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# Ionizing Radiation-Induced Polymerization

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## Abstract

Ionizing radiation can induce some kinds of reactions, other than polymerization, such as dimerization, oligomerization, curing, and grafting. These reactions occur through a regular radical chain causing growth of polymer by three steps, namely, initiation, propagation, and termination. To understand ionizing radiation-induced polymerization, the water radiolysis must be taken into consideration. This chapter explores the mechanism of water molecules radiolysis paying especial attention to the basic regularities of solvent radicals' interaction with the polymer molecules for forming the crosslinked polymer. Water radiolysis is the main engine of the polymerization processes, especially the "free-radical polymerization." The mechanisms of the free-radical polymerization and crosslinking will be discussed in detail later. Since different polymers respond differently to radiation, it is useful to quantify the response, namely in terms of crosslinking and chain scission. A parameter called the G-value is frequently used for this purpose. It represents the chemical yield of crosslinks, scissions and double bonds, etc. For the crosslinked polymer, the crosslinking density increases with increasing the radiation dose, this is reflected by the swelling degree of the polymer while being immersed in a compatible solvent. If crosslinking predominates, the crosslinking density increases and the extent of swelling decreases. If chain scission predominates, the opposite occurs. A further detailed discussion of these aspects is presented throughout this chapter.

**Keywords:** gamma irradiation, polymerization, water radiolysis, radical

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## 1. Introduction

Since the last quarter of the twentieth century, a growing interest in polymerization induced by ionizing radiation has been observed. Throughout this period, researchers have exposed polymeric materials to ionizing radiation and reported the occurring of crosslinking and other

useful effects, e.g., miscibility of blend polymer [1–3] as well as many different applications in the polymer radiation chemistry field [4, 5]. Ionizing radiation is a promising technology for preparation of cost-effective, efficient, safe, and high-quality polymers. The radiation techniques applied for polymerization processes could be carried out using many different types of radiation sources. Ionizing radiations (gamma rays, X-rays, accelerated electrons, and ions beam) initiate polymerization reactions by the formation of very reactive intermediates (energetic radicals). Energetic radicals resulting from ionizing radiation hit molecules causing electrons ejection from a particular orbit, then the atom becomes ionized [6]. As soon as their orbits begin to be ready to overlapping forming new bonds, these electrons may be much more detached by other molecules [7, 8]. This phenomenon occurs when the transferred energy is higher than that of particular orbital electrons. When the energy is not high enough for ionization, electrons are gaining energy and transfer to an upper energy level, resulting in excitation. The ionizing potential for most molecules ranges from 7 to 15 eV [9], while the energies of ionizing irradiators (gamma rays, X-rays, accelerated electrons, and ions beam) range from 1 to 100 MeV [10], so ionization is the predominating process. Energetic radicals with ionized electron excite another molecule upon calling energy transfer. The ionized species associated with the energetic radicals created by irradiation would induce various reactions. This power in a polymerization reaction is an eco-friendly process. Polymers are covalently crosslinked by ionizing radiation at room temperature. The degree of crosslinking is radiation dose-dependent besides other parameters, e.g., temperature and ambience [11].

Radiation crosslinking is a result of the combination of two molecules with active radicals at different three routes (head-to-head, head-to-tail, and tail-to-tail). In an amorphous region, the radical's combination is predominated rather than in crystalline region [12]. Sometimes increase of crystallinity reveals polymer crosslinking. On the other hand, the increase of amorphousity reveals polymer degradation (chain scission) [13]. Whatever, crosslinking or degradation, depends on the polymer nature. Therefore, predomination of radiation crosslinking can be achieved by removing oxidation gas ( $O_2$ ) and replacing it by an inert gas ( $N_2$ ). The percentage of dissolved oxygen could control the degree of polymerization and/or degradation of polymer chains. These processes compete through the breaking or formations of covalent bonds. The formations of new covalent bonds predominate in the case of vinyl monomer or synthetic polymer.

Water radiolysis produces neutral radicals  $H^\bullet$  and  $^\bullet OH$  with hydrated electrons  $e_{hy}$  and molecular products  $H_2$  and  $H_2O_2$ . This means that the radiolysis of water gives several radiation-chemical reactions that have been studied in aqueous solutions, e.g., radiolytic reduction reaction (RRR), radiolytic oxidation reaction (ROR), and radiolytic polymerization reaction (RPR). This chapter discusses three kinds of RPR, namely; radical, cationic, and anionic polymerization.

In order to approach polymerization induced by ionizing radiation in high yield, the selected solvent should be ready for radiation radiolysis and of a high order of dissolving for the desired monomers. However, when switching to poor solvents, this might lead directly to rather broad distributions of polymer molecular weight. Non-polar solvents are ion-pairing or clustering that could interact, by radiolysis, with polymer backbone living a part of solvent

molecules attached to polymer backbone “closely associated with the chain end,” this is the so-called “living polymerization.” Consequently, radiolytic solvents could act as catalysts which govern the kind of polymerization mechanism to be either cationic or anionic when solvents act as Lewis acid or Lewis base, respectively.

