Chapter 1
Fundamental aspects of radiation chemistry, polymers and radiation induced grafting

Keywords: Polymer, Grafting, Hydrogel, Polyelectrolytes, Quaternary ammonium monomer

1.1 Introduction

Polymer surfaces can be modified to achieve a variety of goals, including increasing adhesion, improving wettability and biocompatibility, reducing friction, reducing susceptibility to harsh chemicals or environmental agents, bio-functional surfaces in tissue engineering and antibacterial surfaces. Polymer surfaces may also be modified by functionalization with various chelating groups for their application in the treatment of waste water like toxic metals and dyes from textile effluents to address the serious environmental pollution problem [1, 2]. Surface-modified polymers are of substantial importance in many diverse aspects of modern technology, and whilst there are a number of existing physical and chemical methods like UV, plasma, conventional chemical methods, enzymatic [3] and most recently laser surface modification for surface modification of polymers, the frequent requirement for significant infrastructure, harsh reaction conditions and limitation to specific polymer types led to explore high energy radiation (gamma-ray, electrons beams etc.) based technology known for convenience, high efficiency, high purity, easy and environmental friendly process for such modifications. It started back in 1950s and continued to be a subject of intensive research for obtaining modified materials for various applications based on the wide range of properties available when different polymer chains are connected to form hybrid branched polymers. These surface modifies surfaces have many applications like
antibacterial properties [4], odor absorbent fabrics, ion exchange separation of metal ions, dyes, pesticides, purification of proteins, immobilization of enzymes, extraction of uranium from sea water, recovery of precious/rare earth metals, desalination of seawater, toxic gases [5] and compatibilization in heterogeneous composites. Some of the pioneer progress in the area of radiation induced surface grafting of polymers are elaborated below.

Extensive investigations of adsorbents capable of recovering uranium from seawater which has about 4.5 billion tons of uranium in seawater and aqueous systems have been carried out during the last two decades especially in Takasaki Radiation Chemistry Research Establishment. By using the radiation grafting method, the group from Japan Atomic Energy Research Institute designed a fabric absorbent based to extract uranium from seawater in 2002 [6]. They prepared a polymeric absorbent in a nonwoven fabric by radiation induced grafting of acrylonitrile and subsequently converted to amidoxime group that was capable of forming a complex with uranyl tricarbonate ions. In their marine experiments, the group already has collected one kg of uranium yellow cake. Efforts are being made to decrease the cost and increase the efficiency of uranium uptake by incorporating two amidoxime per monomer unit to increase the capacity of the adsorbent for uranium uptake [7]. Smart polymers, especially PNIPAAM have been grafted by radiation induced polymerization to explore to have smart surfaces for the various applications in the field of tissue engineering by various groups. Okano and Yamato and co-workers have been pioneer in the area of smart polymers cell cultures. This group grafted PNIPAAM, which behave like hydrophobic above 37°C and hydrophilic below 37°C, by radiation induced grafting method. This dual
behavior of the grafted film was applied for the cell culture to avoid the cell adhesion without damaging it [8].

Radiation grafting has also been used to combine the proton-conducting properties of a graft component, hydrophilic polystyrenesulfonate, with the thermal and chemical stability of the partial and fully fluorinated polymer base films together in membranes suitable for the application in Polymer Electrolyte Membrane Fuel Cells (PEMFC) [9]. Considerable work has been recently devoted to develop new cation exchange membranes by radiation-induced graft copolymerization of styrene onto various fluorinated and partially fluorinated polymer films such as PTFE, FEP, PVDF, and ETFE requirements include high ionic conductivity, defined swelling behavior, high chemical resistance, and mechanical integrity and thermal stability [10]. During the last two decades continuous efforts have been made to develop polymers with antimicrobial properties. Positive charge and hydrophobic nature of the antibacterial reagent are important factors of cationic disinfectants [11]. Quaternary ammonium compounds (QACs) have been widely used in water treatment, textiles and food industries because of their low toxicity and broad antibacterial spectrum [12]. In the present thesis surface modification of cottons by covalently attaching QACs has been investigated with high energy gamma radiation technology to smart surfaces with antibacterial properties. These smart surfaces are aimed for adding the antibacterial properties for number of possible applications in the field of healthcare like antibacterial bandages for faster wound healing and antibacterial clothes for undergarments, shoe lining, hospitals and sportswear etc. To add these QACs, radiation induced grafting method was adopted which is further explained in later section of this chapter. Grafted samples, having quaternary ammonium group a strong anion exchanger, have also been
investigated for the treatment of textile effluents containing toxic acid dyes to address the serious problem of environmental pollution.

1.2 Basic aspects of radiation chemistry

Radiation chemistry deals with the study of chemical changes induced by high-energy electromagnetic radiation (\(\gamma\)-rays, X-rays), charged particles (electrons, protons, deuterons, \(\alpha\)-particles) or uncharged particle (neutron), termed as “ionizing radiation”, with energy in the range of \(10^2\) to \(10^7\) eV.

![Chemistry](image)

**Figure 1.1:** Energy ranges for electromagnetic radiation

Interaction of ionizing radiation with atoms and molecules in their path is non-specific and thus non-selective in nature. It can cause ionization and excitation of varied types of molecules and atoms in many possible ways resulting in the formation of a variety of reactive species. Interaction of high energy ionizing radiation are non-selective process because of much higher energy which is much higher than the chemical bond in organic compounds, unlike in photochemistry where one can selectively excite, ionize or break a particular bond in a given molecule by choosing the energy of a photon (figure 1.1).

