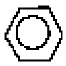
Where, after passing the Co-60 γ-radiation to the LDPE film free radical is formed on the LDPE film, again during irradiation the free radical of Sty and MAn is also formed due to the homolytic cleavage of pi (Π) bonds in both of these compounds. The formed free radicals further combined with each other to form the grafted membrane of low-density polyethylene (LDPE) film with Sty/MAn binary monomer. It seemed that all the grafted process followed the same mechanism.

Free radical Formation



Grafted Product Formation



where,R_1	R_2	P	Intermediate
	H	LDPE	2.2a
$COOCH_3$	CH_3	LDPE	2.2b
	H	PEP	2.2c
$COOCH_3$	CH_3	PEP	2.2d
	H	PPP	2.2e
$COOCH_3$	CH_3	PPP	2.2f
	H	LDPP	2.2g
$COOCH_3$	CH_3	LDPP	2.2h
	H	HPPE	2.2i
$COOCH_3$	CH_3	HPPE	2.2j

Scheme 1.1

2.5 Conclusion:

We have described a very convenient and elegant method for the synthesis of some grafted membrane of low-density polyethylene (LDPE), polyethylene pellet (PEP), polypropylene pellet (PPP), low-density polypropylene (LDPP) and heat pressed polyethylene (HPPE) sheet film with Sty/MAn binary monomer. Some of these grafted products are used as the intermediate products for our target functionalized radiation grafted membrane. These grafted intermediate products were synthesized by readily available starting materials and clean technique i.e., radiation technique and with a good percentage of grafting.

2.6 Experimental:

2.6a. Grafted Polymeric Product of PE-g-P(Sty/MAn)

Materials

Low-density polyethylene film (LDPE) (55 micrometer thickness) was washed with distilled water and then followed by the acetone and finally dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used as received. Styrene (*Sty*) (Merck, Germany), M = 104.06, 11 = 0.79 kg. Methyl methacrylate (*MMA*) GPR, purity 99%, M=100.12 g/mol, 11 = 0.94 kg, (Merck, Germany) was used as received. Acetone was extra pure (Merck, Germany), M = 58.08, 11 = 0.79 kg and used without further purification.

Optimization of radiation dose:

For preparing the graft copolymers radiation-grafting technique was used and for this purpose Co-60 γ-rays were used. For instance, dose optimization was one of the major headache in this study. In that case LDPE sheet were cut first and then followed by washed with acetone, dried in air weighed, which are recorded for determining the grafting percentage. By observing the highest grafting percentage optimum dose were selected. In the dose optimization case, 0.5 - 20 kGy doses were used for all of the grafted copolymers and the optimum dose was 15 kGy.

Graft copolymerization of LDPE:

The graft copolymers were prepared by radiation grafting technique and for this purpose Co-60 γ-rays were used as a radiation source. The identities of Co-60 γ-radiation are energy of 1.17, 1.33 MeV, state metal, half-life 5.26years, specific activity 40-700Ci/g, self-absorption 10% and activity 67kCi. These types of grafting copolymers were prepared by the LDPE film using Co-60 γ-rays at a dose rate of 5 kGy/hr with the Sty/*MAn* binary monomer system. For preparing the Sty/MAn grafting copolymer the strip of LDPE were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) Sty/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.70 g of MAn, 10.30g (or, 13.04 ml) of Sty and 80 g (or, 101.27 ml) of acetone. The comonomer solution was deaerated by bubbling nitrogen then introduced in to the Co-60 γ-rays at the dose of 15 kGy for direct radiation grafting. After completion of the radiation-exposing period, the grafted films were removed and washed thoroughly with acetone to extract the residual monomers and the homo polymers, which were accumulated in the grafted film. For finding more accurate grafting result the films were then further immersed in acetone for 48 hr and then removed the films from acetone and dried then weighed. Finally the degree of grafting value was calculated in percentage. In the purified grafted product the percentage of grafting was 288% and the FTIR spectrum data (Fig.2) is as follows:

IR: υ_{max} 3613, 2858, 2846, 1857, 1707, 1630, 1559, 1435, 1388, 1367, 1067, 1019, 944, 843, 827, 811, 751, 730 cm^{-1}

2.2b. Grafted Polymeric Product of PE-g-P(MMA/MAn)

Graft copolymerization of LDPE:

This type of grafting copolymer of LDPE were prepared by MMA/MAn binary monomer system onto LDPE films using Co-60 γ-rays at a dose rate of 5 kGy/hr dose rate of gamma radiation. For preparing the MMA/MAn grafting copolymer the strips of LDPE were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) MMA/MAn comonomer solution using acetone as a diluent and 80 g (or, 101.27 ml) of acetone. The comonomer solution was deaerated by bubbling nitrogen then introduced in to the Co-60 γ-rays at the dose of 15 kGy for direct radiation grafting. After completion of the radiation-exposing period, the grafted film was removed and washed thoroughly by acetone to extract the residual monomers and the homo polymers, which were accumulated in the grafted films. For finding more accurate grafting result the films were then further immersed in acetone for 48 hr and then removed the films from acetone and dried then weighed finally for calculating the degree of grafting value in percentage. FTIR absorption frequencies (Fig.3) are mentioned below:

IR: υ_{max} 2995.2, 2918.1, 2848.7, 1857.3, 1789.8, 1708.8, 1436.9, 1388.7, 1365.5, 1136.0, 1089.7, 1066.6, 1018.3, 985.6, 943.1, 842.8, 810, 752.2, 731.0, 719.4 cm^{-1}

2.2c. Grafted Polymeric Product of PEP-g-P(Sty/MAn)

Materials

Polyethylene pellet (PEP) was washed with distilled water and then acetone and finally dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used as received. Styrene (*Sty*) (Merck, Germany), M = 104.06, 11 = 0.79 kg.

Graft copolymerization of PEP:

For preparing the Sty/MAn grafting copolymer the PEP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) Sty/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.70 g of MAn, 10.30g (or, 13.04 ml) of Sty and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 3.1%.

2.2d. Grafted Polymeric Product of PEP-g-P(MMA/MAn)

Graft copolymerization of PEP:

For preparing the MMA/MAn grafting copolymer the PEP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) MMA/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.90 g of MAn, 10.10g (or, 13.04 ml) of MMA and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 2.9%.

2.2e. Grafted Polymeric Product of PPP-g-P(Sty/MAn)

Materials

Polypropylene pellet (PPP) was washed with distilled water and then acetone and finally dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used as received. Styrene (*Sty*) (Merck, Germany), M = 104.06, 1l = 0.79 kg.

Graft copolymerization of PPP:

For preparing the Sty/MAn grafting copolymer the PPP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) Sty/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.70 g of MAn, 10.30g (or, 13.04 ml) of Sty and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 2.0%.

2.2f. Grafted Polymeric Product of PPP-g-P(MMA/MAn)

Graft copolymerization of PPP:

For preparing the MMA/MAn grafting copolymer the PPP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) MMA/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.90 g of MAn, 10.10g (or, 10.74 ml) of MMA and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 1.90%.

2.2g. Grafted Polymeric Product of LDPP-g-P(Sty/MAn)

Materials

Low density polypropylene (LDPP) (55 micrometer thickness) films was washed with distilled water and then acetone and finally dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used as received. Styrene (*Sty*) (Merck, Germany), M = 104.06, 1l = 0.79 kg.

Graft copolymerization of LDPP:

For preparing the Sty/MAn grafting copolymer the LDPP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) Sty/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.70 g of MAn, 10.30g (or, 13.04 ml) of Sty and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 10.0%.

2.2h. Grafted Polymeric Product of LDPP-g-P(Sty/MAn)

Graft copolymerization of LDPP:

For preparing the MMA/MAn grafting copolymer the LDPP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) MMA/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.90 g of MAn, 10.10g (or, 10.74 ml) of MMA and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 6.80%.

2.2i. Grafted Polymeric Product of HPPE-g-P(Sty/MAn)

Materials

Heat pressed polyethylene (HPPE) sheet) was washed with distilled water and then acetone and finally dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used as received. Styrene (*Sty*) (Merck, Germany). M = 104.06, 1l = 0.79 kg.

