Ain Shams University

Functionalized Hydrogels and Membranes Prepared by Ionizing Radiations For Possible Use in Biomedical and Industrial Applications

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ACKNOWLEDGEMENT

First of all, thanks to GOD for the infinite helps and persistent supply with patience and efforts to accomplish this work successfully.

I would like to express my deep gratitude and thanks to Prof. Dr. Abo El-Khair B. Mostafa (University College for Women, Ain Shams University) for his supervision, constructive criticism and deep concern in this work.

I am cordially indebted to Prof. Dr. H. Abd El-Rehim and Ass. Prof. Dr. H. Kamal, Department of Polymer Chemistry, National Center for Radiation Research and Technology (NCRRT), for suggesting, planning the point of research, close supervision, and also for the sincere guidance during their direct supervision throughout this work.

Sincere thank to Ass. Prof. Dr. E. Abd El-Wahab (University College for Women, Ain Shams University) for her supervision and encouragement.

Deepest thanks and sincere gratitude are due to Dr. Ghada Adel, Department of Polymer Chemistry, (NCRRT), for co-supervision, valuable discussion, encouragement and critical reading of this work.

Many thanks are also due to all colleagues and staff members of Polymer Chemistry Department, Staff of Central Labs. and groups of irradiation facilities at (NCRRT) for their helps and facilities provided throughout this work. Also, my deepest thanks to Prof. R.Mehnert at IOM, Leipzig, Germany for all facilities provided and helps during my visit of year 2003.

AIM OF THE WORK

Radiation grafting covers a very broad field of polymer chemistry with numerous potential applications of industrial interest. It is a well known method for modification affects the chemical and physical properties of polymer and is of particular interest for achieving specifically desired properties.

Synthetic membranes have achieved a wide range of applications. Such membranes are used for a great variety of separation processes such as dialysis, electrodialysis, hemodialysis, ultra- and hyperfilteration and pervaporation. In such applications the process is generally designated according to the applied driving force such as concentration, electrical potential, or pressure difference across the membrane. Therefore, a great deal of work was spent during the last 40 years for the development of the best possible membranes and hydrogels using almost every available polymeric materials. A large effort is devoted to the production of permselective membranes by grafting of different hydrosoluble monomers onto polymer films.

The suitability of a given membrane for any particular process is determined by several factors. A very important requirement is the chemical stability toward solutions of various pH's, organic solvents, oxidizing agents, and fouling by bacteria. In addition a membrane must show good mechanical properties with the smallest possible thickness and very often low electrical resistance. Other properties such as good dimensional stability under different wetting conditions and flexibility that facilitates handling and use can not be neglected. Fluorine- containing polymers have drawn much attention in the past and gained wide practical use because of their excellent thermal, chemical stability and mechanical properties. Therefore, PFA fluorinated copolymer was chosen in this study to be the base material for the preparation of supported grafted hydrogel and ionic membranes, also PP and LDPE films were used as substrate for the grafting process.

In this connection, the present work deals with the preparation and characterization of radiation graft copolymers which may be suitable as membrane and supported hydrogels for possible use in the field of wastewater treatment from some toxic metals and also in some biomedical applications as in kidney dialysis. In this respect, cationic, anionic and cationic/anionic graft copolymers were prepared by radiation-induced graft copolymerization of acrylic acid (AAc), 4-vinylpyridine (4-VP) and AAc/4VP onto poly(tetrafluoroethylene - perfluorovinylether) (PFA), polypropylene(PP) and low density polyethylene (LDPE) films. Such prepared graft copolymers were investigated in the removal of some alkali metal cations namely; Mg, Ca, K and Na from aqueous solutions. The possibility of their practical uses was also determined and evaluated according to the characteristic properties of the prepared membranes and supported hydrogels and their selectivity towards the removal of such different metal ions.

ABSTRACT

Preparation of graft copolymers by radiation graft copolymerization of acrylic acid (AAc) and 4-vinylpyridine (4-VP) individually or binary monomer mixture in two successive steps onto poly (tetrafluoroethylene - perfluorovinylether) (PFA), polypropylene (PP) and low density polyethylene (LDPE) films was studied. The graft copolymerization was carried out using mutual gamma irradiation technique. The effect of reaction conditions on the grafting yield has been investigated. Further chemical treatments have been carried out to improve the ion-exchange and hydrophilic properties of the prepared graft copolymers.