A thorough knowledge of the processes by which high-energy radiation interacts with matter is a pre-requisite for understanding the radiation chemical effects, as it is the absorbed energy, which results in the observed chemical changes in the substrate. The
extent and process of energy absorption depends upon the nature of radiation and properties of the material. The important parameters on which the interaction will depend are energy, mass and charge of the radiation, and atomic number or electron density of the material [13]. Mechanisms of interaction of (i) electromagnetic radiation (ii) electrons (iii) heavy charged particles and (iv) neutrons, which are of relevance in radiation chemistry, are explained in brief in the following sections.

1.2.1 Interaction of electromagnetic radiation

Electromagnetic radiations of wavelength less than 100 Å belong to the class of ionizing radiation. They are usually called X-rays (extra nuclear origin) or γ rays (produced from the atomic nuclei). The gamma rays emitted by radioactive isotopes are mono-energetic, possessing one or more discrete energies, for example $^{60}$Co emits γ-photons of energy 1.332MeV and 1.173MeV. For a narrow beam, the intensity of gamma radiation transmitted through an absorber is given by

$$I = I_0 e^{-\mu x} \quad (1.1)$$

Where, $I_0$ is the incident radiation intensity, $x$ is the thickness of material through which radiation has traversed and $\mu$ is the linear attenuation coefficient, which is the sum of a number of partial coefficients representing different processes occurring inside the absorber. These are (i) Photoelectric effect, (ii) Compton scattering, (iii) Pair production (iv)coherent scattering and (v) photonuclear reactions. The relative importance of each process depends on the photon energy and the atomic number of the absorbing material. Coherent scattering is of importance for low energy photons (<0.1MeV), photonuclear reactions are possible with photons of energies in the range of 2 to 8MeV for low Z
materials and in the region of 7-20MeV for high Z materials. Thus, for gamma radiation emitted by $^{60}$Co source, only the first three interaction processes are of importance and are discussed below briefly.

(i) **Photoelectric effect:** This process is the principal interaction process at low photon energies. In photoelectric process photon interacts with a bound electron in an atom and transfers all its energy to eject it from the atom (figure 1.2).

![Photoelectric Effect](image)

**Figure 1.2:** Photoelectric Effect

The kinetic energy of the ejected electron ($E_{KE}$) is equal to the difference between the energy of the incident photon ($E_{hv}$) and the binding energy of the electron ($E_{BE}$) as given by equation 1.2.

$$E_{KE} = E_{hv} - E_{BE} \quad (1.2)$$

(ii) **Compton scattering:** Compton scattering is an inelastic scattering, which occurs when a photon with energy $E_0$ interacts with a loosely bound or free electron (as shown in figure 1.3). The resulting photon is deflected with reduced energy $E'$ at an angle $\theta$ to the direction of the incident photon and the electron gets accelerated at an angle $\phi$ with recoil energy $E_e$. The relation between the various parameters is given by equation (1.3). The energy of recoil electron is given by the equation (1.4).
Figure 1.3: Compton Scattering

\[ E' = \frac{E_0}{1 + \left( \frac{E_0}{m_e c^2} \right) (1 - \cos \theta)} \]  

(1.3)

\[ E' = E_0 - E_e^{-} \]  

(1.4)

Compton scattering predominates for photon energies between 30keV to 20MeV for low Z materials like water and polymeric materials.

(iii) **Pair production:** In the pair production process, as diagramed in the figure 1.4 below labeled “Pair Production - Energy Conversion to Mass,” the photon is literally split into an electron and its anti-particle, called a positron. Both have a rest mass energy equivalent of 0.511MeV (2m_e c^2). (Since mass and energy are equivalent, the mass energy equivalent is just the amount of energy that it would take to form the mass of the particle. Pair production is a phenomenon of nature where energy is converted to mass (equation 1.5). It involves the complete absorption of a photon in the vicinity of an atomic nucleus.
\[ E_0 = E_{e^-} + E_{e^+} + 2m_eC^2 \]  \hspace{1cm} (1.5)

The electron and positron can move in opposite directions (at an angle of 180°) meaning they have a total momentum of zero or they can move at an angle of less than 180° resulting in a net combined momentum. However, if the photon had only just enough energy to create the mass of the electron-positron pair then the electron and positron will be at rest. This could violate the conservation of momentum since the photon has momentum and the two resulting particles have none if they are stationary (since momentum = mass × velocity). This means that the pair production must take place near another photon or the nucleus of an atom since they will be able to absorb the momentum of the original photon. In other words, since the momentum of the initial photon must be absorbed by something, pair production by a single photon cannot occur in empty space; the nucleus (or another particle) is needed to conserve both momentum and energy [14]. Thus depending on the incident photon energy, the photon gets attenuated and the total linear attenuation coefficient (\( \mu \)) is given by equation (1.6).

\[ \mu = \tau + \sigma + \kappa \]  \hspace{1cm} (1.6)
Where, \( \tau \), \( \sigma \), \( \kappa \) are the linear attenuation coefficient of photoelectric, Compton and pair production process respectively.

### 1.2.2 Interactions of charged particles

#### (a) Electrons

Electron interacts with matter via four processes namely, emission of Bremsstrahlung radiation, inelastic collision, elastic collision and Cerenkov emission. The relative importance of these processes depends mostly on the energy of the electrons and to a lesser extent on the nature of the absorbing material.

**i) Bremsstrahlung:** High energy electrons passing close to the nucleus of an atom are decelerated due to their interaction with the electric field of the nucleus and radiate electromagnetic radiation called bremsstrahlung radiation. Bremsstrahlung emission is negligible below 100KeV but increases rapidly with increasing energy, and is the dominant process at electron energy between 10-100MeV.