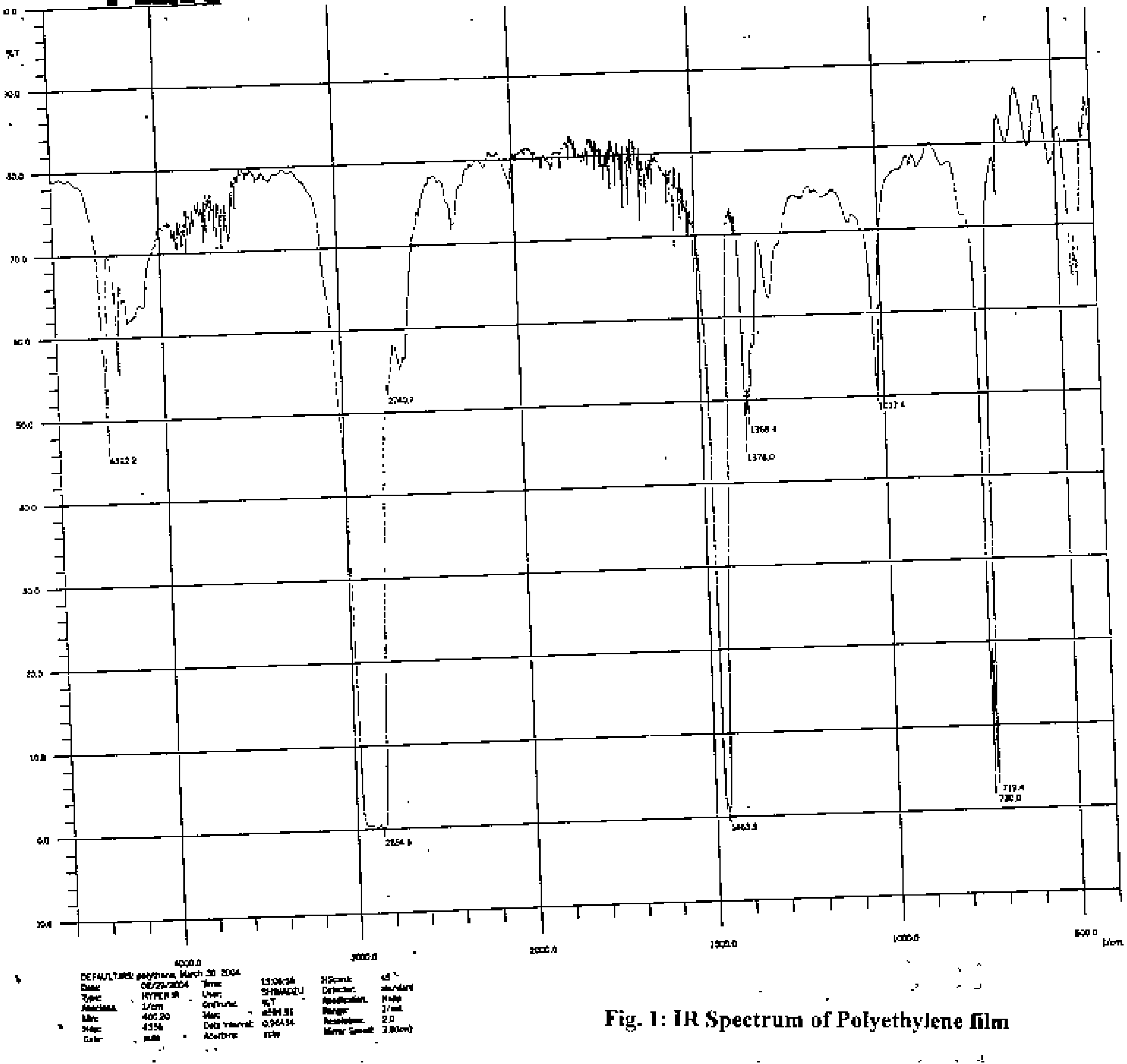
Graft copolymerization of HPPE:

For preparing the Sty/MAn grafting copolymer the LDPP were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) Sty/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.70 g of MAn, 10.30g (or, 13.04 ml) of Sty and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 1.80%.

2.2j. Grafted Polymeric Product of HPPE-g-P(Sty/MAn)

Graft copolymerization of LDPP:

For preparing the MMA/MAn grafting copolymer the HPPE were prepared first and then followed by washed with acetone, dried in air weighed and immersed in the 20% (1:1 mol/mol) MMA/MAn comonomer solution using acetone as a diluent. The 20% comonomer solution was prepared by taking 9.90 g of MAn, 10.10g (or, 10.74 ml) of MMA and 80 g (or, 101.27 ml) of acetone. Then same procedure of 2.2b was applied. In the purified grafted product the percentage of grafting was 1.68%.



No.	Pos. (1/cm)	Inten. (%T)
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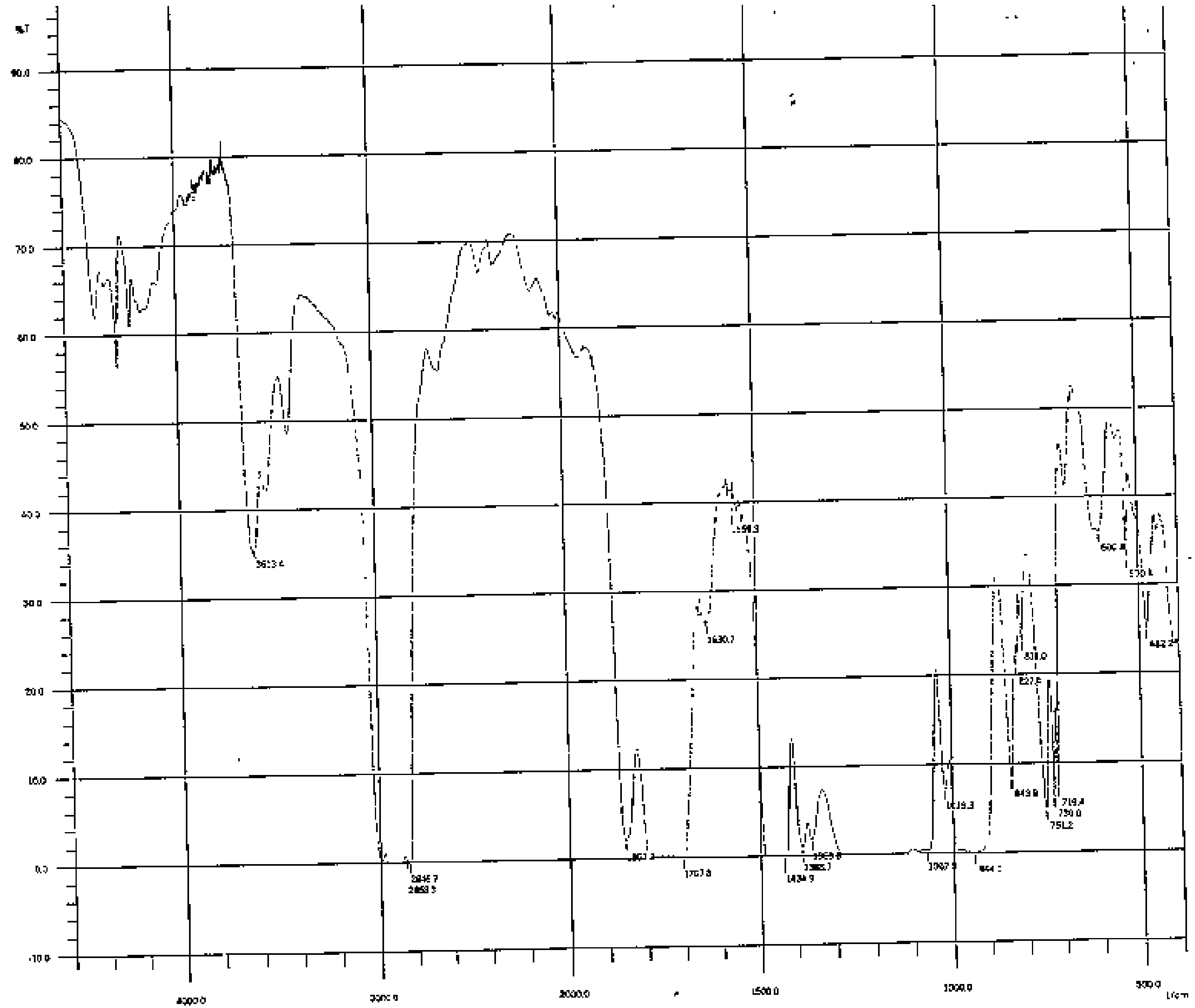
2	730.0	4.378
3	1017.4	50.640
4	1368.4	48.264
5	1378.0	44.901
6	1463.9	0.617
7	2740.7	53.316
8	2854.5	0.217
9	4322.2	47.105

polythene, March 30 2004

Fig. 1: IR Spectrum of Polyethylene film



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N15KGY.IR3  N 15KGY  March 22  2004
Date       02/22/2004   Time           17:44:47   No.Scans      45
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Abscissa   1/cm         Ordinate       %T         Apodization   Happ
Min        400.20       Max            4639.91    Range         1/cm
Pts        4394         Data Interval  0.96434    Resolution    2.0
Gain       auto         Aperture       auto       Mirror Speed  2.8(mm/s)
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No.	Pos. (1/cm)	Inten. (%T)
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2	530.4	33.003
3	600.8	36.021
4	719.4	7.363
5	730.0	6.163
6	751.2	4.762
7	811.0	23.842
8	827.4	21.053
9	843.8	8.414
10	944.1	0.049
11	1019.3	7.183
12	1067.5	0.383
13	1363.6	1.777
14	1388.7	0.974
15	1434.9	0.045
16	1559.3	38.782
17	1630.7	26.380
18	1707.8	0.088
19	1857.3	2.029
20	2846.7	0.026
21	2858.3	0.005
22	3613.4	35.764