Step-growth radical polymerization induced by gamma irradiation occurs in three main stages. The first stage of the reaction is “initiated” by ionizing radiation, in which a radical (molecule with an active center) is formed, typically by radiolysis of an aqueous solvent (mainly water) or by breaking C–H bond in polymer chains. The second stage is “propagation” which begins by attracting an active center that is formed in one monomer molecule with another monomer molecule. The final stage is “termination,” in which the number of radical creation is terminated or the monomer molecules are consumed and mostly all monomers form polymer chains. Furthermore, the degree of polymerization depends on the monomer concentration and manipulation of the radiation dose.

Radiolysis of water is the ionization of water molecules by the absorption of ionizing radiation energy. The ionizing radiation absorbed by the water molecules is the pulse radiolysis technique [14]. The pulse radiolysis of water in high energy electromagnetic wave (ionizing radiation) gives variety of reactive species such as excited molecules, ions, and radicals [15]. It should be observed that radicals are formed by a wide variety of water radiolysis reactions, these species are chemical transformation and physical generation. The physical stage of the primary interaction of ionizing radiation with water molecules result in excitation and ionization as expressed by Eqs. (1) and (2):



This chapter focuses attention on the radiolysis of water as a source of radicals which are responsible for polymerization reactions. ESR spectroscopy is the best detection method for studying radical intermediates in radiolysis [16].

## 2. Photo-initiated induced by UV irradiation

### 2.1. Radical polymerization

Photopolymerization induced by UV irradiation is presented as a green technology characterized by low cost electrical power input and low energy requirements. Low temperature, low noise operation, and no volatile gases are generated. Photopolymerization is performed by water photolysis, practically the excited water molecule was generated ( $\text{H}_2\text{O}^*$ ) through the UV radiation ( $\lambda < 240 \text{ nm}$ ) absorption process (Eq. (3)). The water molecules in the excited state are mainly located on the water surface that exposed to UV, and with the course of time, energy will transfer to bulk molecules of water to produce (reactive species) radicals ( $\text{H}^\bullet$  and  $\bullet\text{OH}$ ). The predominant photolysis reaction of UV in water molecules is homolytic bond scission (Eq. (4)). The excited

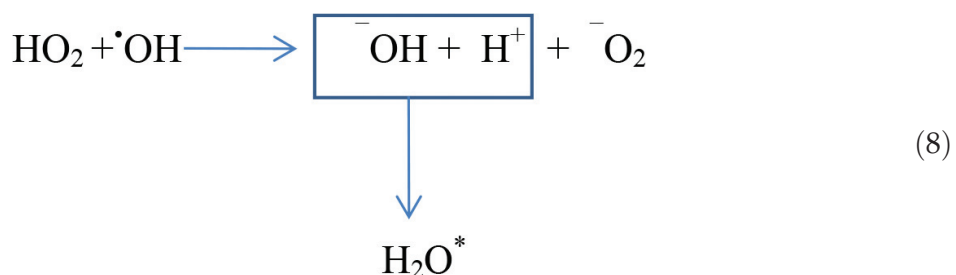
water molecules ( $\text{H}_2\text{O}^*$ ) can undergo further photolysis producing reduction/oxidation agents ( $\text{H}^+$  and  $^-\text{OH}$ ) by intra-molecular electron transfer (as summarized in Eq. (5)). The following equations are the most common water photolysis impact of UV absorption:



In dissolving oxygen, the energy transfer processes to oxygen molecules forms dioxygen radical anion (superoxide radical) is possible according to Eq. (6). In case of complete energy transfer, relatively long-lived water molecules are produced in excited state, as the so-called the triplet state.



All the above reactions may be recombined with each other's in unlimited hypothesis, as expressed in Eqs. (7) and (8). This recombination gives excited ( $\text{H}_2\text{O}^*$ ) water molecules



The hydroxyl radical ( $^\bullet\text{OH}$ ) has a limited mobility and mainly abstract hydrogen atoms (H) for forming  $\text{H}_2\text{O}$ . On the other hand, the number of reduction/oxidation agents ( $\text{H}^+$  and  $^-\text{OH}$ ) increases as the addition of oxygen to the water solutions increases. Obviously, at low concentration of dissolved oxygen, the crosslinked polymer is obtained. Therefore, under condition of sufficient dissolved oxygen, photo-oxidative degradation process may predominate. This is beneficial for water treatment and elimination of organic compounds pollutants; but sometimes, a part of the dissolved organic pollutants was found to precipitate, probably as a result of functional groups condensation (acetic acid, oxalic acid, n-butanoic acid, and malonic acid) which were the most abundant degradation products detected. The photo-oxidative degradation process  $\text{C}-\text{C}$  yields a macroradical  $\text{C}^\bullet-\text{C}^\bullet$  by bond session. This macroradical molecule may be recombined in the absence of oxygen (polymerization). In the presence of oxygen, the peroxy radicals  $\text{C}-\text{O}-\text{O}^\bullet$  may be formed (photo-oxidative degradation) [17]. Particularly, the photons that cause degradation are found in all electromagnetic radiations and can be enhanced at elevated temperatures. So, in polymerization reaction, the concentration of oxygen should be controlled in order to improve the polymerization induced by UV irradiation.

