Chapter 15

ESTABLISHED AND EMERGING APPLICATIONS OF RADIATION-INDUCED GRAFT POLYMERIZATION

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1. INTRODUCTION

Among various physical and chemical methods, radiation-induced graft polymerization (RIGP) has advantages over the other grafting techniques. Radiation-induced grafting is a means of modifying base polymers wherein grafts can result in a combination of properites related both to the base polymer backbone and to the grafted chains. Through the proper choice of monomers with appropriate functionalities, new properties such as biocompatibility, hydrophilicity, hydrophobicity, adhesion, friction resistance, barrier properties, *etc*. can be incorporated onto the radiation-activated polymers, especially very inert ones, as fluoropolymers, by graft copolymerization.

Radiation-induced graft copolymerization has been used to produce graft copolymers with diverse functionalities, properties and configurations that meet the requirements of a variety of specific separation and purification applications which are of industrial interest. Various functional copolymers in form of selective membranes, ion-exchange resins, adsorbents and polymer electrolytes and solid polymer catalysts were found to be suitable for applications in the fields of water treatment, in the chemical industry, in environmental decontamination and in biotechnology and medicine. Details of the preparation and applications of a variety of functional copolymers obtained by radiation-induced graft copolymerization for separation and purification can be found in a review article published by Nasef and Güven [1].

Radiation-induced graft polymerization has been developing in three main directions: (i) polymeric membranes, (ii) polymeric sorbents, and (iii) graft polymers for medical and biotechnology applications. Among these applications, membranes play a key role in separation and purificaton processes. Specialty membranes have become an essential part of our daily life because of their use in areas such as biotechnology, nanotechnology and membrane-based energy devices, in addition to different membrane-based separation and purification processes. The development of these uses is very cost-effective due to low energy requirements for grafting and the ease of scale-up of membrane modular design. Various types of membranes have been developed for the use in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation, electrodialysis, solid polymer electrolytes, fuel cell applications, membrane-based sensors, medical uses such as artificial organs, controlled release drugs and tissue engineering. Among these membranes, ion-exchange membranes are among the most advanced separation membranes. Ion-exchange membranes are used to solve two important environmental problems: (i) the recovery and enrichment of valuable ions, and (ii) the removal of undesirable, hazardous ions from aqueous streams, especially the extraction of toxic metal ions from effluents. Such membranes or adsorbents in general have potential use as new functional materials in the separation of ionic species, mostly encountered in the solutions containing multiple components.

Many industries, such as electronics, fiber optics, and other materials based areas as nanotechnology as well as pharmaceutical and food processing have increasing requirements for extremely high purity materials. Parts per million levels of impurities are now common, and the need for parts per billion or less concentrations of impurities is becoming more frequent.

For a wide range of applications, the most desired properties required for successful ion-exchange membranes are [2]:

- High permeability selectivity – an ion-exchange membrane should be highly permeable to counter-ion, but should be impermeable to co-ions.
- Low electrical resistance – an ion-exchange membrane should have low electrical resistance and hence less potential drop during electro-membrane processes.
- Good mechanical stability – the membrane should be mechanically strong and should have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions.
- High chemical stability – the membrane should be stable over a wide pH range from 0 to 14 and in the presence of oxidizing agents.

All of the above listed properties may not be found in conventional commodity polymers. Hence the existing polymers need to be modified to cope with these expectations. For most of the applications, modification of surfaces only would be sufficient to meet these requirements. In polymer technology, surface modifications can be easily performed by grafting of a polymer to impart the properties lacking in the base polymer. Grafting of a second polymer chain on another polymeric substrate can be achieved by various free radical polymerization techniques.

Radiation-induced graft copolymerization has been used very often to prepare various types of membranes. However, most of the radiation-grafted membranes are ion-exchange materials because functional monomers can be easily grafted onto prefabricated polymer films, a process that is difficult to perform using other grafting techniques. The consistent and growing demand for ion-exchange membranes in separation, electrochemical and biological applications along with the high cost of commercial perfluorinated ionomeric membranes have driven research to develop alternative, less expensive membranes. A number of radiation-grafted neutral and specialty functional membranes have also been made and generated potential in various applications [3]. These applications that have already reached an industrial level of acceptance together with those with high market potential as highlighted below.

2. RADIATION-GRAFTED MATERIALS FOR SEPARATION AND PURIFICATION

In the design and development of radiation-grafted materials to be used in separation processes two approaches have been considered, either to collect valuable metal ions or to remove hazardous ionic species from aqueous media. The most remarkable application for the collection of valuable metal ions is the recovery of uranyl ions from seawater which can be used in the conversion into uranium oxide to be used as nuclear fuel. This topic has been elaborated in detail by the researchers from the Takasaki Radiation Chemistry Research Establishment of the Japan Atomic Energy Authority for the last couple of decades [4].