N 15KGY, March 22, 2004

Fig. 2: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 15 kGy dose

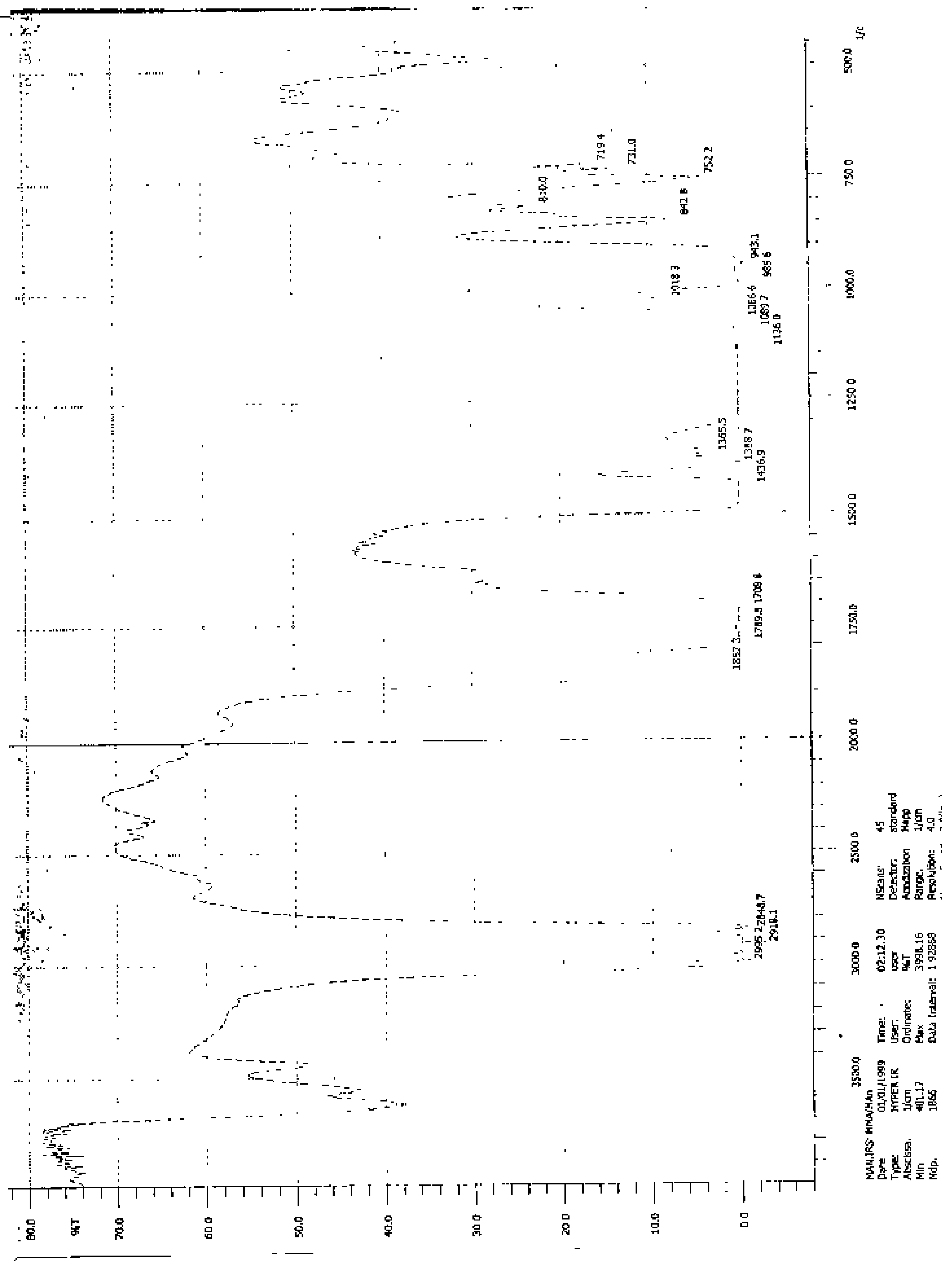
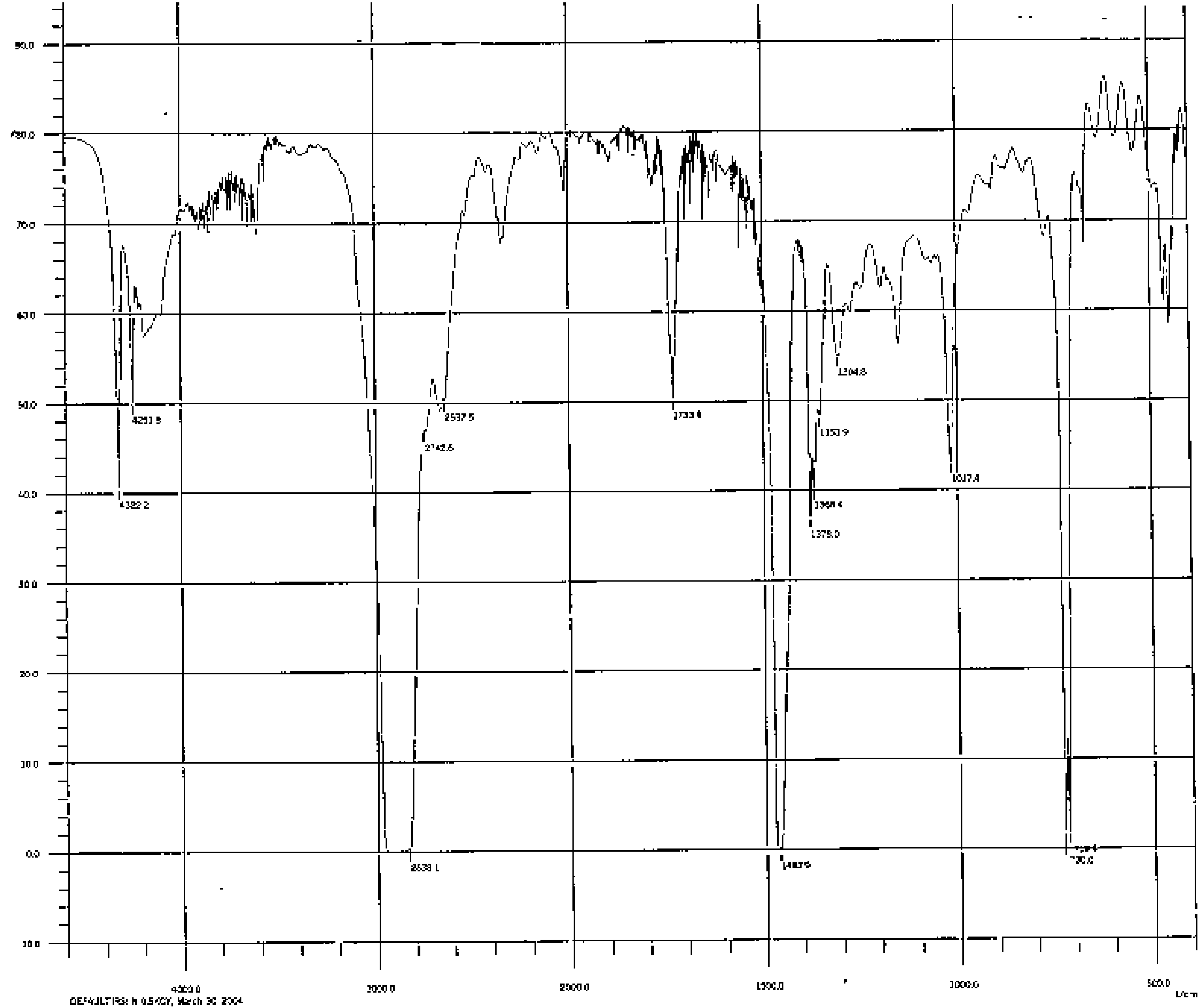


Fig. 3: IR Spectrum of Grafted Polymeric Product of PE-g-P (MMA/MAn) at 15 kGy dose



DEFAULTIRS: N 0.5KGY, March 30 2004

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Ndp	4356	Data Interval	0.96434	Resolution	2.0
Gain	auto	Aperture	auto	Mirror Speed	2.8(mm)