The role of the polymerization reaction initiation induced by UV irradiation “photoinitiator” is delayed with converting the photon energy into a chemical energy in the form of a “reactive

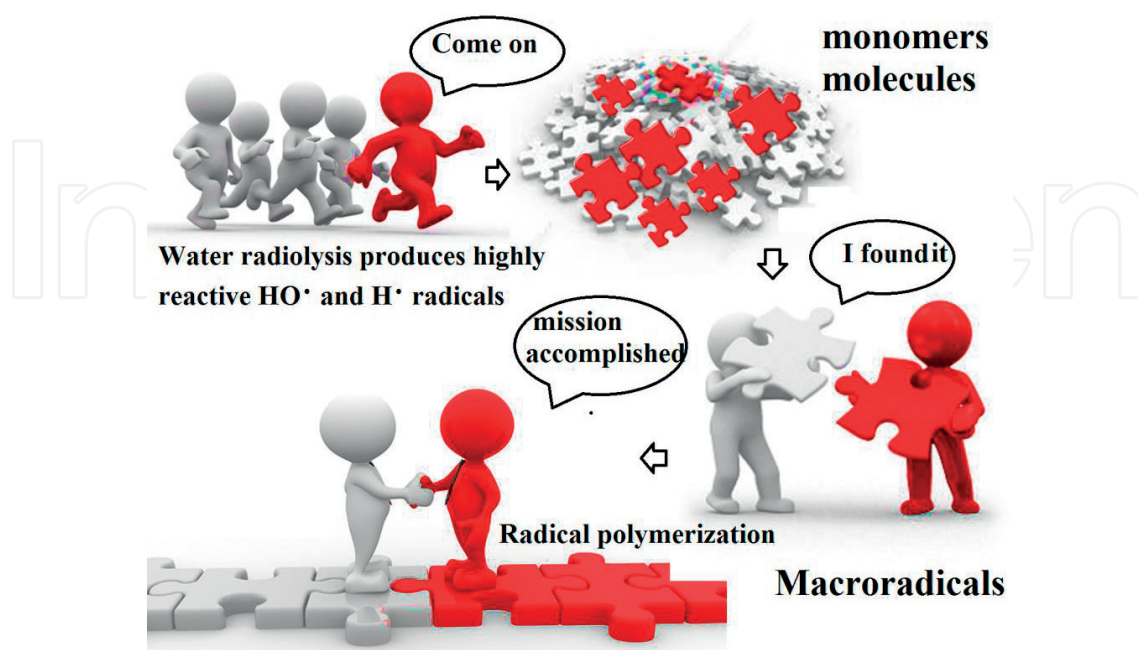


center.” When a water molecule absorbed photon in UV range in the absence of oxygen, it becomes excited and forms ( $\cdot\text{OH}$  and  $\cdot\text{H}$ ) species with a high quantum yield [18]. The photoinitiator should exhibit an energetic wavelength, and undergo a rapid water photolysis to generate the initiating ( $\cdot\text{OH}$  and  $\cdot\text{H}$ ). Subsequent polymerization goes on when reacting with a monomer molecule to start monomers combination and build 3D polymer network [19]. In this process, the polymers chains are crosslinked by forming covalent bonds cross chains [20].

The radical polymerization process is outlined in **Figures 1** and **2**, water excitation by absorbing UV leads to formation of free radicals as a first stage. In this typical step, the energetic radicals transfer to monomer molecules that undergo unimolecular bond formation upon irradiation. The polymerization process is complete with integration of monomer molecules. **Figure 2** shows water ionization by the UV rays that are capable to generate an active center (energetic radicals). These radicals pass energy to a monomer molecule that keeps the polymerization reaction going on. A “reactive” photoinitiator reacts with a monomer molecule to start a polymer chain formation, and the polymerization process begins with transferring the energetic radicals to monomer molecules. The crosslinked density is high in the deeper level rather than the surface level depending on oxygen concentration. While in free oxygen system, the crosslinked density is expected to be higher in the surface level rather than in the deeper level due to further yield of radicals on the side exposed to UV radiation.