2.1. RADIATION-GRAFTED MATERIALS FOR RECOVERY OF URANIUM FROM SEAWATER

Although the concentration of uranyl ions in seawater is around 3 ppb, considering the vast volume of oceans and other seas, the total amount of uranium in seawater has been calculated to be 4.5 billion tons, which corresponds to 1000 times the amount available from terrestrial sources. The recovery of a rare earth metal like uranium from seawater has been considered a promising way to secure future fuel needs for atomic energy. In the development of an adsorbent for the selective adsorption of uranyl ions, the presence of other ions such as sodium, potassium, calcium and magnesium which are abundant in seawater has to be taken into account. Amidoxime (AO) adsorbents are considered as the most appropriate material for the recovery of uranium from seawater. Amidoxime groups are obtained by the chemical conversion of nitrile groups. Thus a nitrile group carrying monomer, such as acrylonitrile (AN), has been the monomer of choice for radiation grafting onto polyethylene

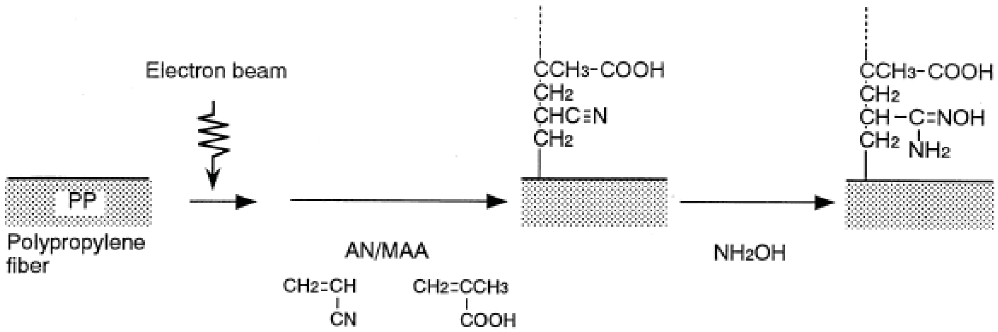

Fig.1. A simplified scheme for the preparation of amidoxime fibers by radiation-induced grafting.

(PE) or polypropylene (PP) fabrics for the preparation of amidoxime adsorbents. Adsorbents having AO groups exhibit a high selectivity for uranium complexes which exist as the tricarbonate-uranyl(VI) complex, $[UO_2(CO_3)_3]^{4-}$, in seawater. The adsorbed uranyl ions are easily recovered by elution with acid solutions. Polyethylene-coated polypropylene non-woven fibers (NF) are generally preferred as substrate materials for the radiation grafting of acrylonitrile monomer because of their environmental stability, chemical inertness, ease of radiation grafting and economics. The hydrophilicity of the adsorbents can be appended simply by using a monomer containing a hydrophilic group, such as 2-hydroxyethyl methacrylate or methacrylic acid (MAA) together with acrylonitrile. The hydrophilic amidoxime fibers are effective in accelerating uranium diffusion into the pores of the fibers. Katakai *et al.* [5] prepared MAA-cografted amidoxime fibers and demonstrated that these fibers exhibited an adsorption rate about four times that of fibers grafted with just amidoxime. A simplified scheme for the preparation of hydrophilic amidoxime fibers by radiation-induced grafting is shown in Fig.1.

The uranyl ion adsorption performance of adsorbents prepared by using different compositions of AN and MAA as monomers were tested and it was found that adsorbents prepared by using the ratio of AN/MAA at 60/40 showed the highest performance [6].

Kavakli *et al.* prepared a new type of fibrous adsorbent by incorporating two adjacent amidoxime groups in a repeating unit by radiation-induced graft polymerization [7]. The unique advantage of these polymers is that they contained double the amidoxime groups per repeating unit, an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit to improve the recovery of uranium and other transition metal ions from seawater and aqueous media at very low concentration levels (in ppb) more efficiently [8].

In the resultant structure shown in Fig.2, this adsorbent is enriched with amidoxime groups and the resulting adsorption efficiency for uranyl ions is more than 50% higher than adsorbents carrying a single amidoxime group per

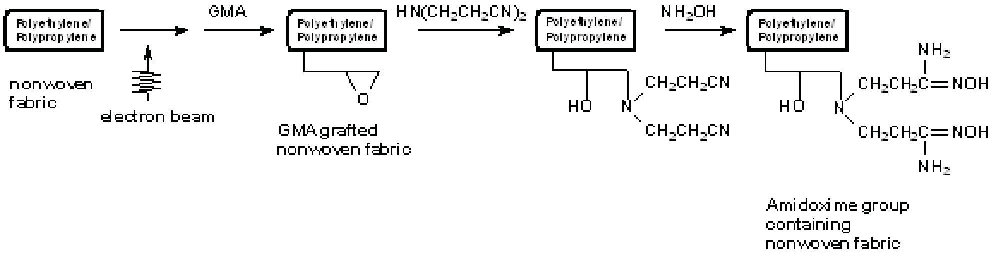

Fig.2. Scheme showing the synthesis of a novel non-woven adsorbent with enriched amidoxime groups.

repeat unit. There have been numerous attempts to develop special adsorbents for the uptake of uranyl ions from aqueous solutions and seawater. A comparative evaluation has been made to see which grafted groups have the best uranyl ion adsorption capacity.

2.2. COLLECTION OF URANIUM FROM SEAWATER

Most of the work on development and application of amidoxime adsorbents for the removal of uranium from seawater has been carried out by the Japanese scientists for the last three decades. Their findings are described below.