No.	Pos. (1/cm)	Intest.
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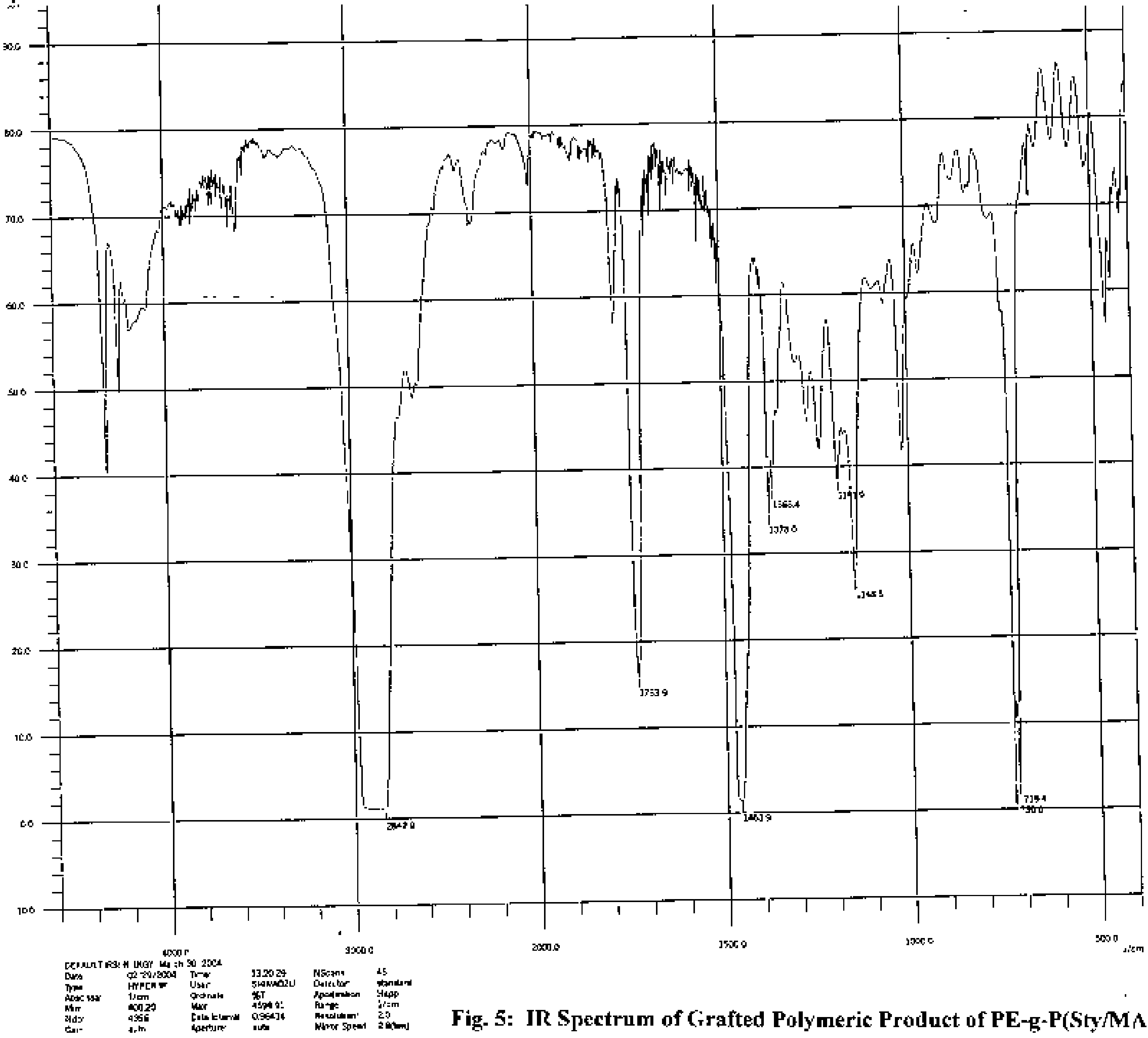
2	730 0	1.854
3	1017.4	43 09
4	1304 8	54 98
5	1353.9	48 29
6	1368.4	40.24
7	1378 0	36 92
8	1463.9	0.069
9	1733.9	50 38
10	2637 5	50 28
11	2742 6	46 87
12	2838.1	0.127
13	4251.8	50 10
14	4322.2	40 6

N 0 5KGY, March 30 2004

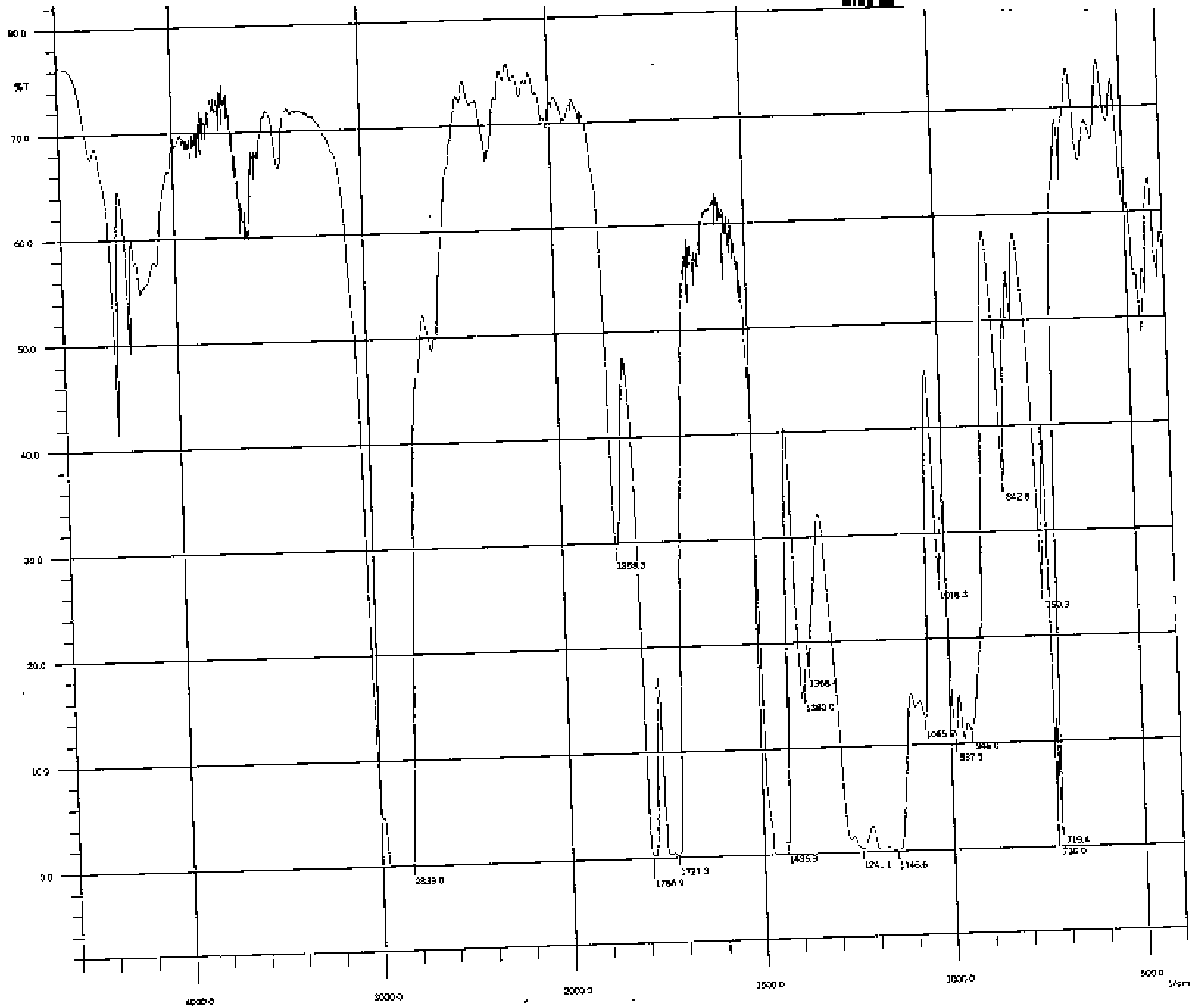
Fig. 4: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 0.5 kGy dose



No.	Pos. (1/cm)	Area
1	719.4	2.982
2	730.0	3.049
3	1148.5	26.950
4	1191.9	38.504
5	1368.4	37.537
6	1378.0	34.622
7	1463.9	1.300
8	1733.9	15.945
9	2842.9	1.032