**ii) Inelastic collision:** This is the major process for electrons having energy more than that at which bremsstrahlung emission occurs. The average amount of kinetic energy lost per unit length by electron through coulomb interaction with atomic electrons in a medium is defined as the specific energy loss or stopping power \( (S) \) of the medium and is defined by the Bethe’s equation (1.7).

\[
S = \frac{dE}{dx} = \frac{2\pi e^4 N_o Z}{m_o v^2} \left[ \ln \frac{m_o v^2 E}{2l^2(1-\beta^2)} - (2\sqrt{1-\beta^2} - 1 + \beta^2) \ln (2 + 1 - \beta^2 + \frac{1}{8} (1-\sqrt{1-\beta^2})^2) \right]
\]

(1.7)

Where, \( e \) and \( m_o \) represents the charge rest mass of electron, \( v \) is the velocity of electron, \( N_o \) is the number of atoms \( \text{cm}^{-3} \) in the medium, \( Z \) is the atomic number and \( l \) is the mean...
excitation potential of the electrons in the stopping material, $\beta$ is the ratio of $v$ to the speed of light $c$ and is numerically represented in equation (1.8)

$$\beta = \sqrt{1 - \left(\frac{m_0 c^2}{E - m_0 c^2}\right)^2} \quad (1.8)$$

(iii) Elastic collision: This is a quite frequent phenomenon because of the small mass of electrons and happens when electrons get deflected by the electrostatic field of an atomic nucleus. This essentially leads to a change in the direction of motion of electrons and is more probable for electrons with low energy and target with high atomic number.

(iv) Cerenkov emission: Electrons with velocity higher than that of light in a particular medium interacts and emits electromagnetic radiation, called Cerenkov radiation. This phenomenon is responsible for the blue glow observed around high intensity $\gamma$-sources stored under water.

(b) Heavy charged particles

The interaction of heavy charged particles with matter is the same as that of electrons, i.e., Bremsstrahlung emission, inelastic collision and elastic scattering. The most important among these processes by which charged particle interact with matter is inelastic collision. As heavy charged particles have higher mass than electrons, for a given energy, they have a much higher linear energy transfer (LET), which give rise to high local concentration of primary species and leads to recombination in spurs to yield molecular products.

(c) Neutrons

Neutrons do not produce ionization directly in matter but interact almost exclusively with the atomic nuclei of the material. The main processes by which neutron interacts with matter are: elastic scattering, inelastic scattering, nuclear reaction and
capture. The products of neutron interactions often cause ionization and thus produce typical radiation chemical changes. The main products of neutron interactions being protons and heavy positive ions, the chemical effects of neutron interactions are similar to those of charged particles.

1.2.3 Distribution of active species in the system – track structure

The electrons from Compton scattering of $^{60}$Co $\gamma$-rays have an average energy of 440keV. These electrons, also termed as $\delta$-rays, bring about further ionization and excitation. Such events along the main track or the $\delta$-ray branch track are called isolated spurs. In water, the isolated spurs contain on an average ~ 6 active species and ~ 100eV energy is involved. When $\delta$-ray electron energy is < 5keV, its penetration becomes very less and the spurs so formed in close vicinity overlap and take cylindrical shape, known as short tracks. As the electron energy becomes less than 500eV, even denser regions of ionization, which look like large spurs, called as blobs, are produced (figure 1.5).

![Figure 1.5](image)

**Figure 1.5**: Distribution of ions and exited species along the track of fast electron; (●) represents the ions and (⭐) represents the excited species
The typical energy distribution ratio for a 440keV electron in water is spur (64%), short tracks (25%) and blobs (11%). In contrast to this, for heavy charged particles (high LET), more energy will be deposited in blobs and short tracks than in isolated spurs.

1.3 Radiation dosimetry

Management of the physical, chemical or biological changes produced by ionizing radiation necessitates knowledge of the amount of energy absorbed per unit mass of the absorber, and distribution of the absorbed energy in the absorbing material. Radiation dosimetry constitutes determination of these quantities.

(i) Absorbed dose: The absorbed dose is the amount of energy absorbed per unit mass of the irradiated material. The SI unit for the absorbed dose is Joules per kilogram (Jkg\(^{-1}\)), which is known as gray (Gy). The old unit is rad (1 rad = 0.01Gy).

(ii) Absorbed dose rate: The absorbed dose rate is the absorbed dose per unit time.

1.3.1 Radiation-chemical yield

Traditionally, radiation chemical yields have been reported in terms of G values, which represents the number of molecules of the product formed or changed per 100eV of energy absorbed [14]. The SI unit of radiation chemical yield is defined as change in the number of moles of material formed or decomposed by energy absorption of 1Joule. G-values reported in terms of number of species formed per 100eV can be converted to SI units using the following relationship (1.9).

\[
G(\text{mol J}^{-1}) = G(\text{as 100ev}) \times 1.036 \times 10^{-7}
\]  

(1.9)

1.3.2 Gamma Radiation Dosimetry (Fricke Dosimeter)

The radiation-induced oxidation of the ferrous ions to the ferric ions in aqueous solutions forms the basis of Fricke dosimeter [15]. The standard Fricke dosimeter consists
of an aerated solution of $1.0 \times 10^{-3}$ mol dm$^{-3}$ ferrous ammonium sulphate, $1.0 \times 10^{-3}$ mol dm$^{-3}$ NaCl and $0.4$ mol dm$^{-3}$ sulphuric acid. The yield of Fe$^{3+}$ ions produced is determined by absorption spectrophotometry employing Beer's law ($\Delta A = \Delta \varepsilon \cdot c \cdot l$) at 30 nm with $\varepsilon(\text{Fe}^{3+}) = 220.5 \pm 0.3$ m$^2$/mol$^{-1}$ and $\varepsilon(\text{Fe}^{2+}) = 0.1$m$^2$/mol$^{-1}$ at 25$^\circ$C. The G(Fe$^{3+}$) value accepted for electron and photon radiation in the range 1 to 30 MeV is $3.52 \times 10^4$ m$^2$/J$^{-1}$ at 25$^\circ$C [16]. The Fricke dosimeter can be used to accurately determine dose only up to 400Gy because of depletion of oxygen present in the system. Fricke dosimeter is independent of dose rate between 0.2 to $2.0 \times 10^6$ Gys$^{-1}$. A modified version of Fricke dosimeter, also called as super Fricke dosimeter, containing $10^{-2}$ mol dm$^{-3}$ ferrous ions, oxygenated but without any sodium chloride, is dose rate independent up to absorbed dose rates of the order of $10^8$ Gys$^{-1}$. The upper limit of absorbed dose that can be measured using a super Fricke dosimeter is 2.0kGy.