To elucidate the possibility of practical use of the prepared graft copolymers as membrane and supported hydrogel, their physical and chemical properties such as swelling in water, mechanical and thermal properties and thermal stability were investigated. The graft copolymers have been characterized using infrared spectroscopy FTIR, thermal gravimetric analysis (TGA) and differential scanning calorimetric (DSC) to determine the structural changes as a result of grafting. Some properties of the graft copolymers have been studied as a function of grafting yield such as, water uptake and mechanical properties. The applicability of the prepared membranes and supported hydrogels was studied in terms of its possible use in the removal of metal ions from wastewater (aqueous metal salts were used as a model for wastewater). The factors that influence the ion-exchange property during the treatment of wastewater such as time, temperature, metal feed concentration and degree of grafting were investigated. Results of this study showed that the prepared grafted membranes and supported hydrogels possessed good thermal stability, acceptable tensile strength and good affinity towards the removal of alkali metals from their wastes which make them acceptable for practical uses.

CHAPTER I
INTRODUCTION

I.1. General Principles of Grafting

Graft copolymerization offers an unequaled versatility and specificity for incorporating new molecular functionalities into the existing polymers in a well-controlled manner (1). Grafting is used in situations where the requirements for bulk and surface properties cannot be readily met using a single polymeric material. In fact, surface modification by graft copolymerization offers a simple and unique method for redesigning and reengineering the surface molecules of all polymers, including the most inert fluoropolymers (2, 3) The beauty of grafting is that it is possible to construct a material whose bulk is comprised of one polymer type but the surface is made of a different polymer type. Grafting allows the selection of virtually any combination of bulk and surface material. Using this approach, one begins with a bulk material (often chosen on the basis of good mechanical strength and low cost), and then "grows" a second polymer type on the surface of material. Much geometry, including films, powders and macroscopic objects has surface grafts attached in this way. A wide range of graft layers has been produced by varying available parameters: utilizing different monomers or combinations of monomers, adding crosslinking agents, choosing conditions to vary the depth of penetration of monomer into the bulk, etc. The nature of the monomers in this context plays an important role. Many of the grafting processes that have been reported to date have involved relatively hydrophobic polymers which have been given a hydrophilic surface layer using a monomer such as an acrylate, to facilitate interaction with aqueous or ionic substrates.

Grafting process can take place in two different ways, i.e. ‘surface grafting’ and ‘bulk grafting’. Surface grafting occurs onto the surface of the polymer whereas bulk grafting occurs deep-rooted into the polymer matrix. In case of membrane modification, surface grafting is more suitable than the bulk grafting for biomedical applications.

Surface graft copolymerization is a simpler and more versatile technique than that of the coupling reactions, and has been explored much more extensively. Graft copolymerization of monomers normally requires only the generation of active species on the substrate surface to initiate the polymerization. It is based most commonly on the free radical reaction of vinyl or acrylic monomers, although cationic and anionic polymerization mechanisms can also be used. For graft copolymerization via the free radical mechanism, either free radicals or peroxides have to be generated in the surface region of the substrate to initiate chain growth. Surface graft copolymerization proceeds via the diffusion of monomers, present either in vapor or in solution, to the substrate surface and react with the active centers there, which is regenerated after each monomer addition, the reaction continues and the chains propagate from the substrate surface. In addition to chain growth from the surface, ungrafted homopolymer chains are also produced and can become adsorbed on the substrate but they must be removed by vigorous extraction.

Surface modification of polymer by grafting has incorporated the feature of surface molecular design into the traditional approaches. Through the intelligent choice of functional monomers for graft copolymerization or polymers for grafting, new surface functionalities, such as biocompatibility and physiological activity, metal-free conductivity, and bondability to metals, can be readily incorporated into the existing polymers.

The radicals that contacted with the substrate surface will create unpaired electrons by abstraction of hydrogen from the polymer chains at the surface **(4)**. In the case of initiation by surface pre-activation, the peroxide and hydroperoxide species required for the initiation of surface graft copolymerization are usually generated on the substrate surface may with high-energy radiation, such as gamma-rays**(5)** electron and ion beams**(6)**. The effects of the various surface oxidation processes on hydrocarbon and fluoropolymers have been compared **(7- 9)**. When the pretreated surface is exposed to radiation in the presence of a thoroughly degassed monomer or monomer solution, the decomposition of the surface peroxide species readily results in the initiation of surface graft copolymerization. A kinetic model of free-radical surface graft copolymerization, based on a conservational polymerization and molecular-weight distribution numerical algorithm, has been developed **(10)**.

The improvement in properties of the grafted copolymer depends on the nature, amount and chain length of the grafted branches as well as on the type of distribution of the grafted monomer in the base polymers. The properties which might be incorporated into the base polymer are determined by the evaluation of various parameters e.g. elongation, elasticity, permeability, etc. To set up a correction between the physical properties and structural changes, knowledge of the model of distribution of the monomers in the trunk polymer is essential.

Moreover, the structural changes are also dependent on the nature of the base polymer as well as the monomer, the method of graft copolymerization, medium in which reaction occurs, and the extent of graft copolymerization, (11).