N 1KGY, March 30 2004

Fig. 5: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 1 kGy dose

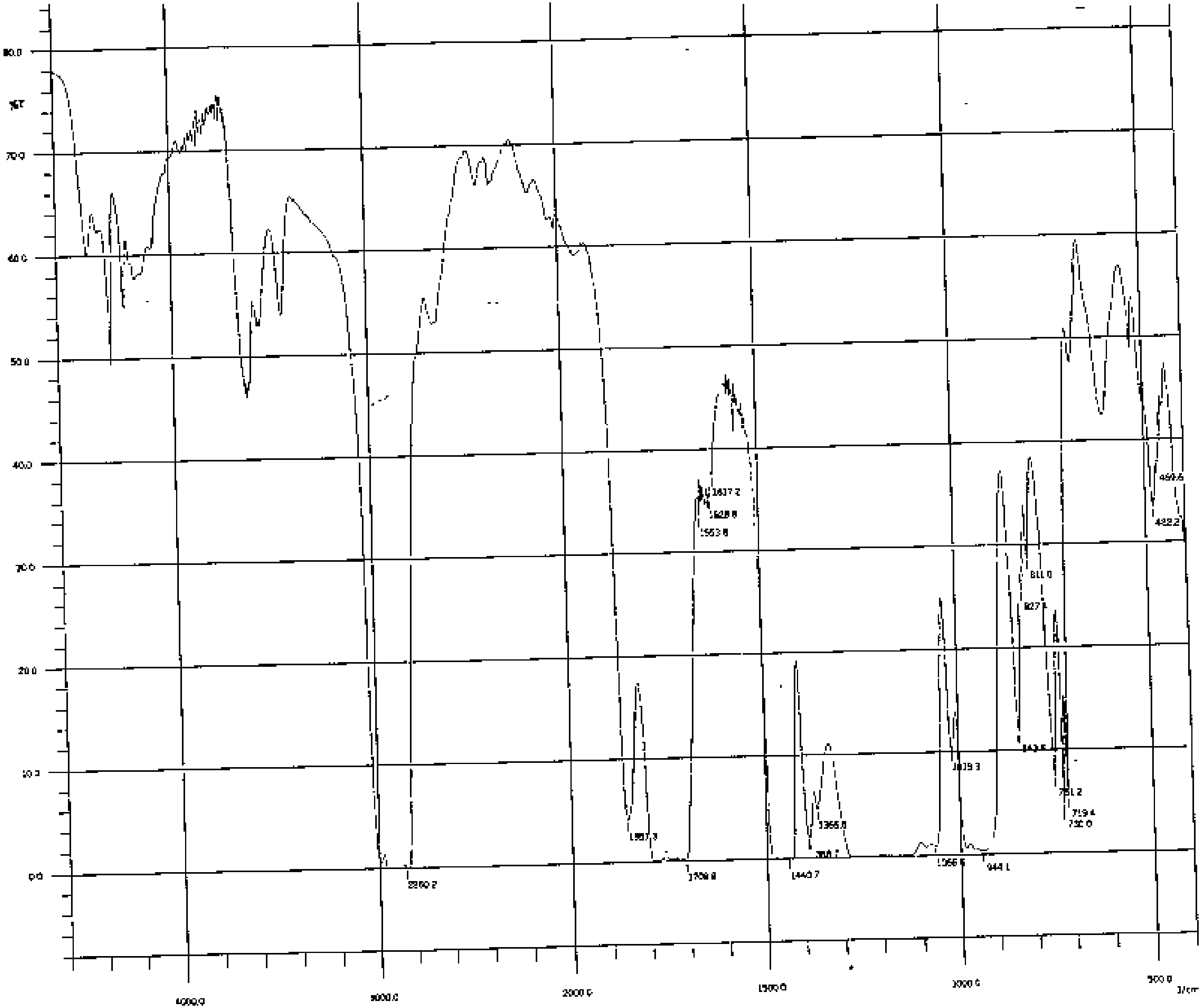


DEFAULTIRS N5KGY March 30 2004					
Date	03/29/2004	Time	13.13.22	NScans	45
Type	HYPER IR	User	SHIMADZU	Detector	standard
Abscissa	1/cm	Ordinate	%T	Apodization	Happ
Min	400.23	Max	4503.91	Range	1/cm
Max	4.356	Data Interval	0.96434	Resolution	2.0
Color	auto	Aperture	auto	Mirror Speed	2.8(low)

No.	Pos. (1/cm)	Inten. (%T)
1	719.4	2.088
2	730.0	2.255
3	750.3	24.451
4	842.8	34.789
5	946.0	11.250
6	987.5	10.727
7	1018.3	25.617
8	1065.6	12.481
9	1146.6	0.144
10	1241.1	0.276
11	1368.4	17.643
12	1380.0	15.363
13	1436.9	1.056
14	1721.3	0.219
15	1786.9	0.253
16	1858.3	29.361
17	2839.0	0.108

N 5KGY, March 30, 2004

Fig. 6: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 5 kGy dose



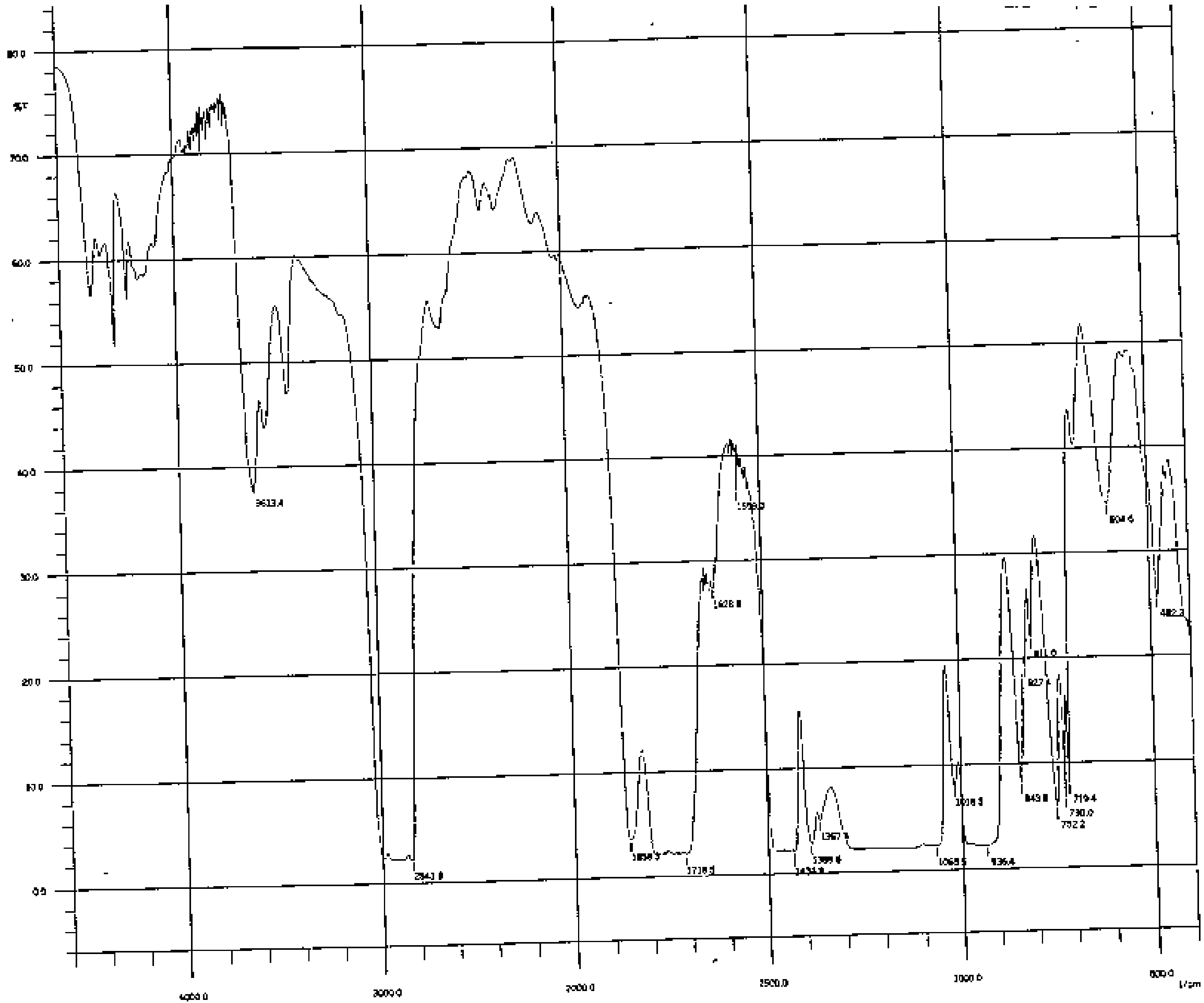
No.	Pos. (1/cm)	Inten (%T)
1	469.6	37.785
2	482.2	33.445
3	719.4	5.429
4	730.0	4.803
5	751.2	7.430
6	811.0	28.646
7	827.4	25.606
8	843.8	11.784
9	944.1	0.303
10	1019.3	10.157
11	1066.6	0.903
12	1365.5	4.786
13	1388.7	1.978
14	1440.7	0.003
15	1617.2	37.452
16	1628.8	35.245
17	1653.8	33.499
18	1708.8	0.089
19	1857.3	4.107
20	2860.2	0.012