1.4 Radiation chemistry of water

Understanding of radiation chemistry of water is of importance as water is present in most biological and chemical systems. For water, the sequence of events like formation and solvation of the primary species, and the time scale of events initiated either by fast electrons from an accelerator or by $^{60}$Co gamma-rays is illustrated in figure 1.6. High energy radiation is deposited in energy in $10^{-16}$ seconds in the substrate forming positively charged ions, electrons and excited species. Energetically unstable positively charged ions (H$_2$O$^+$) undergo ion-molecule reaction in $10^{-14}$ seconds producing $^\bullet$OH radicals [17]. The excited water molecules decompose in $10^{-14}$ seconds yielding H$^\bullet$ and $^\bullet$OH radicals. The electron released during ionization can also bring about further ionization provided it has sufficient kinetic energy. Eventually, its energy will fall below
the ionization threshold of water and then it dissipates rest of its energy by exciting vibrational and rotational modes of the solvent molecules. Finally, it would be localized in a potential energy well long enough to become solvated as a result of molecular dipoles rotating under the influence of the negative charge, and thus get stabilized [18]. The electrons get thermalised in about $10^{-13}$ seconds and subsequently get hydrated or solvated in less than $10^{-12}$ seconds and called hydrated electron ($e_{\text{aq}}^-$) [19].

![Diagram of water radiolysis and formation of primary species](image)

**Figure 1.6:** Sequence of events in water Radiolysis and formation of primary species from $10^{-16}$ to $10^{-7}$ second.

These species viz. hydrated electrons, hydrogen atoms and hydroxyl radicals, formed in the spurs, can react with one another to reform water or molecular products, $H_2$ and $H_2O_2$, while the remaining escape into the bulk solution. This spur expansion is complete in about $10^{-7}$ s. The reactions occurring during spur expansion are listed in
Table 1.1. After about $10^{-7}$ second, the species are distributed homogeneously in the bulk and are known as primary species. Main species produced are hydrated electrons ($e_{aq}^-$), OH$, H^+$ and molecular products H$_2$ and H$_2$O$_2$. These species can subsequently react with solutes present in the system. In water, $10^{-7}$ seconds is the lifetime of the radicals reacting at a diffusion-controlled rate with a solute whose concentration is $10^{-3}$ mol dm$^{-3}$. Under these conditions the G-values of $e_{aq}^-$, H$^+$ and $^\circ$OH radicals at $10^{-7}$ second are shown in the figure 1.7.

Table 1.1 Spur Reactions in Water

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k \times 10^{-10}$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2^\circ$OH</td>
<td>0.55</td>
</tr>
<tr>
<td>$e_{aq}^- + ^\circ$OH $\rightarrow$ OH$^-$</td>
<td>3.0</td>
</tr>
<tr>
<td>$e_{aq}^- + H_3O^+ \rightarrow H^+ + H_2O$</td>
<td>2.3</td>
</tr>
<tr>
<td>$e_{aq}^- + H^+ \rightarrow H_2 + OH^-$</td>
<td>2.5</td>
</tr>
<tr>
<td>$H^+ + H^+ \rightarrow H_2$</td>
<td>1.3</td>
</tr>
<tr>
<td>$^\circ$OH + $^\circ$OH $\rightarrow$ H$_2$O$_2$</td>
<td>0.53</td>
</tr>
<tr>
<td>$^\circ$OH + H$^+$ $\rightarrow$ H$_2$O</td>
<td>3.2</td>
</tr>
<tr>
<td>H$_3$O$^+ + OH^- \rightarrow 2$H$_2$O</td>
<td>14.3</td>
</tr>
</tbody>
</table>

1.4.1 Primary yields

Primary yields are the yields of the species remaining when all spur reactions are complete, that is, $\sim 10^{-7}$ seconds after the ionization event. At this time the radiolytic change in water is represented by:

\[ H_2O \rightarrow e_{aq}^-, H^+, OH, HO^2, H_2O_2, H_2, H_3O^+ \]

The gamma or EB and the material balance equations are:

\[ G(-H_2O) = 2 \ G(H_2) + G(H^+) + G(e_{aq}^-) - G(HO^2) \]
\[ = 2 \, G \, (H_2O_2) \, + \, G(\cdot OH) \, + \, 2G(HO_2^\cdot) \]  
\[ \text{(1.10)} \]

or if \( HO_2 \) is neglected, which is justified for low LET radiation

\[ G \, (-H_2O) \, = \, 2 \, G \, (H_2) \, + \, G \, (H^\cdot) \, + \, G \, (e_{aq}^-) \]

\[ = \, 2 \, G \, (H_2O_2) \, + \, G \, (\cdot OH) \]  
\[ \text{(1.11)} \]

Primary yields were measured particularly for low LET radiations using scavengers in dilute solutions. In very dilute solutions the radical and molecular yields are constant, but in the presence of a reactive solute at concentrations more than \( 10^{-2}\text{mol dm}^{-3} \), the yields of \( H_2 \) and \( H_2O_2 \) decrease and radical yields increase due to spur scavenging by the solute molecules [20].