The amidoxime adsorbent fabric was prepared in a pilot facility at the Takasaki Radiation Chemistry Research Establishment in Japan. Rolls of polyethylene non-woven fabric, 200 m long and 1.5 m wide, were pre-irradiated by gamma rays to a dose of 200 kGy. The irradiated fabrics were then reacted with a monomer mixture of acrylonitrile and methacrylic acid. The grafting reaction proceeded for 5 h with the non-woven exposed to the monomer mixture and a degree of grafting of 120% was achieved. After amidoximation, a uranium adsorbent fabric of 6000 m^2 and 700 kg in weight was obtained for use in a marine experiment [9]. The collection system was composed of a floating frame carrying cages loaded with the adsorbent fabrics. At the end of about 20 to 30 days of seawater contact, the adsorbent fabrics were fractionally eluted by 0.5 M HCl to collect uranyl ions. The average capacity of the adsorbent was found to be 0.5 g-U/kg-adsorbent after 30 days of soaking. In order to reduce the operational costs, instead of using floating frames containing adsorbent beds, a new type of braid adsorbent was developed by the same group of researchers. The amidoximated braid type non-woven adsorbents of 60 m long were anchored at the sea bottom near Okinawa island in Japan and capacity of this type of adsorbent was determined to be 1.5 g-U/kg-adsorbent for 30 days' soaking which is three times higher than floating technique.

A group from the Oak Ridge National Laboratory, USA, presented a detailed cost analysis to verify the technical and economic feasibility of uranium recovery from seawater based on marine experiments performed at various locations [10]. Improvements in adsorbent performance, measured by number of viable reuses, degradation rate, and adsorption capacity, are considered as key factors that can reduce the costs of recovering uranium. The authors emphasized that as long as uranium recovery levels are in the range of grams per kilogram of adsorbent, minimizing the costs of fabrication of the adsorbant should be a key objective. The cost of producing the adsorbent itself was estimated by Schneider and Sachde at US$5.4/kg-adsorbent [10]. As the technology continues to develop, two pathways will be considered. If adsorbant capacity could be increased dramatically, this might lead to a very high-loading, single use material. Under this pathway, reducing adsorbent fabrication costs would benefit the uranium recovery cost most signicantly. Alternatively, the focus could turn to a very durable material that can sustain many uses without capacity loss. In this case, because the material would be moored at sea many times over its life cycle, deployment and mooring become the critical cost driver. Adsorption capacity and number of recycles are thus the main cost drivers for uranium recovery from seawater. The authors suggest that these economic analyses provide the motivation to develop robust adsorbents which can have high uranium capacity and which can be regenerated and recycled many times [10].

2.3. SCANDIUM RECOVERY FROM HOT SPRINGS

Scandium is the 30th most abundant element on the earth's crust. However, ores containing scandium as the main component are extremely rare, and scandium is primarily obtained as a by-product of uranium extraction from uranium ores. Thus, the price of scandium is 10 times higher than the price of gold, even though scandium is 1000 times more abundant. Because of the high price of scandium, advances in the research and development of its applications have been limited, with exceptions, such as new applications in catalysis. The conventional processes for recovering useful rare earth metals have disadvantages of not only environmental pollution, but also poor recovery efficiency at low capacity and low adsorption rates; therefore, finding adsorbents that can efficiently recover these metals, particularly scandium, by adsorption would be beneficial. In Japan, hot springs contain many dissolved metals such as vanadium and scandium. If these metals can be collected from hot springs, the industrial demand could be met. A suitable metal adsorbent was synthesized by radiation-induced graft polymerization by the direct grafting of 2-hydroxyethyl methacrylate phosphoric acid onto non-woven fabrics [11]. To test the performance of this newly produced adsorbent, a pilot-scale adsorption facility was installed. The hot spring water (pH 1.4) pumped from Yukawa river flowing through Kusatsu town in Japan was passed through the column filled with the adsorbent at a flow rate of 2.5 to 10 L/h (space velocity, SV: 60 to

500 h^{-1}). The breakthrough point and capacity were found to be almost same as those on a lab scale. Notably, the adsorbent volumes after scale-up were as much as 7500 times larger, and no decrease in performance was observed. From these results, if the column exchange time is set at 4 h, the total amount of scandium that can be collected per column was 100 mg. This system would allow scandium to be collected at 200 g/yr per column [11].

2.4. ARSENIC GRAFT ADSORBENTS

Various oxidation states of arsenic (As), which is a highly toxic element, exist in surface and ground waters all around the world. The most commonly used removal techniques for As(V) involve coagulation and ion-exchange of granular resins. However, it is difficult to remove As(V) to a low concentration rapidly with these techniques. Therefore, a new fibrous adsorbent using radiation-induced graft polymerization has been developed to effectively remove As(V) from water [12]. Synthesis of arsenic adsorbents at the pilot scale was carried out by radiation-induced graft polymerization of 2-hydroxyethyl methacrylate phosphoric acid monomer which consists of phosphoric acid mono-(50%) and di-(50%) ethyl methacrylate esters onto a non-woven cotton fabric (NCF), and then followed by chemical modification through contact with a zirconium (Zr) solution. The apparatus, which was equipped with reaction tanks, a washing tank and a pump, can produce up to 0.3-14 m size of the As(V) adsorbent in one reaction. A degree of grafting of 150% was obtained at an irradiation dose of 20 kGy with 5% of monomer solution made with deionized water for 1 h at 40°C. Finally, after Zr(IV) was loaded onto a NCF with 5 mmol/L of Zr(IV) solution, the graft adsorbent for the removal of As(V) was produced on a pilot scale. The adsorbent which was synthesized in pilot scale was evaluated in batch mode adsorption with 1 ppm (mg/l) of As(V) solution for 2 h at room temperature. The result was an adsorption capacity for As(V) for 0.02 mmol/g-adsorbent.