N 10KGY, March 30, 2004

N10KGY.IRS N 10KGY, March 30, 2004

Date	02/29/2004	Time	12:27:40	NScans	45
Type	HYPER IR	User	SHIMADZU	Detector	standard S
Abscissa	1/cm	Ordinate	%T	Apodization	Happ
Min	400.29	Max	4599.91	Range	1/cm
Ndp	4356	Data Interval	0.96434	Resolution	2.0
Gain	auto	Aperture	auto	Mirror Speed	2.8(cm)

Fig. 7: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 10 kGy dose



DEFAULT.03, N 20KGY, March 30, 2004

Date	02/29/2004	Time	12:31:21	NScans	45
Type	HYPER IR	User	SHIMADZU	Detector	standard
Abscissa	1/cm	Ordinate	%T	Apodization	Happ
Min	409.20	Max	4599.91	Range	1/cm
Nop	4356	Data Interval	0.96434	Resolution	2.0
Gain	auto	Aperture	auto	Mirror Speed	2.8(mm)

No.	Pos. (1/cm)	Intst. (%
1	482.2	25.599
2	604.6	34.676
3	719.4	8.041
4	730.0	6.717
5	752.2	5.896
6	811.0	21.998
7	827.4	19.231
8	843.8	8.180
9	936.4	2.234
10	1018.3	7.998
11	1068.5	2.355
12	1367.4	5.039
13	1389.6	2.833
14	1434.9	2.110
15	1559.3	36.787
16	1628.8	27.454
17	1716.5	2.084
18	1858.3	3.556
19	2843.8	2.246
20	3613.4	38.182

N 20KGY, March 30, 2004

Fig. 8: IR Spectrum of Grafted Polymeric Product of PE-g-P(Sty/MAn) at 20 kGy dose

SECTION: 3

3. Present Work: Synthesis of Chelating Functionalized Polyethylene Grafted Polymers with Some Ammonia Derivatives.

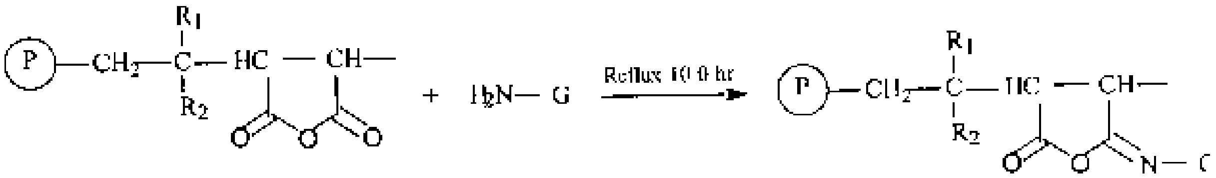
3.1 Rationale:

Metals are among the most important trace level constituents of natural water[54]. Many heavy metals are quite toxic and drinking water standards for these metals allow only a low level. In recent years a great deal of interest has been observed in relation to the applicability of chelating agents for removal or separation of metal ions from heavy metal contaminated water[55-59]. Among many sorptive materials various forms of synthetic polymers containing complexing molecules which are abundant at low cost have emerged as one of the most important matrices for the synthesis of new sorbents Chelates forming polymeric ligands have been extensively studied by several authors and many reviews are available in the field [60-67]. Several heavy metal ions such as Hg, Pb and Cu were extracted using thiol chelating resins[68] and chelating resins supporting dithiocarbamate and methyl thiourea [69]. Recently there has been substantial growth in interest in the use of radiation induced graft copolymerization of functionalized monomer onto polymer membranes for preparing chelating sorbent materials [69-72]. Graft copolymers involving maleic anhydride moieties have been the subject of considerable interest, because these anhydride moieties contain reactive carbonyl groups which are subjected to numerous reactions. In this respect radiation induced graft copolymerization of styrene/maleic anhydride (Sty/MAn) commoner and another pair of methyl methacrylate/maleic anhydride (MMA/MAn) onto polyethylene film was studied. Varieties of ammonia derivatives, such as hydrazine, phenylhydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride and S-Benzyl-thiouroniumchloride were introduced into the graft copolymer and the possibility of their practical uses in selectivity of arsenic and some toxic metal ions are investigated.

3.2 Results and Discussion:

3.2a Polyethylene Grafted Polymer of Sty/MAn Chelating Functionalized with hydrazine

According to the **Scheme 2**, here we demonstrate an approach where the chelating functionalization of the radiation grafted membrane of polyethylene film with binary monomer of styrene and maleic anhydride. In this purpose the grafted intermediate products were used for the completion of the chelating functionalized reaction. By this technique, there is an increase of molecular weight. Therefore, it is reasonable to describe the conversion of maleic anhydride groups in graft copolymer chains by the increasing percentage of the membrane weight.



Scheme 2

It can be seen that the grafted intermediate product easily combines with the hydrazine and give the condensation reaction resulting the formation of condensed product with hydrazine. This condensation product was then used for the removal of some heavy metals.

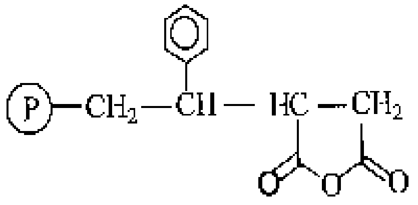
Polyethylene Grafted Polymer of Sty/MAn Chelating Functionalized with Other Ammonia Derivatives

According to the **Scheme 2**, it can be seen that the grafted intermediate product easily combines with the phenyl hydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride, *S*- Benzyl- thiouronium chloride and give the condensation reaction resulting the formation of condensed products with the respective ammonia derivatives. These condensation products (3.2b -3.2h) were then used for the removal of arsenic and some heavy metals.

3.2.1. Starting Materials:

Synthesis of Chelating Functionalized Polyethylene Grafted Polymers with Some Ammonia Derivatives.

The starting material for this chelating functionalization step was the grafted intermediate product of **PE-g-P**, and hydragene. The structures of those materials are shown below:



(PE-g-P)

$H_2N—NH_2$

Hydrazine

$H_2N—NHPh$

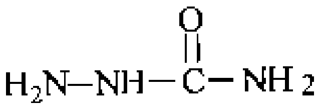
Phenylhydrazine

NH_2OH

Hydroxylamine

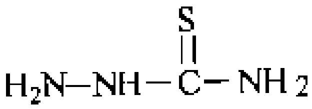
$H_2N—NHOH{\cdot}HCl$

Hydroxylamine hydrochloride



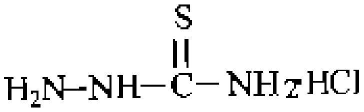
$H_2N–NH–\overset{\overset{\displaystyle O}{||}}{C}–NH_2$

Semicarbazide



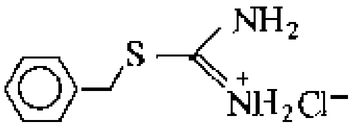
$H_2N–NH–\overset{\overset{\displaystyle S}{||}}{C}–NH_2$

Thiosemicarbazide



$H_2N–NH–\overset{\overset{\displaystyle S}{||}}{C}–NH_2{\cdot}HCl$

Thiosemicarbazide hydrochloride



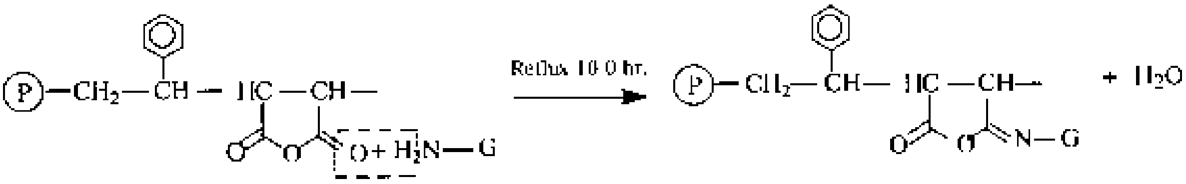
S-Benzyl-thiouronium chloride

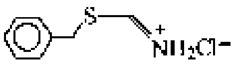
3.3. Characterization of the Product:

We have synthesized the chelating functionalized polymeric materials of low-density polyethylene (LDPE) film with Sty/MAn binary monomer system and the chelate formation accomplished through some ammonia derivatives. These products were characterized through gravimetric method. The spectroscopic method was not applied for characterizing these compounds. The sample products were not compatible for recording the IR spectrum because the chelating functionalized products were not permit the infrared ray. There by, through the gravimetric technique, the chelating functionalized products were characterized. In gravimetric method, it is reasonably described the conversion of maleic anhydride groups into condensed products in graft copolymer chains by the increasing percentage of the membrane weight.

3.4. Mechanism:

The simple mechanism for the chelating functionalized condensation reaction are shown below, where the oxygen atom of anhydride moieties and the hydrogen of hydragene combine with each other and finally give the chelating functionalized grafted product through the removal of water.