**1.4.2 Important reducing radicals in aqueous solutions**

The hydrated electron, \( e_{aq}^- \), and the hydrogen atom (\( H^\cdot \)) are the primary radicals falling in this category. The redox-potential value \( \xi^\circ = -2.9 \text{ V vs NHE} \) for \( e_{aq}^- \) suggests that it is a powerful reducing agent (Table 1.2). Its reactions with solutes are best understood in terms of availability of a suitable vacant orbital in the solute molecule (\( S \)) for the electron to get localized. A typical reaction is represented as in equation (1.12) where the \( n \) represents the positive charge on the solute.

\[ e_{aq}^- + S^n \rightarrow S^{n-1} \]  
\[ \text{(1.12)} \]

The rate constant values for typical hydrated electron reactions support the above requirement. For water, the rate constant, \( k \) is only \( 16 \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) as a low-lying vacant orbital is absent in water. It also explains the sufficiently long half-life of \( e_{aq}^- \) in water. With solutes having low lying \( \pi^* \) orbital, the \( k \) value approaches the diffusion controlled limit. In neutral and acidic pH, the \( H^\cdot \) is an important reducing species with its redox
potential value, $\xi^o = -2.3$ V vs NHE (Table 1.3). It can be thought of as a weak acid with pK$_a$ of 9.6. While it readily reduces substrates with more positive redox potential, the corresponding rates are slower than for e$_{aq}^-$ reactions. With substrate having center of unsaturation, it is known to add readily to form H-adduct.

**Table 1.2** Properties of e$_{aq}^-$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of charge distribution</td>
<td>0.25-0.30 nm</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$4.9 \times 10^{-5}$ cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Spectral characteristics</td>
<td>e$<em>{aq}^-$, $\lambda</em>{max} = 715$ nm, $\varepsilon = 1.85 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Redox potential (Vs NHE)</td>
<td>$\xi^o$ (e$_{aq}^-$ + H$^+$ $\rightarrow$ $\frac{1}{2}$ H$_2$ + H$_2$O) - 2.9 V</td>
</tr>
<tr>
<td>Half life: pH $\geq$ 7.0</td>
<td>$6.6 \times 10^{-4}$ seconds.</td>
</tr>
</tbody>
</table>

From a solute devoid of $\pi$ electrons, it abstracts hydrogen atom giving rise to a solute transient radical. Optical absorption of H$^*$ lies around 200 nm with very low extinction coefficient, which is normally not accessible with the available experimental facilities. Thus, measurements of H$^*$ reaction parameters are made by competition kinetics method or from the transient formation kinetics.

**Table 1.3** Properties of H$^*$ atom

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion constant</td>
<td>$8.0 \times 10^{-5}$ cm$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Spectral characteristics</td>
<td>H$^*$, $\lambda_{max} = 200$ nm</td>
</tr>
<tr>
<td>Reduction potentials (vs. NHE)</td>
<td>$\xi^o$ (e$_{aq}^-$ + H$_3$O$^+$ $\rightarrow$ H + H$_2$O) - 2.3 V</td>
</tr>
<tr>
<td>pK$_a$:</td>
<td>9.6</td>
</tr>
</tbody>
</table>
1.4.3 Important oxidizing radicals in aqueous solutions

Hydroxyl radical (•OH) is a strong oxidizing radical (ξ° = 2.8 V vs NHE) and like H•, it absorbs in the far UV, therefore, its kinetic parameters are also estimated by competition kinetics or transient formation kinetics. In strongly basic solution (pH > 11.9), it is deprotonated to give O•−. The properties of •OH radical are listed in Table 1.4.

Table 1.4 Properties of •OH radical

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion constant</td>
<td>2.2 x 10⁻⁵ cm² s⁻¹</td>
</tr>
<tr>
<td>Spectral characteristics</td>
<td>•OH, λ_max = 235 nm, ε = 530 dm³ mol⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>Reduction potentials (vs. NHE)</td>
<td>ξ° (e⁻ + •OH + H⁺ → H₂O) + 2.8V, acid</td>
</tr>
<tr>
<td></td>
<td>(e⁻ + •OH → OH⁻) + 1.8 V, alkali</td>
</tr>
<tr>
<td>pKₐ:</td>
<td>(•OH ⇌ O•− + H⁺) 11.9</td>
</tr>
</tbody>
</table>

1.5. Radiation effects on Polymers

It has been approximately 50 years since researchers first began exposing polymeric materials to ionizing radiation, and reporting the occurrence of cross linking [21], surface modification (grafting and curing) [22, 23] and other useful effects. Today, a substantial commercial industry is in place based on processing of polymers with radiation like radiation cross-linked wire and cables, smart surfaces for tissue engineering, separation of toxic metal ions, treatment of textile effluents, fuel cells etc.

Irradiation of polymers causes modification of properties which is currently the basis of major industries in heat shrinkable film and tubing, crosslinked polymers and graft copolymers [24]. Irradiation of polymers with high energy radiation leads to the formation of very reactive intermediates in the forms of excited states, ions and free
radicals. These intermediates are almost instantaneously guided in several reaction pathways which result in the arrangement or formation of new bonds structures. The ultimate effects of these reactions are the formation of oxidized products, grafts copolymer, crosslinking and scissioning of main or side chains which is also called degradation. Schematic of various processes has been shown in the figure 1.7. Generally, scission and crosslinking coexist, although the prevalence of each relies on many factors, such as the initial molecular structure, polymer morphology and the experimental irradiation conditions of treatment before, during and after irradiation and close control of these factors make the modification of polymers possible by radiation processing [25]. The degree or dominance of these transformations depends on the nature of the polymer and the conditions [26].