## 2.2. Cationic polymerization

Besides photo-initiated radical polymerization that has been outlined, there are other two photo-polymerization processes; cationic and anionic polymerizations will be discussed in this section. Additives sensitive to UV radiation were required to promote cationic and anionic polymerization. In **Figures 3** and **4**, the common ultraviolet (UV) initiation agents are present



**Figure 1.** Imagination of the setup of radical polymerization.

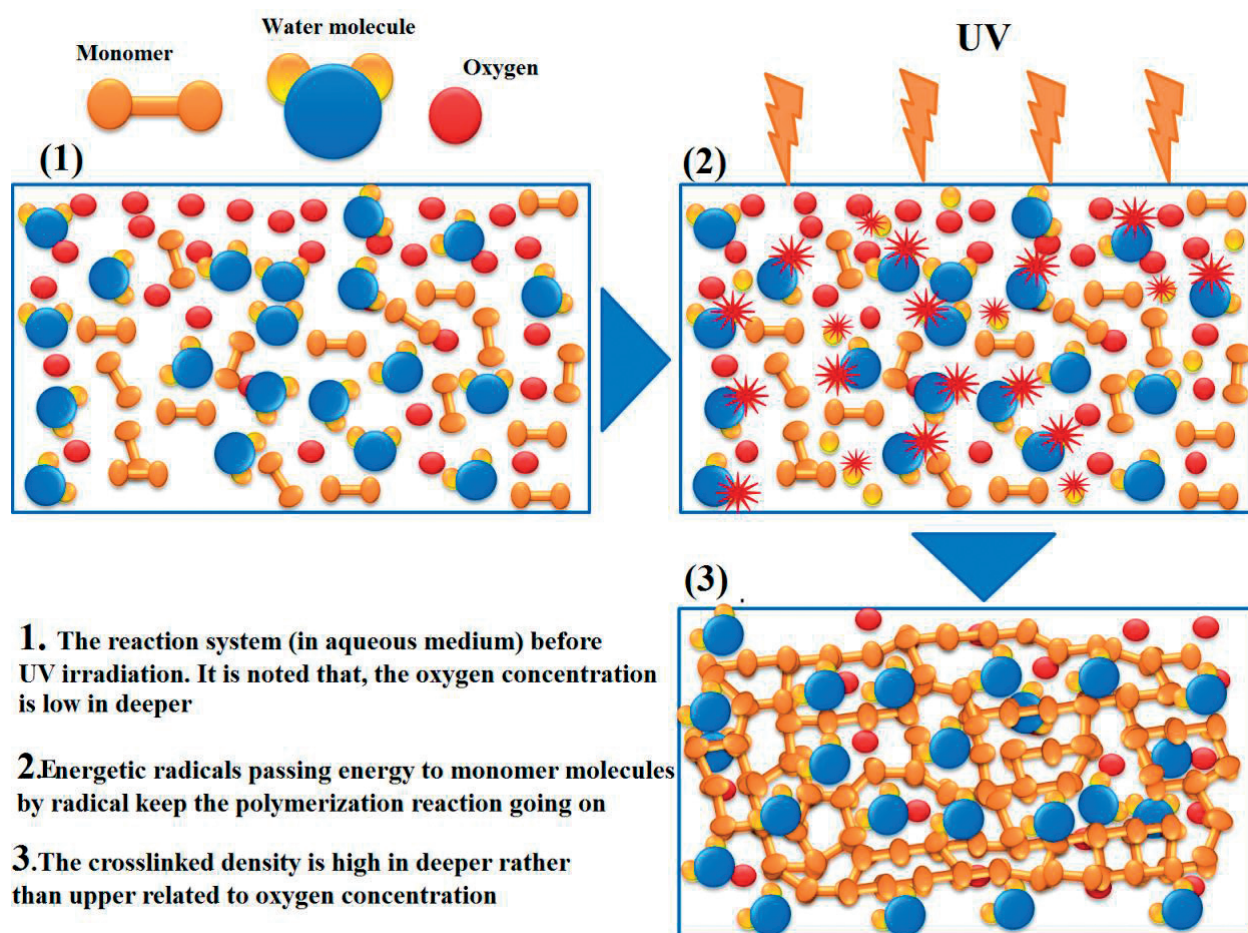


Figure 2. Proposed radical photo-polymerization induced by UV radiation.

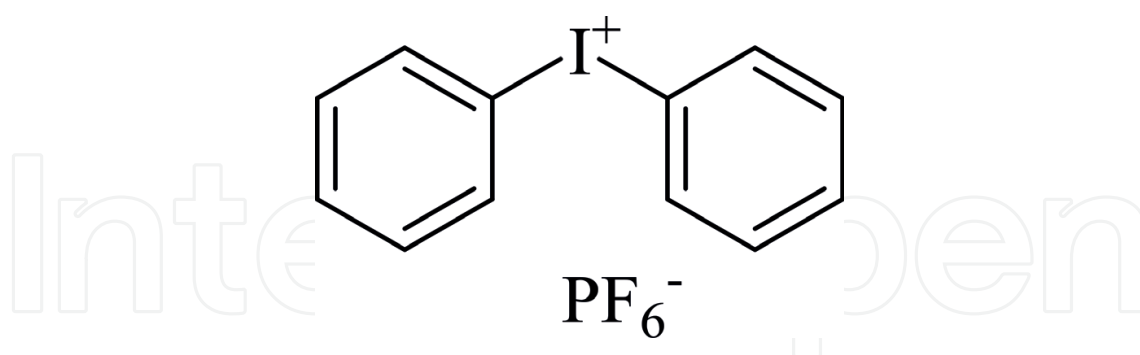
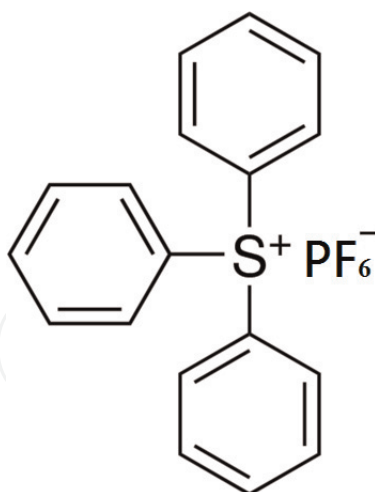