G	**Chelating Product**	**G**	**Chelating Product**
NH_2	3a	$NHCONH_2$	3e
NHPh	3b	$NHCSNH_2$	3f
OH	3c	$NHCSNH_2.HCl$	3g
OH.HCl	3d		3h

3.5 Conclusion:

We have described a very convenient and elegant method for the synthesis of chelating functionalized polymeric materials of low-density polyethylene (LDPE) film with Sty/MAn binary monomer system and the chelate formation accomplished through some ammonia derivatives, such as hydrazine, phenylhydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride and *S*-benzyl-thiouronium chloride. These chelating functionalized products were used as the absorbent and for removing the arsenic and some heavy metals from the aqueous solution. These chelating functionalized products were synthesized by readily available starting materials and clean technique.

3.6 Experimental:

Materials

The intermediate grafted product of **PE-g-P** with Sty/Man was washed with acetone and then dried in air. Maleic anhydride (*MAn*), purity 97% (BDH, Poole, England), M = 98.06 g/mol, was used. Hydragene (Merck, Germany), M = 32.05 g/mol, Phenyl hydragene (Merck, Germany), M = 108.14 g/mol, Hydroxylamine (Merck, Germany), M = 33.03 g/mol, Hydroxylamine hydrochloride (Merck, Germany). M = 84.51 g/mol. Semicarbazide (Merck, Germany), M = 75.07 g/mol, Thiosemicarbazide (Merck, Germany), M = 91.13 g/mol, Thiosemicarbazide hydrochloride (Merck, Germany), M = 127.59 g/mol and *S*-Benzyl thiouronium chloride were purchased from the local market, and used without any further purification. Ethanol absolute (Merck, Germany) were purchased from local market, M = 46.07g/mol, 1l = 0.79 kg and used without further purification. Acetone was extra pure

(Merck, Germany), M = 58.08. II = 0.79 kg and other solvents also used without further purification. Styrene (*Sty*) (Merck, Germany), M = 58.08, II = 0.79 kg. Dimethyl formamide (DMF), dioxane also used as solvents. Different solution of metals: Cr, Cu, Fe, Mn, Ni and Pb solutions were prepared from the respective salts.

3a. Chelating fictionalization of PE-g-P (Sty/MAn) with hydrazine:

To improve the chelating functionality of the prepared grafted film PE-g-P (Sty/MAn) were reacted with hydragene. The reactions were performed in solutions of 70ml DMF/dioxane (v/v) co-solvent and 0.32 g (0.01-mol) hydragene. The prepared solution was placed in a round bottom flask and stirred for 5 min before adding the grafted copolymer films (weight of the membrane was about 0.5g; degree of grafting 288). The reactions were kept at 70^0C for 10h. After completion of the reaction, the membranes were rinsed with ethanol, dried and weighed.

Chelating fictionalization of PE-g-P (Sty/MAn) with Other Ammonia Derivatives:

To improve the chelating functionality of the prepared grafted film PE-g-P (Sty/MAn) were reacted with phenylhydragene, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride and *S*-benzyl-thiouronium chloride. The reactions were performed in solutions of 70ml DMF/dioxane (v/v) co-solvent and 0.01-mol mole of respective ammonia derivatives. The products were then processed according to the previously mentioned procedure.

SECTION: 4

4. Present Work: Synthesis of Radiation Processed Hydrogel for the removal of Arsenic and some Heavy Metals.

4.1 Rationale:

Generally 'hydro' means water and 'gel' means jelly like substance. Hydrogel is a three-dimensional network structure of polymer containing a significant amount of water. The convenient tool for modification of polymeric material is radiation and this modification is accomplished through crosslinking, grafting and degradation. It has been recognized that the ionizing radiation is a very suitable tool for the preparation of hydrogel especially for biomedical application[46-49]. This process has versatile advantages. for example: easy process control, simultaneous crosslinking of the polymer to hydrogel formation and sterility of the product with high degree of assurance level, no necessity to add any initiators, no waste. and the technology is environment friendly since it leaves no residue or pollutant in the environment etc[46,47]. The necessary requirement to produce a usable hydrogel is the formation of cross-links between different polymer chains, resulting in a three-dimensional network structure [46-48,50]. This requirement is achieved by the irradiation of aqueous solution of polymeric materials (polyvinyl alcohol, in our study) through gamma rays or electron beam. Those irradiation techniques are able to control the degree and nature of cross-links, the parameter, which control the swelling capacity, mechanical properties and pore sizes in the hydrogel [48,49]. During irradiation of aqueous solution of polymeric materials the major portion of energy is absorbed for water forming free radicals and molecular products [50-53].

Metals are among the most important trace level constituents of natural water[54]. Many heavy metals are quite toxic and drinking water standards for these metals allow only a low level. In recent years a great deal of interest has been observed in relation to the applicability of chelating agents for removal or separation of metal ions from heavy metal contaminated water[55-59]. Among many sorptive materials various forms of synthetic polymers containing complexing molecules which are abundant at low cost have emerged as one of the most important matrices for the synthesis of new sorbents chelate forming polymeric ligands have been extensively studied by several authors and many reviews are available in the field[60-67]. Several heavy metal ions such as Hg, Pb and Cu were extracted using thiol chelating resins[68] and chelating resins supporting dithiocarbamate and methyl thiourea[69]. Recently there has been substantial growth in interest in the use of radiation induced graft polymerization of functionalized monomer onto polymer membranes for chelating sorbent materials[69-72]. So in this purpose the hydroxyl group containing PVA hydrogel is able to absorb the arsenic and some heavy metals through the showing of chelating capacity.

4.2 Results and Discussion:

When polymeric aqueous solution is subjected to ionizing radiation, highly reactive hydroxyl radicals, which react quickly with PVA than with polysaccharides, are produced. PVA is crosslinked predominantly at low dose and after that, carrageenan degradation occurs. This degradation was no longer protected by PVA, but the flour retained in almost unchanged state. The gel fraction (ratio of the extracted and unextracted gel weight) of PVA/flour hydrogel is increased with decreased carrageenan content.

Polysaccharides, which were added in the formulation, can improve the strength and flexibility of the prepared hydrogel, but these advantages were not possible from sans polysaccharides. Addition of two biodegradable polysaccharides instead of single polysaccharide has extra advantages, due to the fact that the use of these two could adsorb the cations and show the exchange property with anions. Even, the high molecular weight and branched polysaccharide, flour entrapped in the gel network structure and become part of the hydrogel. Hence, it could reduce the crosslinking density in the prepared hydrogel.

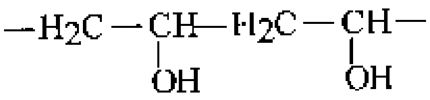
Anion exchanging behavior can be explained from the structure of the carrageenan polysaccharide and the radiation effect on it. Carrageenan is one of the most abundant hydrophilic polysaccharide and composed of D-galactose units linked alternately with α-1,3 and β-1,4 linkages. Due to their half-ester sulfate moieties, it is strongly an anionic polymer. During irradiation, the weaker chemical bond between C_1 and C_4 of the carrageenan molecule breaks down [52]. After breaking, the small carrageenan molecules with anionic half-ester sulfate moieties are entangled into the network structure of hydrogel, and then the forces influencing the swelling behavior rapidly increases due to localization of charges within the hydrogel [53], as well as the avail able arsenic species in water can exchange with the sulfate anion of the carrageen.

Another target of this work is the removal of arsenic and some heavy metals by the radiation processed hydrogel, and this purpose is achieved by the synthesized radiation processed hydrogel explained above. Now, hydrogel removed the heavy metals from contaminated water, due to the adsorption of metal through the hydroxyl group of PVA hydrogel.

4.2.1. Starting Materials:

Synthesis of Chelating Functionalized PVA Hydrogel for Removing the Arsenic and Some Heavy Metals from Aqueous Solution:

The starting materials are for this chelating functionalization step; poly vinyl alcohol (PVA), carrageenan and flour.



$$-H_2C-\underset{\displaystyle OH}{\underset{|}{CH}}-H_2C-\underset{\displaystyle OH}{\underset{|}{CH}}-$$

(PVA)

4.3. Characterization of the Product:

The hydrogel product was characterized through gravimetric method only. The spectroscopic methods were not applied for characterizing this product because the sample product was not compatible for recording the IR spectrum. Due to the applied radiation dose. there ,is an increase of gel content, so by the gravimetric technique, the chelating functionalized product characterized easily. Therefore, it is reasonable to describe the conversion of monomers in grafting copolymer products by increasing the percentage of gel content.