2.5. ADSORBENT FOR CESIUM

As a result of a nuclear accident that took place in Fukushima Daiichi Nuclear Power Station in March 2011, a significant amount of radioactive cesium (Cs) was released into the surroundings. An extremely vital task for the restoration process was to secure safe water sources. Japanese researchers immediately developed a Cs adsorbent for producing drinking water. The adsorbent was synthesized using radiation-induced graft polymerization of glycidyl methacrylate (GMA) with ammonium 12-molybdophosphate (AMP) onto a non-woven polyethylene fabric (NFPE) [13]. The radiation crosslinked poly-

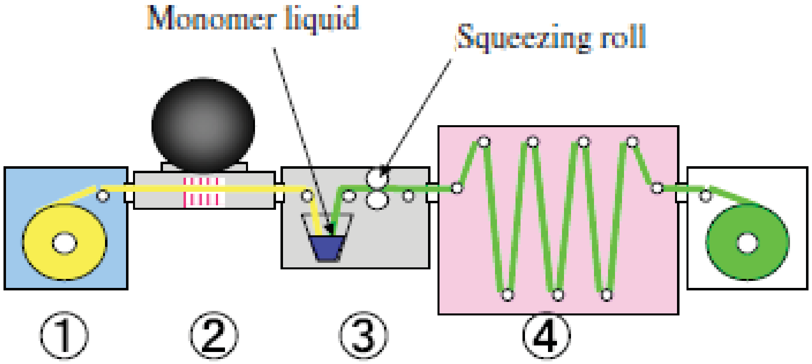

Fig.3. Schematic presentation of continuous radiation grafting system used by the Ebara Company [14] for the production of specialty membranes: 1 – trunk polymer feeding, 2 – electron accelerator, 3 – monomer impregnating zone, 4 – grafting reaction zone.

ethylene non-woven provided the adsorbent with a high stability of the loaded AMP. The Cs adsorption performances were evaluated using batch and column tests with various cesium solutions. The amount of adsorbed Cs was substantial enough for use in a wide pH range and even in the presence of coexistent ions. The amount of desorbed molybdenum from the Cs adsorbent was at a minimum at pH ranging from 5.8 to 8.6 (drinking water standard).

Figure 3 presents the scheme of continuous radiation grafting system used by the Ebara Company [14] for the production of specialty membranes.

2.6. ULTRA-PURE WATER PRODUCTION

Fine patterning in the electronics industry requires the use of ultra-pure water. Ultra-pure water is typically made by removing the contaminations such as metal ions, organic carbon, and small solid substance that may be present in wash water. The metal ions are generally removed by using a column packed with cation-exchange resins. Closely packed resins reduce the flow rate of water. To overcome this limitation in flow rate, an ion-exchange of a fibrous adsorbent was made by radiation-induced graft polymerization. An ion-exchange sulfonic acid group was bound onto a high density polyethylene non--woven fabric by radiation-induced grafting of glycidyl methacrylate and subsequent sulfonic acid chemical modification. The cation-exchange fabric was evaluated for adsorption of sodium ions in an experimental column. The effect of concentration, flow rate, and column height was investigated in terms of water purification. Total organic carbon eluted from the resulting ion-exchange fabric (IEF) could be reduced to concentrations less than 1 ppb after washing with organic solvents. Adsorption performance of the ion-exchange fabric was evaluated using a 10 ppb Na + solution. The results showed that the IEF made by graft polymerization was suitable for water purification in producing ultra-pure water [15].

2.7. AIR FILTERS

A facility for the continuous production of radiation-grafted non-woven fabrics is installed in Japan for making NH_3 gas removal filters for a large-scale integrated circuit facility. In this facility, the substrate is irradiated with a 300 keV electron beam (EB) in an inert atmosphere and then dipped into a monomer solution. The grafting proceeds as the monomer impregnates the non-woven while in the reactor [14]. The monomer is completely consumed during this grafting process, such that the removal of residual monomer is not necessary. The maximum production rate for this facility is 20 m/min. The grafted product can adsorb NH_3 quicker than conventional adsorbents such as charcoals and organic acid treated charcoal. Its adsorption capacity is 150 times higher than that of charcoal. As a spin-off technology, antimicrobial fabrics were also produced by radiation-grafting of N-vinyl pyrrolidone onto a non-woven polypropylene fabric and subsequent treatment with iodine. These fabrics have been commercialized to produce antimicrobial masks since 2002.