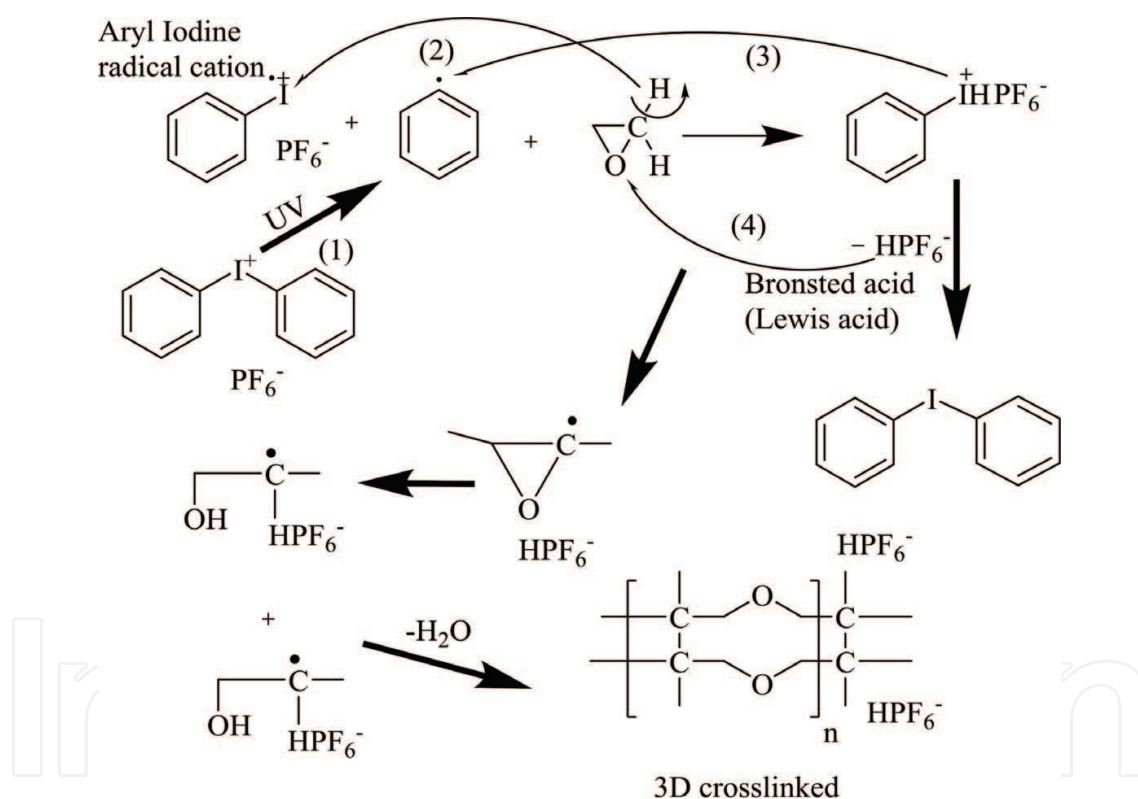
Figure 3. DPI diphenyliodonium hexafluorophosphate.

in two forms of onium salt: diphenyliodonium DPI (Ph<sub>2</sub>I<sup>+</sup>) and triphenylsulfonium DPS (Ph<sub>3</sub>S<sup>+</sup>) used as cationic photoinitiator under UV radiation [21–25]. Those are able to generate both protonic acids (carbonium ions) and free radicals (**Figure 5**).

This polymerization process is also called free-radical promoted cationic polymerization. This process undergoes more rapid polymerization, for example, in the curing process of epoxy resins, the ring opens and initiates both radical and cationic polymerization mechanism. Onium salt is sometimes called the curing agent, especially, for epoxy resin curing. **Figure 4**



**Figure 4.** DPS triphenylsulfonium hexafluorophosphate.



Curing of epoxy is very rapid due to radicals driven cationic  
 photopolymerization

**Figure 5.** A proposed mechanism of radical cationic photopolymerization induced by UV radiation of epoxy resin.

shows the generation of a Bronsted acid (Lewis acid) when DPI and DPS exposed to UV radiation [26–28].