The properties of the graft copolymer change according to the combination of trunk polymers/monomers and the reaction conditions such as the irradiation dose, dose rate, temperature and concentration of monomer. In addition, the absolute values of these properties depend on the method of measurement. Therefore, an accumulation of data in this field may be necessary for establishing the reaction condition for the synthesis of the desired membranes by radiation - induced grafting (12).

I.2. Radiation Grafting Technique

Radiation is a powerful source of energy for chemical processing applications. Thus, it can be applied in different industrial areas and can initiate chemical reactions which have led to the large-scale use of radiation for various industrial processes. Radiation provides a highly advantageous means of grafting. A large concentration of free radicals is produced in the irradiated material without the use of chemical initiators. These radicals undergo reaction with a monomer to produce macromolecular chains that are covalently bound to the irradiated specimen. Generally with the radiation technique, absorption of energy by the backbone polymer initiates a free radical process. The use of radiation-grafted copolymers, as membranes is just an attempt to get a compromise between good mechanical and chemical properties as well as membrane properties.

Radiation grafting is one of the most promising methods because of its easy handling at room temperature, large penetration in polymer matrix, rapid and uniform formation of active sites for initiating grafting throughout the matrix, under appropriate experimental conditions for homogeneous diffusion of monomer in the polymer. Modification of polymer properties can be accomplished not only at the surface but also throughout the internal phase of polymer **(13)**.

Careful selection of proper dose and intensity of the radiation can control the size of the grafted domain in the copolymer matrix. It is, therefore, possible to introduce membrane properties into a film without much influencing important characteristics of the trunk polymer, such as thermal stability and chemical resistance **(14)**.

Radiation graft copolymerization can be carried out by using three main methods: -

1) Direct or simultaneous radiation grafting in which the polymer substrate is irradiated in the presence of monomer or monomer-containing solution; often the solution contains an inhibitor to retard the homopolymerization in the liquid phase.

2) Pre-irradiation grafting method, in which the polymer first irradiated under vacuum or in inert atmosphere at low temperature and then subsequently placed into contact with the monomer solution at appropriate reaction temperature and time intervals.

3) Peroxidation grafting method, in which the material is irradiated in the presence of air. The grafting step can be performed much later; peroxides formed during irradiation can be activated by elevated temperature to form radicals at the desired time (5).

Thus radiation-induced grafting is a versatile technique to modify the properties of polymeric membranes. These membranes play a very important role in various separation processes such as desalting of brackish and sea water, separation of gases, separation of wafer from organic and inorganic mixture, waste water treatment, battery technology, etc.

Grafting of hydrophilic monomers onto high-surface-area substrates to yield materials of high ion-binding capacity has been the subject of many publications (15- 27). These materials have been developed for use in removal of heavy and toxic metal ions from industrial wastewater, and for capture of U ions in the treatment of liquid radioactive waste. Ion-binding materials prepared in this way are also being tested for harvesting uranium from the ocean and for use as battery membranes.

Research on grafted materials to meet a variety of other surface property requirements remains active; examples in recent years include membranes for gas separation(28), adhesive layers(29), enhanced binding of liquid crystal layers (30, 31) , and surface attachment of organic layers to inorganic fillers to enhance compatibility with polymer matrices(32 ,33). Methods for making grafting technology more versatile are also under ongoing development. Recent reports continue to explore the use of multifunctional additives and charge-transfer complexes to enhance grafting yield (34- 36). The use of supercritical CO_2 to enhance monomer penetration into the surface undergoing grafting (37), and the use of heavy ion beam irradiation to yield surfaces with only partial graft coverage (39– 40) have been explored. The addition of acids and salts to enhance grafting yield is a widely used technique (41).

Fluorinated polymers, such as poly (tetrafluoroethylene) (PTFE), are not susceptible to surface oxidation by ozone and corona treatments. The active species for surface graft copolymerization of fluoropolymers are effectively produced only by plasma, Ar^+ beam, γ-rays and electron beam treatments (42- 45). The fluorinated polymers, however, often suffer serious chain scission upon exposure to vacuum ultraviolet. The influence of grafting parameters, such as pre-irradiation dose, monomer concentration, and grafting temperature on the graft yield of hydrophilic N-vinyl-2-pyrrolidone polymer on g-ray pre-irradiated PTFE and poly(tetrafluoroethylene-hexafluoropropylene) films have been studied in detail(46) .

I.3. Characterization of Hydrogel

Hydrogels are typically synthesized by one of the two well-established procedures: (a) polymerization and simultaneous or post-polymerization cross-linking of hydrophilic monomers and (b) modification of hydrophilicity of existing polymers with potential hydrogel properties by grafting with hydrophilic monomers. The preparation of hydrogels by radiation treatment of aqueous solution of hydrophilic monomers or polymers carries some advantages over the conventional techniques, it doesn't require initiators, crosslinkers and can be used practically with any vinyl