1.5.1 Crosslinking and degrading polymers

Polymers are generally divided into two groups: crosslinking type (which predominantly crosslink) and degrading type (which predominantly undergo chain scission). In general, polymer chain with at least one hydrogen atom (as in the structure I) with each carbon atom undergo crosslinks and if a tetra-substituted carbon atom is present in the repeat unit (as in the structure II), the polymer degrades predominantly.

\[
\text{Structure I (crosslinking)}: \quad [-\text{CH}_2\text{-CH}_2\text{-}]_n \quad \text{R} \\
\text{Structure II (degrading)}: \quad [-\text{CH}_2\text{-C}_2\text{-}]_n \quad \text{R}
\]

Thus, polyethylene, polystyrene, are crosslinking type of polymers, and polymethyl methacrylate, polytetrafluoroethylene are degrading type of polymers. In general, crosslinking reactions in polymers are favored by the presence of unsaturated
groups particularly vinyl groups, absence of oxygen, high chain mobility and molecular entanglements. Chain scission on the other hand is favored by restrictions to chain rotation i.e. glassy state, high levels of crystallinity and presence of oxygen. Usually radiation stability of the polymer increases in the presence of aromatic ring in its structure. Crosslinking reaction transforms a linear polymer into a single three-dimensional molecule with significantly different properties. The crosslinked structure has ultra high molecular mass, is practically insoluble in any solvent and has improved mechanical properties. Degradation on the other hand results in a reduction of molecular mass as chains are fractured and results in a general degradation of the physical properties of the polymer.

Crosslinking reactions have been intensively studied for a long time, and continue to this date for the improvement of the thermal resistance, mechanical, physicochemical properties of polymers. The desired change of physical and mechanical features is induced and can be tuned by the choice of individual irradiation parameters. There are number of applications of cross-linking, mainly with radiation technology, like wire and cable insulation, heat shrinkable products, polymeric positive temperature coefficient products, gaskets and seals, hydrogels, vulcanization etc. Other cross linking applications like hydrogel will be further elaborated in respective chapter. The opposite of crosslinking chain, scission is the basis of other radiation treatment aimed at enhancing processing characteristics of polymers. For example, radiation degradation of Polytetrafluoroethylene (PTFE) found large applications for thickener of various oils, lubricants, material for coatings and inks [27].
Figure 1.7: Schematic diagram for radiation effect on polymers

There were number of problems with the high MW PTFE in grease and other lubricants. Grease containing degraded PTFE was claimed by US patent in 1966. It was claimed that PTFE retained its low coefficient of frictions even with loss of tensile strength and was easier to disperse in a lubricant than high MW PTFE. It was also observed that degraded PTFE gives smoother grease and reduce the amount of PTFE required [28].

1.5.2 Surface modification

(a) Basics of Radiation Induced grafting

Graft copolymers are branched copolymers in which the branches are of a different type from the base polymer to add the desired functionality for various directed applications. In graft copolymerization, the role of the trunk polymer is to provide an appropriate practical shape and dimension and to maintain physical and chemical stability, whereas, the grafted polymer branch adds various functionalities.
There are various methods for the graft polymerization like conventional method, radiation induced method, plasma induced method, enzymatic method [3] etc. But using high energy radiation is hot topic nowadays in which radiation chemist produces radicals by breaking C-H bonds on a trunk polymer by irradiating it with ionization radiation (gamma rays or electron beams). Then a polymer branch with desired functional capabilities is grafted onto the trunk polymer as shown in figure 1.8.

![Diagram of Radiation induced Graft Copolymerization](image)

Figure 1.8: Radiation induced Graft Copolymerization

Therefore, one can easily and effectively incorporate the desired properties onto a polymer backbone using graft polymerization by selecting suitable monomer without destroying or affecting the basic properties of the of the trunk polymer, e.g. crystallinity, melting point or mechanical properties [29-31].

(b) Classification of graft polymerization

Radiation grafting technique can be classified into two categories in terms of irradiation opportunity [5].

(i) Simultaneous or mutual irradiation grafting: Simultaneous irradiation is the simplest irradiation technique for preparation of graft copolymers. In this method a polymer backbone is irradiated in the presence of a monomer available in different forms: vapor, liquid or in bulk solution. Irradiation can be carried out in air, inert atmosphere (e.g. N₂) or preferably under vacuum leading to the formation of active free radicals on
both polymer backbone and monomer units (figure 1.9a). In this method, the trunk polymer in contact of a monomer is irradiated simultaneously. The best condition for the method is preferred for base polymer having higher G-value as compared to the monomer to be grafted.

![Backbone and monomer are simultaneously irradiated](image)

**Figure 1.9a:** Schematic diagram for Mutual Irradiation Grafting

(ii) **Pre-irradiation grafting:** In this method, the trunk polymer is first irradiated to generate reactive radical sites and then brought into contact with the monomer (figure 1.9b). The best condition for the method is preferred for base polymer having lower G-value as compared to the monomer to be grafted.

![Radicals are generated & dipped in Monomer solution](image)

**Fig 1.9b:** Schematic diagram for Post Irradiation Grafting
(c) Parameters affecting Graft Polymerization

There are number of parameters, which strongly affect radiation-induced graft copolymerization process and subsequently the grafting yield in the copolymer membranes. Variation of parameters as mentioned in figure 1.10 causes considerable changes in the amount of degree of grafting in the resulting membranes and therefore, control of the compositions and the properties of the membranes can be achieved. A combination of parameters has to be adapted to achieve successful grafting reactions and obtain desired membrane structure economically. This includes parameters directly related to irradiation source and others related to the grafting mixture and its components.