4.4. Mechanism:

The radicals (·OH, ·H) abstract hydrogen from the polymer chain and thus produced a carbon-centered radicals in polymer chains and these carbon-centered radicals on polymer chain further decay by forming intermolecular crosslinking, results to increase in molecular weight and finally a hydrogel. Sometimes intramolecular and disproportionation reactions also take place. These reactions may be controlled, by the high dose rate (electron beam) and lower concentration, favors intramolecular crosslinking whereas the low dose rate (gamma radiation) and higher concentration favors intermolecular crosslinking, which is used for making PVA/polysaccharide biomaterials like wound dressing. The biodegradable polymers, such as PVA, PVP are converted to CO_2 and H_2O by digestion and bacterial degradation in the soil. So, considering their environment friendly nature such kinds of polymers have been effectively used to develop hydrogel. which can accelerate the healing of wounds. Generally, hydrogel contains 30-90% water that entrapped in the three dimensional network structure of PVA hydrogel. This large water content makes them biocompatible and is preferred as biomaterials. Even the biodegradations of such biomaterials are not affected by formed crosslinked network structure.

4.5 Conclusion:

By applying the chelating functionalized radiation processed hydrogel materials we can remove arsenic and some heavy metals. We have described a very convenient method for the synthesis of chelating functionalized PVA hydrogel as well as the synthesized material has the affinity towards the removal of arsenic and some heavy metals from the contaminated water. This chelating functionalized product was synthesized by readily available starting materials and clean technique.

4.6 Experimental:

Materials

Kappa-carrageenan was obtained from Shemberg Corp., Phillippines and PVA from BDH, Poole, England. The polysaccharide (flour) (food grade), Nutrient Agar (Oxoid, England) and Potato Dextrose Agar (Oxoid, England) were purchased from the local market. All the materials were used without any purification.

Sample Preparation and Irradiation

PVA was added slowly in hot deionized water with continuous stirring followed by 1% polysaccharide (flour) from the previously prepared stock solution and finally 1% carrageenan. This solution was allowed to stand for over night to mix well and then autoclaved at 121°C & 15 psi for 15 minutes. After autoclave, the hot aqueous solution of this mixture were poured in disposable polyethylene terephthalate (PET) trays and allowed to cool. These were sealed in polyethylene bags and irradiated with gamma rays generated from a ^{60}Co source. After irradiation various properties of the resulting hydrogel were measured.

SECTION: 5

5. Present Work: Application of the synthesized Products.

Arsenic and heavy metals are harmful as well as the level of drinking water standards is deteriorated due to the presence of these metals[19,73]. In recent years, a great deal of interest has been observed in relation to the applicability of chelating agents for removal or separation of metal ions from contaminated water[19, 20 21]. Similarly much efforts in the investigation in connection to eliminate arsenic from water have also been given[25,74]. It is worthwhile to note that many sorptive materials, made of various forms of synthetic polymers containing complexing molecules, which are abundant at low cost, have immersed as one of the most important matrices that play important role to absorb the desired elements. Three major categories, which are usually followed to eliminate arsenic from water, are chemical precipitation, adsorption and membrane separation/filtration[75]. Research on cation-exchange membrane, has grown much attention for selective removal of some heavy metal ions (Fe, Cu, Pb, Hg, etc.) and radioactive element from aqueous solution[20 21 76]. Recently, anion exchange methods have been recognized as an excellent technology for arsenic removal when arsenic species are in anionic state[75]. Though much research merely on the identification and determination of arsenic and heavy metals in the contaminated water has been done in Bangladesh[76], but the number of specific work is very few to remove arsenic from this contaminated water so far in this country. Therefore, the present work will be undertaken to do research for the removal of arsenic/heavy metals from water.

Because of various types of ligands, which have been introduced into polymers to be used, as chelating polymer is an important factor to determine how much affinity showing such graft polymer to remove a specific metal ion from the solution.

Studying the sorption capacity of the sorbent towards various metal ions is carried out by equilibrating a fixed amount of the sorbent (0.5g) with different metal ion solutions of 100 ppm concentration for 12h. The maximum metal uptake of different metals by these treated membranes is shown in the respective table.

The graft polymer films treated with hydrazine, phenylhydrazine, hydroxylamine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide, thiosemicarbazide hydrochloride show the affinity by the adsorption of different metals. The chemisorption capacities of the sorbents towards Cu(II), Fe(III), Ni(II), Pb(II), Mn(II), Cr(III) is found to be different with various chelating groups. For PE-g-P(Sty/MAn) graft copolymer treated with NH_2OH and $NH_2OH.HCl$ the sorption of Fe(III) ions is higher than other metals. However, in the case of PE-g-P(Sty/MAn) grafted films treated with semicarbazide, thiosemicarbazide and thiosemicarbazide hydrochloride the sorption of Cu(II) is higher than other metals under investigation. Meanwhile, for grafted films treated with hydrazine and phenylhydrazine the chemisorption of Pb is higher than other metals. The aforementioned results can be explained according to the ligand type and the structure of chelate.

The reaction of various ligands with different metal ions or metal complexes usually results in various coordination structures. Therefore, the coordination structure of graft copolymer-Cu complex is different from that of Fe(III) and /or other metal used.

It is reported that Cu(II) can commonly be 4-or 6-coordinate and exist in any of several geometries. However, Fe(III) is most commonly 6-coordinate octahedral [21].

On the other hand, the importance of both inherent acidity and a second hard soft factor is well known by the Irving-Williams' series and some oxygen, nitrogen and sulfur chelates.

The Irving-Williams' series of increasing stability on the increasing of inherent acidity of the metal (largely due to decreasing size). Superimposed upon this is a hardness-softness factor in which the softer species coming later in the series of favoured ligands S>N>O [21]. The harder, early transition metals ions (few d electrons) preferentially bind in order of O>N>S. Therefore, the films containing ligands of oxygen-donating atoms such as NH_2OH treated films and/or hydrogel (which also contain hydroxyl group) prefer Fe(III) ions which have few d-electrons than other metals.

However, softer species such as Cu(II) (which is of high d-electron) prefer ligands containing S and/or N atoms to chelate with.

The absorption of metal ions on treated films containing O donor (hard base) atoms prefer the hard acid metal ions the in order of Fe(III)>Mn(II)>Cr(III)>Cu(II). Accordingly, their behavior followed the Irving-Williams' series. However the adsorption of metal ions on the NH_2OH–treated films and/or hydrogel which contain donating oxygen atoms only was in the order of Fe(III)>Mn(II)>Cr(III)>Cu(II) only exception of Ni(II).

The selectivity and affinity of the polymer towards Fe(III) or other metals investigated here can be attributed according to the valence and atomic radii of metal, stability constant, temperature and structure of chelate.

The increase in oxidation state causes a shrink in size, not only because the ion becomes smaller as it loses electron density, but also the increase of the cationic charge pulls the anions in closer. Therefore, the selectivity of Fe(III) ion by chelating polymeric materials containing O donating ligands can be attributed according to high valence and low atomic radii of Fe(III).

Table 1: Results of arsenic Removal:

Sorbent	Removal %
Hydrogel	34.54
Hydroxylamine hydrochloride treated Sty/MAn grafted membrane	25.312
Hydroxylamine hydrochloride treated MMA/MAn grafted membrane	19.125
S-Benzyl-thiouronium chloride treated Sty/MAn grafted membrane	5.280

Table 2: Radiation grafted membrane treated with hydrazine:

Metal	Removal %
Pb	10.92
Fe	10.13
Cu	9.17
Ni	8.34
Mn	7.09
Cr	6.35

Table 3: Radiation grafted membrane treated with phenylhydrazine:

Metal	Removal %
Pb	10.11
Fe	9.89
Cu	9.04
Ni	7.79
Mn	6.97
Cr	6.17

Table 4: Radiation grafted membrane treated with hydroxylamine:

Metal	Removal %
Fe	13.27
Mn	12.3
Cr	11.88
Cu	11.59
Pb	8.34
Ni	6.07

Table 5: Radiation grafted membrane treated with hydroxylamine hydrochloride:

Metal	Removal %
Fe	12.98
Mn	11.77
Cr	11.52
Cu	10.31
Pb	7.98
Ni	6.72

Table 6: Radiation grafted membrane treated with semicarbazide:

Metal	Removal %
Cu	21.36
Ni	19.37
Fe	14.22
Mn	11.85
Cr	10.15
Pb	9.33

Table 7: Radiation grafted membrane treated with thiosemicarbazide:

Metal	Removal %
Cu	19.57
Ni	17.21
Fe	10.79
Mn	10.12
Cr	8.99
Pb	8.57

Table 8: Radiation grafted membrane treated with thiosemicarbazide hydrochloride:

Metal	Removal %
Cu	18.32
Ni	17.02
Fe	9.38
Mn	8.95
Cr	7.37
Pb	6.16

Table 9: Removal percentages of metal by hydrogel

Metal	Removal %
Fe	59.03
Mn	54.92
Cr	41.46
Cu	33.89
Pb	32.08
Ni	21.86

Table 10: Effect of binary monomer unit on graft copolymerization

Radiation dose (kGy)	Grafting percentage of MAn-Styrene	Grafting percentage of MAn-MMA
0.50	2.06	1.72
1.00	5.24	4.76
5.00	58.77	41.90
10.0	180.17	159.75
15.0	288.18	253.00
20.0	328.81	295.38

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