As depicted in **Figure 5**, an aryl iodine radical cation and aryl radical are formed by the photolysis of DPI salt (1). Both of these are highly reactive species which separate protons



from the monomer (2) generating bronsted acid ( $\text{HPF}_6$ )<sup>−</sup> and formatting diaryl iodine (3). The polymerization reaction rapidly involves by protonation of the epoxide oxygen with the very powerful acid (4). It is obvious that the cationic polymerization of epoxies is highly quantitative and very rapid, with low activation energy [29]. For clarity, the concurrent radical and cationic reactions in hybrid systems have dramatically changed the rate of photo-polymerization [30].

**Figure 5** shows a proposed mechanism of radical cationic photo-polymerization induced by UV radiation of epoxy resin.

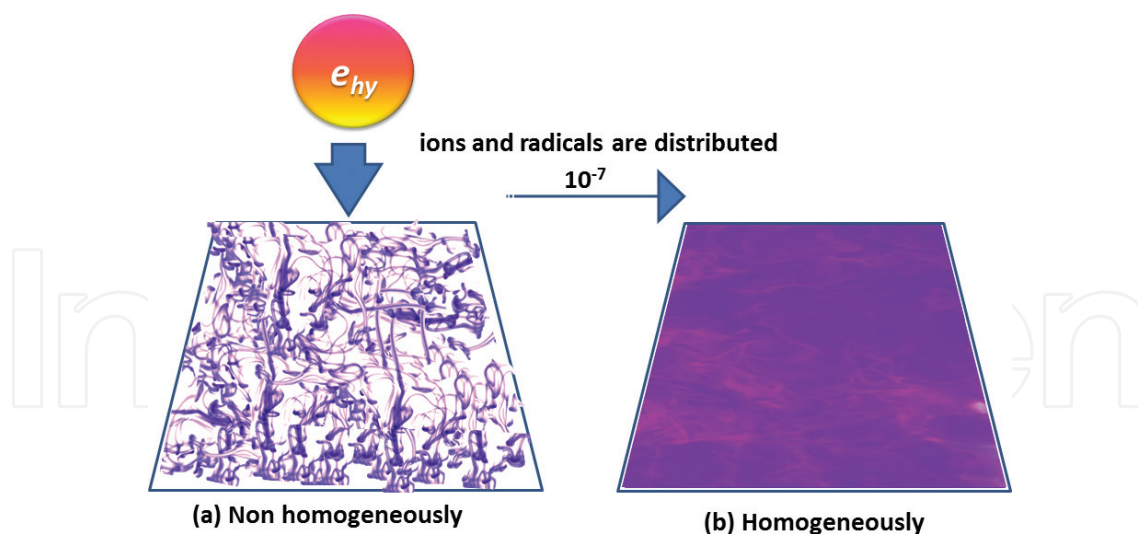
### 2.3. Anionic polymerization

Free cationic and radical photopolymerizations have been extensively applied in this context, whereas photo-induced anionic polymerization was limited in scope and application [31]. Kahveci et al. used a combination of cationic photo-polymerization and anionic opening ring polymerization mechanisms to confirm the amphiphilic graft copolymers of poly(ethylene oxide)-g-poly(isobutyl vinyl ether) (PEO-g-PIBVE) [32]. First, poly(ethylene oxide-co-ethoxyl vinyl glycidyl ether) was synthesized by anionic ring-opening co-polymerization of corresponding monomers using radiation for reaction initiation. Random anionic ring-opening co-polymerization of a mixture of the gaseous EO (b.p. 11°C) and the respective co-monomer in an appropriate solvent can be initiated by an alkali-metal alkoxide [33]. The vinyl ether moieties were then cationic photo polymerized using diphenyliodonium iodide photoinitiator. It is clear that photoinitiator was only used for cationic polymerization, while anionic polymerization takes place spontaneously by ring opening in mild conditions. Further investigation is needed to cover unexplored areas in the field of photo-induced polymerization [34]. Radicals promote cationic photo-polymerization, since it has been demonstrated to be a very effective method for the preparation of well-defined high molecular weight epoxy resin [35].

## 3. Electron beam

In order to complete the image of radiation-induced polymerization, another radiolysis system should be taken into consideration is electron beam. Electrons are generated in a linear beam form causing a powerful and fast water radiolysis that produce hydrated electrons ( $e_{hy}$ ). Most solvents are of a continuum for some polarity properties. The hydrated electron ( $e_{hy}$ ) is very reductive chemical species, once the solvated electron hits water molecules, water becomes ionized [36]. This depends on the time consumed for interaction and the average distance between the solvated electron ( $e_{hy}$ ) and the water ions.