**Figure 1.10:** Schematic representation of parameters affecting the degree of grafting prepared by radiation-induced graft copolymerization.
Figure 1.10 shows a schematic representation of parameters affecting the degree of grafting in membranes prepared by radiation-induced graft copolymerization [32]. The effect of each one of these parameters on the degree of grafting of the membrane is discussed in the corresponding chapters.

(d) **Advantages of radiation grafting:** Radiation grafting is superior to other conventional grafting techniques because of the following reasons:

(i) Selective absorption, low penetration and requirement of additive like photo initiators or photo sensitizers make the photo initiation process a handicap one. However, radiation induced grafting methods are limitless, owing to the unselective absorption of radiation energy in matter, and can in principle, be used to prepare any desired combination of polymers. Unlike conventional grafting methods, radiation grafting reaction can either be conducted homogeneously throughout thick layers of polymers or limited to the surface zone of desired thickness only, depending upon the type of radiation, the total energy absorbed, the depth of penetration and radiation sensitivity of trunk polymer and monomer.

(ii) Some polymers such as solid fiber are difficult to be grafted by chemical initiators, because they can hardly induce reactive centers homogeneously in the solid fiber. As far as radiation grafting is concerned, it is easier, especially for gamma radiation and high-energy electrons, which have high penetration power, to induce radicals homogeneously onto any arbitrary shapes of polymers, such as a hollow fiber, woven/non-woven fabric and films.

(iii) Radiation grafting does not require any additives such as initiators or sensitizers, unlike photo grafting or thermal grafting methods. Therefore, in radiation grafting
method, high purity copolymer is obtained, which have vast applications as biocompatible and bio-functional materials where impurity of any type is not acceptable.

1.6 Hydrogel

At present there is no precise and limiting definition of the term hydrogel but it is commonly defined as three dimensional networks of cross-linked hydrophilic polymer chains that imbibe substantial amounts of water (>20%) without losing its physical integrity. Hydrogels are highly absorbent (>99.9% water) based on natural or synthetic polymers. It is a solid material in dried state, but when water is added; the hydrogel swells until it reaches the swelling equilibrium as shown in figure 1.1. Hydrogels also possess a degree of flexibility very similar to natural living tissue, due to their high water content, more than any other type of synthetic biomaterial. Due to this resemblance to living tissues, hydrogel have a number of biomedical applications, such as wound care products, dental and ophthalmic materials, drug delivery systems, elements of implants, constituents of hybrid-type organs, as well as stimuli-sensitive systems superabsorbents etc. with a number of products being commercially available [33].

Among the above mentioned applications of hydrogel, most notably, research has been advanced in the commercialization of burns and wound dressing hydrogels. In India, wound dressing material has been commercialized with the brand name ‘HI-ZEL’ by Varshney and group [34]. These hydrogel maintain a moist environment, barrier to bacterial contamination, excess to oxygen, transparent in nature, which allows monitoring the healing progress of wound without removing the dressing. Most importantly faster wound healing was reported than dry gauze dressing [35].
Figure 1.11: Schematic representation of gel structure before and after swelling

Another fascinating class of hydrogel which is subject of extensive investigation is responsive to small transition in solvent composition, pH, temperature, and intensity of light as well as magnetic and electric fields called Stimuli Responsive Hydrogel. For example, the change in pH causes volume transition in polyacrylic acid hydrogel as shown in figure 1.12. Depending on the pH of the medium as the polyacrylic acid goes from non-ionized state (relaxed configuration) to ionized state (stretched configuration), the polyacrylic matrix may swell or de-swell. The applications of such hydrogels in devices as actuators, artificial muscles, controlled drug delivery; controlled molecular separators have been suggested [36]. Carenza and group have reported control release of insulin in response to glucose blood levels in their vivo studies on diabetic rats.

The properties, which decide the applications of a hydrogels, are: equilibrium degree of swelling, swelling kinetics, permeability, biocompatibility, mechanical and optical properties and change in extent of swelling with external environment like pH, ionic strength, temperature.

The introduction of ionic monomers results in gels which normally swell more than the non-ionic gels [37-39]. Incorporation of monomers like acrylic acid and methacrylic acid produces anionic polyelectrolyte gels, whose ionization is a function of pH, thermo
responsive gels poly-N-isopropylacrylamide (PNIPAM) are the functions of temperature which undergo phase transition in pure water, from a swollen state at low temperature to a collapsed state at high temperature [40] by breaking hydrogen bonding at higher temperature whereas incorporation of the sulfonate, tertiary and quaternary amines group produces polyelectrolyte gels relatively insensitive to pH [41]. Poly(2-hydroxyethyl methacrylate) (PHEMA) based gels have been the subject of interest for scientists and technologists because of their versatile properties, such as biocompatibility, good mechanical strength, high gel fraction, and ease of synthesis. However, low swelling of non-ionic polymer matrix like PHEMA at higher crosslinking extent restricts their applications where high swelling is desired. This problem can be overcome by either functionalization of the base matrix or by co-polymerization with ionic monomers. The introduction of ionic monomers results in gels which normally swell more than the non-ionic gels [37-39].