3. RADIATION-GRAFTED MEMBRANES FOR BATTERY AND FUEL CELL APPLICATIONS

3.1. MEMBRANES FOR BATTERIES

A battery is mainly composed of an anode (negative electrode), a cathode (positive electrode) and an electrolyte. There is also a separator and whose main function is to physically separate the positive and negative electrodes and prevent electrical short circuits while permitting the flow of ionic charge carriers necessary to complete the circuit. The separator, which is a film or membrane, must be a very good electrical insulator but also capable of conducting ions, and should be chemically and electrochemically stable. There are commercially available membranes meeting the requirements for fuel cell and battery applications and Nafion, a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer, is a frequently used separator membrane in fuel cells. Due to chemical, physical and mechanical property requirements for these applications, the base material is almost always a fluorinated polymer. Further modification of fluorinated polymers can best be achieved by radiation-induced grafting. In this way radiation-grafted membranes comparable in properties with that of Nafion are under development.

The most commercially successful radiation-grafted battery separators are for alkaline button type batteries where polyethylene is grafted with poly(acrylic acid) [16]. Lithium-ion (Li-ion) battery cells consist of a positive electrode, a negative electrode, a separator, and a non-aqueous liquid electrolyte. Microporous polyolefin separators have been widely used in Li-ion batteries because of their chemical and electrochemical properties. Microporous polyolefin separators have a low affinity for polar liquid electrolytes and a good thermal stability for the various applications. Some commercial polyolefin separators may shrink significantly at high temperatures leading to direct contact between the electrodes of opposite polarity. The separator should not shrink much at higher temperatures in order to ensure the safe operation of Li-ion batteries. In addition, the separators should have a thermal shutdown to insure a battery's safety. Poly(methyl methacrylate), PMMA-grafted PE separators were prepared by a research team at the Korea Atomic Energy Research Institute **(**KAERI), Korea [17], *via* irradiation of PE and then the grafting of methyl methacrylate to make a separator. The physical, chemical and electrochemical properties of the modified separators were tested. The results of these tests confirmed that the PE-g-PMMA separators showed better electrochemical stability than a PE separator. A PP-based battery separator was prepared by mutual irradiation grafting of acrylic acid (AA) onto microporous polypropylene films by the Bhabha Atomic Research Center in India [18]. The AA-grafted PP sheet was tested for its performance under actual battery conditions related to the battery separator membrane presently used by the battery industry in India. Samples grafted to > 20% gave satisfactory results. A sample grafted to ~20% was also used for a complete battery system consisting of 17 Ni and 16 Cd electrodes. The performance of the radiation-modified PP separator was found to be comparable to batteries made using a commercial battery separator that are being used in industry.

3.2. POLYELECTROLYTE MEMBRANES FOR FUEL CELLS

Fuel cells are a promising technology that can provide electrical energy that can satisfy the growing demand for emission free energy systems. Polymer electrolyte membranes are one of the key components in the development of fuel cells and there is a growing demand for more efficient, reliable and environmentally friendly energy systems. Amongst various methods, radiation-induced grafting is an attractive way for making polymer electrolyte materials to be used in fuel cells. Fluoropolymers, composed of synthetic polymers with structures of carbon–fluorine bonds, such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), poly(vinylidene fluoride) (PVDF), poly(ethylene-alt-

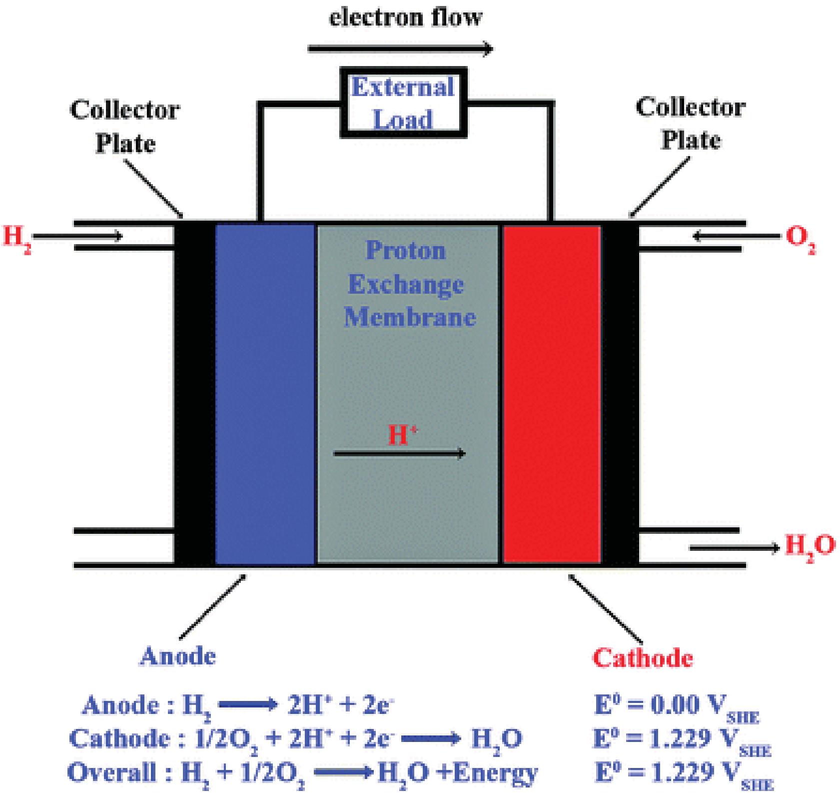

Fig.4. Sketch showing the assembly of a typical PEMFC and the electrochemical reactions involved.