The emitting powerful electron (more than 1 MeV electron) from electron accelerator hits water molecule and then scatters. The energy of electron is lost as a result of bordering a pathway for secondary electrons. Secondary electrons keep their own powerful energy, causing water ionization and forming copious quantities of variety of reactive species (e.g.,  $\text{H}_2$ ,  $\text{H}_2\text{O}^+$ ,  $\text{H}_2\text{O}_2$ ,

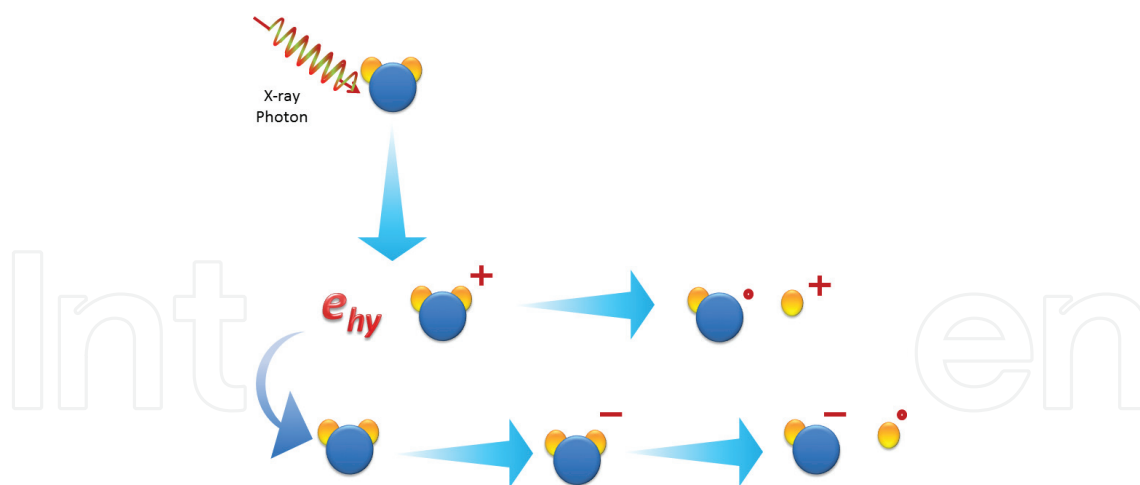


**Figure 6.** Inhomogeneous distribution of ionizing events ( $e_{hy}$ ) and its diffusion with time ( $\sim 10^{-7}$ ) and reactions reach the formation homogenous distribution.

$\text{OH}^-$ ,  $\text{H}_3\text{O}^+$  and  $\bullet\text{OH}$ , etc.) [37]. Particularly, the chemical reactions (radiolysis) occur when the reactive species of ions and radicals are distributed nonhomogeneously in “clusters” of excitations/ionization (i.e., spurs), and homogeneously after the reactive species have diffused and thermalized [38]. Spurs were used to describe the high energy electron passed through liquids. It is well-known that the ionizing and exciting species are, in fact, nonhomogeneous and occur in clusters called “spurs.” The electron is similar to a “stone” hit in the surface of the water pool, by the time the resulting “splashes” induced by “the stone hit” will expand and eventually overlap with their neighbors to result in a homogenous distribution (**Figure 6**). However, this simple picture is not true in some cases; the irradiation of nonaqueous systems does not yield as a clear picture concerning spurs as the case in the water.

#### 4. X-ray

Risse and Fricke [39, 40] had studied the radiolysis of water by X-rays in a closed vessel. Bubbles of hydrogen and carbon dioxide gas resulting from irradiation are found [41]. X-ray photons are highly powerful causing radiolysis of water to create an ion pair  $(\text{H}_2\text{O})^+$  ( $e_{hy}$ ). The amount of ionization species produced is affected by the amount of energetic photons absorbed. **Figure 7** shows that the positive and negative water molecules are unstable. These can break apart into smaller molecules. Free radicals can be formed by this breakup. Several chemical reactions might occur (oxidation reduction) by ( $\text{OH}^-$ ,  $\text{H}^+$ , and  $e_{hy}$ ) beside polymerization takes place by ( $\bullet\text{OH}$  and  $\bullet\text{H}$  and  $e_{hy}$ ) [42]. Also, the radiolysis products may recombine individually, forming gases such as  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  [43], and hence the bubbles are formed due to an evolving mixture of  $\text{H}_2$  and  $\text{O}_2$  gases.  $\text{H}_2$  present in the solution, or the “ $e_{hy}$ ,” may cause reduction reactions.