In the present study, poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (MAETC), a strong cationic polyelectrolyte, was incorporated in Poly(2-hydroxyethyl methacrylate) (PHEMA) based gels by radiation induced polymerization to improve the swelling extent and also to add ionic strength responsive properties. Electrostatic interactions between the ionized groups, as well as the presence of small electrolyte ions in the nearby solution, convey to polyelectrolyte system a host of properties distinct from those displayed by neutral polymer systems. Industrial applications and academic interests lead to more studies on the polyelectrolyte behavior in solutions, gels, adsorbed layers, and grafted brushes.
1.7 Quaternary cationic polyelectrolytes

Cationic polyelectrolytes are polymers with basic groups, either a weak amine or a quaternary ammonium groups, situated along the main chain of the polymer. Therefore they retain many of the properties of polymer from which they are derived, but these properties are considerably modified by the presence of the basic groups. Examples of weak cationic polyelectrolytes are polyvinylamine, polyethyleneamine, and poly (4-vinyl-pyridine), where examples of strong polyelectrolytes are polyvinyl-bezyltrimethylammonium chloride and polyvinylmethylpyridinium bromide. Quaternary ammonium cations, also known as quats and corresponding polymer containing quaternary ammonium cations as polyquats, are positively charged polyatomic ions of the structure NR₄⁺, R being an alkyl group or an aryl group [42]. Unlike the ammonium ion (NH₄⁺) and the primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution.

**Figure: 1.12:** Effect of pH on pH stimuli Hydrogel
1.7.1 Quaternary ammonium compounds as an anti-microbial compounds

Antimicrobial agent or germicides are the chemicals which inhibit or kill microorganisms’ e.g bacteria, fungi or viruses. Halogens (iodine, chlorine), alcohols, peroxxygen compounds (H₂O₂, peracetic acid), phenolic compounds, aldehydes and ionic surfactants are the well-known examples of antimicrobial agent. Among the various classes of surfactants, the cationic, and more particularly the quaternary ammonium compounds are the most effective germicides. Quaternary ammonium compounds (QACs) are amphoteric surfactants that are widely used for the control of bacterial growth in clinical and industrial environments [43]. Quaternary ammonium compounds have a broad spectrum of antimicrobial activity against both Gram-positive and Gram-negative bacteria. As compared with small molecule antimicrobial agents, polymeric antimicrobials have advantages, such as that they are nonvolatile, chemically stable, have long-term antimicrobial activity, and are hard to permeate through the skin [11]. These compounds kill or inhibit the growth of both gram-positive and gram-negative bacteria, and are effective over wide pH range. On the other hand, the anionic surfactants are frequently effective against gram-positive bacteria but very rarely effective against gram-negative bacteria. Their action tends to be much slower than that of the cationic surfactants and more susceptible to the changes in the pH of the system [44].

1.7.2 Mechanism of the germicidal action

Although large amount of work has been carried out to study the biochemical mechanism by which cationic surfactants exert their germicidal action, no complete theory has yet been developed. It appears probable that the surfactant can attack the cell through many different routes, and the particular mechanism, which is effective in a single case, depends on the organism and the concentration of the surfactant. Simple
adsorption may not be sufficient disturbing to kill unless it seriously upsets the osmotic balance between the organism and the medium. This class of chemical reduces the surface tension at the interfaces, and is attracted to the negatively charged surfaces, including microorganism. Some of the mechanism suggested include: (i) denaturation of the cell proteins. (ii) Combination of the cationic compound with the cell lipids. (iii) Interference with the enzyme balance within the organism and affecting the metabolic reactions of the cell (iv) Interference with the osmotic balance in such a manner as to release vital solute materials outward through the cell wall, finally causing death [45, 46]. Most of these compounds bearing quaternary ammonium groups appear to act by interacting with and disrupting negatively charged bacterial cell membrane followed by release of K+ ions and other cytoplasmic constituents, resulting in immediate death of the bacterial cell. In contrast to the soluble polycations, insoluble quaternary ammonium macromolecules act on the surface of the microbial cell and display their antimicrobial activity only on contact without permeation [47]. An alternative mechanism of action was proposed by Kugler et al. for cationic surfaces which appear to induce an ion exchange between the positive charges and cations within the membrane. Upon approaching a cationic surface, the structurally essential divalent cations of the membrane are relieved of their role in charge neutralization of the membrane components and are thus free to diffuse out of the membrane. The loss of these structural cations results in a loss of membrane integrity [48].

1.8 Scope of the thesis

As discussed in the earlier part of this chapter, water-soluble polyelectrolytes have been suggested as important polymeric materials having immense potential in
different field of life. New method of synthesis of polyelectrolytes, their gels and grafted copolymers using radiation polymerization method have been developed.

High energy gamma radiation has been used to initiate the synthesis HEMA-co-MAETC hydrogels of good swelling extent and mechanical strength which has number of advantages over conventional methods viz. high purity products, easy process control, room temperature synthesis and possibility of sterilization during synthesis. The properties, which decide the applications of a hydrogels, are: equilibrium degree of swelling, swelling kinetics, permeability and hence incorporation of strong polyelectrolyte PMAETC has been studied extensively. Equilibrium swelling study gives the idea about the equilibrium degree of swelling (EDS) of the hydrogel, which is the one important factor that decides the application of the gel matrices. On the other hand, dynamic swelling kinetics provides information regarding solvent sorption rate (diffusion constant), the rate of approach to the EDS and transport mechanism (type of diffusion) controlling the solvent sorption. Therefore, equilibrium swelling and dynamic swelling studies of any gel are of vital importance for developing technological applications. The equilibrium and dynamic swelling study of polyampholytic gels were carried out in different experimental conditions.

PMAETC and PAETC have a strong anion exchanger (quaternary ammonium) group and also exhibit anti-microbial activity. Therefore, PMAETC and PAETC were grafted onto cotton cellulose matrix, which is the most abundant biopolymer in the nature but very prone to attack by the microorganisms like bacteria, fungi, by mutual radiation grafting method in order to incorporate bactericidal. The grafted samples were then tested for antibacterial property group of gram positive and gram negative bacteria. In the last, one of the monomer VBT containing quaternary ammonium groups, a strong anion
exchanger which is grafted onto cotton, has been investigated for the treatment of textile effluents containing acid dyes.