-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA), and poly(tetrafluoroethylene) (PTFE), are very attractive materials as substrates for radiation-induced grafting because of their high thermal stability, good mechanical properties, and excellent chemical resistance. There are many studies in the literature reporting the use of various fluoropolymer films together with styrene for the preparation of proton exchange membranes (PEM) for use in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). Styrene is the most extensively used monomer to make proton exchange membranes by radiation grafting since it is available at reasonable cost, has established kinetics and the grafted styrene can be readily modified to introduce a variety of functionalities. A simplified sketch of PEMFC assembly and relevant reactions occurring at the anode and cathode generating electricity are shown in Fig.4.

The proton conducting membrane separates the anode and the cathode compartments such that it is impermeable to the fuels (methanol and oxygen) and has a high permeability for protons. With radiation-induced grafting of monomers onto FEP and ETFE films followed by sulfonation, proton exchange membranes for fuel cell application can be made. The use of commercial FEP and ETFE films avoids the problem of shaping the graft polymer into thin membranes of uniform thickness.

One of the most expensive components of a fuel cell is the proton conducting membrane. These are presently available at US\$600-800/m^2, *e.g.* Nafion, and this has to be reduced to ~US\$150/m^2 for the fuel cell technology to become more commercially viable [19]. Much work has been carried out in the search of more inexpensive membranes with comparable or better performance than those presently available. Fuel cell membranes based on fluorinated polymers made by radiation-induced grafting of monomers has been considered to be a very promising technique due to the advantages inherent in radiation grafting. Many reviews have been published covering the preparation, characterization, and performance assessment of radiation-grafted membranes obtained by radiation-induced grafting of styrene or its substituents with and without comonomers onto FEP and ETFE films in PEMFC [20-22]. The first radiation-grafted PEM was made by the radiation-induced grafting of styrene onto PE films with subsequent sulfonation. This was followed by a large number of studies using various substrate films made of hydrocarbon and fluorocarbon polymers in addition to commercial engineering plastics. The preparation of PEMs is carried out in two steps: (i) grafting and (ii) sulfonation. The stability of radiation-grafted membranes has been a subject of intensive research during the last decade and the following strategies have been established to enhance stability of membranes for PEMFC [23]:

- radiation-induced grafting of monomer with crosslinking followed by sulfonation,
- radiation-induced grafting onto new or modified polymer substrates followed by sulfonation,
- applying new radiation grafting techniques.

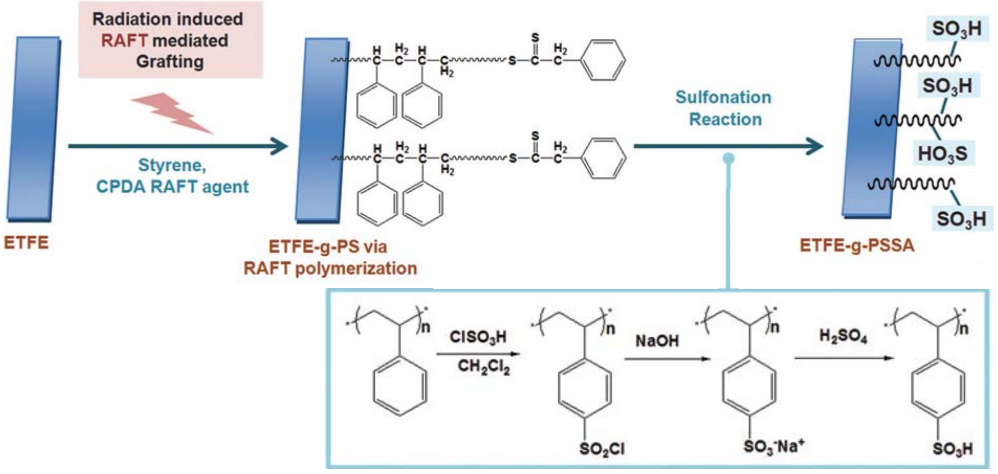

Fig.5. A scheme of the RAFT-mediated grafting process of styrene from ETFE surface and eventual sulfonation.

A comprehensive review on this subject, elaborating all the issues mentioned above, has been published by Nasef in *Chemical Reviews* [24]. The use of new radiation grafting techniques seems to have great potential for making fuel cell membranes with enhanced properties. We have shown that when free radical polymerization reactions involved in the grafting process can be controlled by so-called reversible addition-fragmentation chain transfer (RAFT) mechanism, the average molecular weight and distribution of graft chains can be controlled. Such a precise control of grafting imparts better properties to the membrane compared to grafting in the absence of RAFT polymerization [25]. Figure 5 shows a scheme of the RAFT-mediated grafting process of styrene from ETFE surface and eventual sulfonation.

By controlling the radiation-induced graft polymerization, it was shown that the introduction of RAFT polymerization in the PEM fuel cell preparation process enhanced the structural uniformity and performance in terms of proton conductivity compared to conventional methods.

4. RADIATION GRAFTING FOR HEALTH-CARE APPLICATIONS

4.1. RADIATION-GRAFTED CELL CULTURE DISHES

When tissue engineering was first proposed in the 1980s, the key materials used were biodegradable polymeric scaffolds. By combining preformed polymeric scaffolds and specific cell types, various tissues have been reconstructed. After transplantation of tissue-engineered contructs into hosts, the scaffolds degrade over weeks or months. The space formerly occupied by the scaffolds is filled with proliferated cells and deposited extracellular matrix (ECM) such as collagen. However this gave rise to the development of cell sheet engineering in trying to find solutions to avoid these limitations. In tissue reconstruction cell sheets are used but not single cells. Cell sheets are prepared on cell culture dishes having temperature responsive surfaces. Imparting thermo-responsive properties to the surfaces of culture dishes is best achieved by radiation-induced grafting of a thermo-reponsive polymer called poly(N-isopropylacrylamide) (PNiPAAm), on the surfaces where cells will be grown. This revolutionary approach was applied for the first time by Okano *et al.* [26]. This polymer exhibits a lower critical solution temperature around 32°C which means it acquires hydrophobic properties (polymer coils contracted) above this temperature and hydrophilic below it (polymer coils expanded), as shown in Fig.6.

The cell sheets grown at 37°C on the grafted polymer in a fully hydrophobic state can be easily detached by lowering the temperature below 32°C

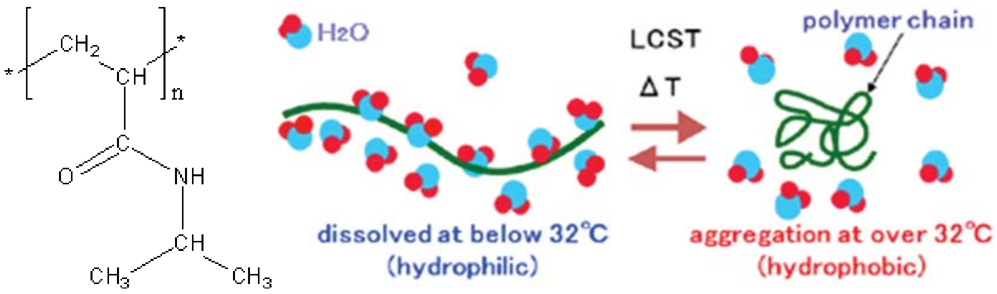

Fig.6. Chemical formula of poly(N-isopropylacrylamide) and its thermo-responsive behavior.

with polymer being transformed into hydrophilic state. Thus, the thermo-responsive behavior of poly(N-isopropylacrylamide) allows noninvasive control of cell attachment and detachment by only changing the temperature across 32°C without using any enzymatic treatment. The success of this technique depends strongly on the frequency of graft chains and their chain lengths [27].

As shown schematically in Fig.7, if the cell sheets grown on the surface of the culture dish were to be removed by using enzymes, the sheets disintegrate into individual cells (Fig.7A). However, by using the temperature responsive behavior of thin poly(N-isopropylacrylamide) layer grafted onto polystyrene culture dishes, sheets can be easily removed in tact (Fig.7B). For cell cultures, commercially available tissue culture polystyrene or polystyrene substrates are generally used for attachment of poly(N-isopropylacrylamide) on the surfaces. Using grafting methods, glass, silicon and poly(ethylene terephthalate) (PET) are also used as substrates. A review by Okano *et al.* focuses on the preparation and characteristics of poly(N-isopropylacrylamide)-modified surfaces and

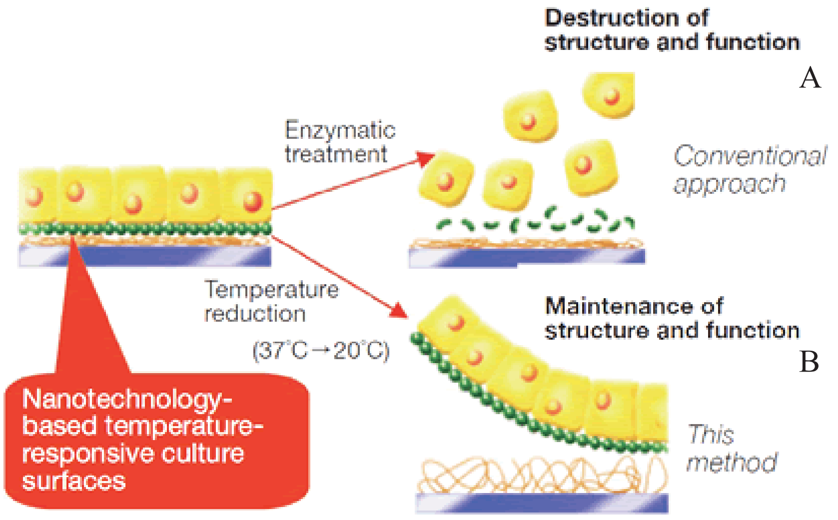

Fig.7. Noninvasive harvesting of cell sheets from PNiPAAm-grafted surfaces of cell culture dishes by temperature reduction.

discusses the effect of surface properties on cell adhesion and release [28]. Developments in improving the grafted surfaces for cell culture and for the clinical use of cell sheets harvested from the substrate surfaces are discussed. Among the clinical applications, culturing of epithelial cell sheets to heal damaged corneal surfaces, preparation of oral mucosal cell sheets to prevent post-operation inflammation, periodontal ligament cell sheets that are employed to induce tissue healing with bone, and periodontal ligament are listed [29].

4.2. ANTIBACTERIAL AND ANTIMICROBIAL SURFACES BY RADIATION GRAFTING

Worldwide, infectious diseases kill more people than any other single cause. These diseases are of particular significance in hospitals where there is considerable effort in warding off infections. Infections are triggered by germs (bacteria, viruses, fungi and protozoa), which are found everywhere, in air, soil and water. Generally, infections are combated with antimicrobial agents. In brief, the use of potent and/or specific antimicrobial systems helps to mitigate, combat and/or eradicate these infections, which means an improvement in the state of well-being. The use of polymeric materials with antimicrobial properties is of interest from both the academic and the industrial point of view. Reviews of the antimicrobial polymeric systems can be found in the literature [30, 31]. Polymers can act as a matrix for holding antimicrobial agents. Polymers with antimicrobial activity themselves is an area of research that is focused on solving the problem of contamination by microorganisms. This is a longer-term activity. Most bacterial cell walls are negatively charged, containing phosphatidylethanolamine (70%) as the major component; hence most antimicrobial polymers are positively charged. Polymers with quaternary ammonium groups are probably the most explored type of polymeric biocides. It is generally accepted that the mechanism of the bactericidal action of the polycationic biocides involves destructive interaction with the cell wall and/or cytoplasmic membranes [32].

As a typical application of radiation-induced grafting for producing antimicrobial fabrics, Ebara Clean Environment Co., Ltd. has made functional PE fabrics based a non-woven material using radiation-induced grafting of N-vinyl pyrrolidone with subsequent treatment with iodine to render it antimicrobal. To meet the huge demand for the antimicrobial materials used in face masks against the H1N1 epidemic in 2009, operational procedures were improved for high throughput reaching 133 000 m^2 [33].

To impart antibacterial properties to cotton which is a fabric widely used as a clothing material, mutual radiation grafting technique using ^{60}Co gamma radiation has been used to carry out grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton cellulose substrate. The VBT-grafted cotton samples showed excellent antibacterial activity against strains like *Escherichia* *coli* and *Staphylococcus aureus*. Samples with 25% VBT grafting showed a 6 log reduction in bacterial counts within 6 h of exposure time. The antibacterial activity of the grafted cotton samples was retained after several cycles of washing using a commercial detergent and drying [34]. The same group used gamma radiation to covalently link polymer chains of [2-(methacryloyloxy) ethyl]trimethylammonium chloride (MAETC) to cotton fabric by mutual radiation grafting. Radiation-polymerized poly(MAETC) and MAETC-g-cotton samples were tested for their antibacterial efficacy against various bacteria and were found to possess significant antibacterial activity [35]. In a similar study, a quaternary ammonium salt containing a monomer, that is [2-(acryloyloxy) ethyl)]trimethylammonium chloride (AETC), was grafted to cotton fabric by mutual radiation grafting using 2-hydroxyethyl methacrylate (2-HEMA) monomer to facilitate the grafting. Radiation-grafted poly(AETC) and AETC-g-cotton samples showed good antibacterial activity against gram-positive bacteria like *Staphylococcus aureus* and *Bacillus cereus* [36].

The development of antimicrobial polymers for food packaging has generated interest in maintaining the quality of food during long-term storage. One of the requirements of the food packaging has been to use antimicrobial packaging so that microbial infection can be prevented or controlled in food items during storage. This has resulted in a huge amount of work to incorporate antimicrobial agents into polymers and polymeric devices, so that they acquire ability to kill as well as inhibit the growth of microbes. The incorporation of antimicrobial agents on the surface of packaging materials seems to be an appropriate route. This can be achieved by either blending the antimicrobial agent into the polymer, or by immobilization of the agent on the polymer surface. Immobilization of any agent to the surface of a polymer is best achieved by radiation-induced grafting. PP surfaces were radiation-grafted with [2-(methacryloyloxy)ethyl]trimethylammonium chloride, which is a monomer with quaternary ammonium salt (QAS), for antimicrobial applications [37]. With a similar aim, radiation-induced grafting has been used to covalently bond low density polyethylene with antimicrobial additive, sorbic acid (SA), to develop a non-migrating antimicrobial active film [38]. Silver nanoparticles have found various uses because of their effective biocidal ability. The use of silver nanoparticles can be best done by surface grafting an appropriate polymer. Poly(acrylic acid) (PAA) chains were grafted onto PET film *via* γ-ray-induced graft copolymerization. The grafted PAA chains on PET film were neutralized by aqueous ammonia and then carboxylate anions were used to complex with silver ions from the silver nitrate solution. After chemical reduction of these silver ions, silver nanoparticles were immobilized on the surface of PET film. The amount of loaded silver nanoparticles can be controlled by the amount of grafted PAA, *i.e.* the degree of grafting of the PAA. The PET-g-PAA/Ag hybrid films possessed excellent bactericidal activity. The loaded silver nanoparticles were stable enough after ultra-sonication and then aging in air for 3 months [39].

5. CONCLUSIONS

Radiation-induced grafting is a simple technique for modifying base polymers because grafting may result in the combination of properties related to the backbone of the base polymer and of the grafted chains. Through the careful choice of monomers with appropriate functional groups, new molecular functionalities can be bound onto the surfaces of polymers *via* graft copolymerization. These combinations end up in countless industrial, environmental and health-care related applications. By the introduction of recently developed techniques for bringing a precise control over the molecular weight and narrow distribution of the graft chains, the prospect for radiation-induced controlled grafting is very high and will be used in the preparation of advanced materials.

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