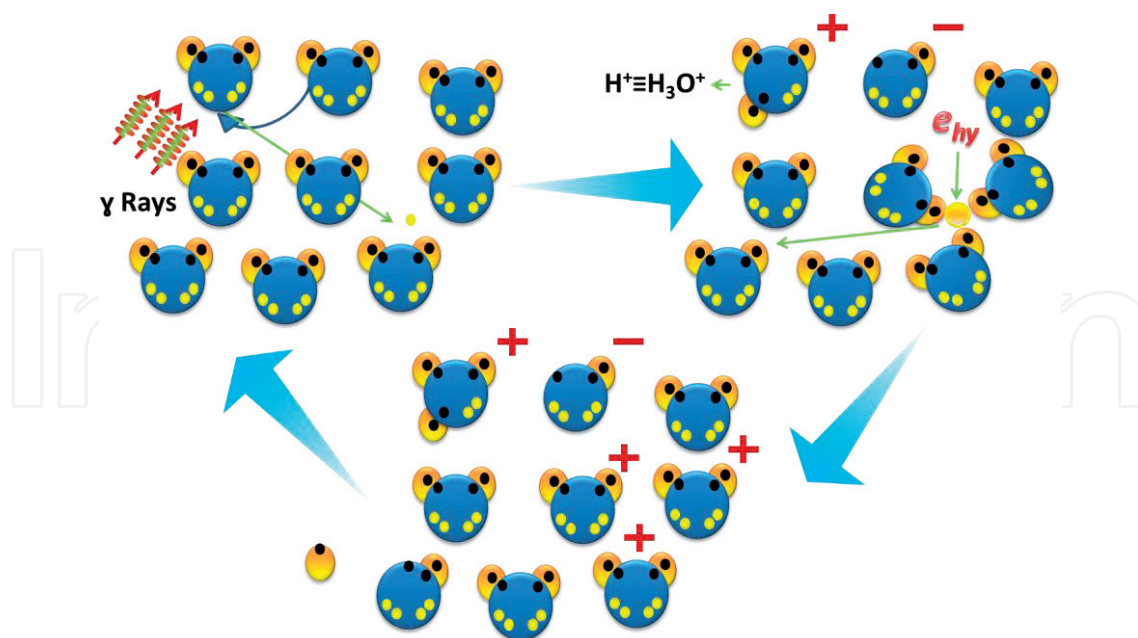
**Figure 7.** In radiolysis, bulk water is ionized to form an  $(\text{H}_2\text{O}^+)_{aq}/(e^-)_{aq}$  pair. The  $(\text{H}_2\text{O}^+)_{aq}$  quickly converts to  $(\cdot\text{OH})$  and  $\cdot\text{H}$  to become  $(\text{H}_2)_{aq}$ . And, the hydrated electron ( $e_{hy}$ ) hits another water molecule to become  $(\text{H}_2\text{O}^-)_{aq}$ , which converts to  $(\text{OH}^-)$  and  $\cdot\text{H}$  to become  $(\text{H}_2)_{aq}$ .

## 5. Gamma radiation

Radioisotopes, e.g., (Co-60  $t_{1/2} = 5.3$  years, Cs-137  $t_{1/2} = 30$  years, and Ir-192  $t_{1/2} = 74$  days) are considered as the sources of gamma rays. The radiation chemistry of polymers dissolved in water is the chemistry of reactions with  $\cdot\text{OH}$ ,  $\cdot\text{H}$ , and  $e_{hy}$ . The effect of ionizing radiation on water was first studied in 1913 by Duane and Scheuer [44] and the results were confirmed by Lanning and Lind after 25 years at 1938 [45]. Several chemical reactions occur in irradiated systems both indirect and direct reactions which take place homogeneously. The latter reactions are studied in details for the case of water radiolysis by  $\gamma$ -irradiation. The ultra-pure water irradiated by  $\gamma$  rays produces 11 reactive species resulted from 20 reactions, while in acidic water it produces 7 reactive species resulted from 10 reactions [46].

In ultra-pure irradiated water, there are no impurities that can scavenge radicals and prevent the tracks of radiolysis to expand. The increase of radical concentrations leads to a homogeneous radical-radical combination ( $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_2$ ). The excess radicals also react with the products of ( $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_2$ ) in homogeneous reactions. All of these phenomena must be considered in polymerization reaction induced by gamma irradiation. Two cases have been established in the polymerization induced by ionizing radiation, namely, crosslinking and degradation. In the polymerization system that starts with crosslinkable monomer or polymer, the system will consume radicals ( $\cdot\text{H}$  and  $\cdot\text{OH}$ ) in polymerization reaction and limits build-up of ( $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_2$ ). While in the system that tends to degradable polymer such as natural polymer, the yield of radicals' duplicates and the breaks of C–C bonds increase and tend to enhance the polymer degradation by formation of a net of oxidative species such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ , and  $\text{O}_3$ .

It is interesting to investigate the proposed mechanism of the polymerization reaction induced by gamma irradiation in an aqueous system. This section, presents the steps of common three polymerization mechanisms (radical, cationic, and anionic). It should be observed that polymerization reaction randomly forms covalent bonds cross the monomer and short chains in space.



**Figure 8.** The close system of water radiolysis induced by gamma rays.

A background of water radiolysis is expected to fluctuate a detection of the majority of primary products of water ions formation (H<sub>3</sub>O<sup>+</sup>, HO<sup>-</sup>, H<sup>+</sup> ions, and e<sub>hy</sub>). A track of initial species formation is shown in **Figure 8**.

Ionization of H<sub>2</sub>O occurs as: H<sup>+</sup> ≡ H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup>. The question here is how this really happened in ultra-pure water solution that contains water molecules? The oxygen molecule with two lone pair of electrons and two hydrogen atoms react with another water molecule under the impact of high power electromagnetic wave (ionizing radiation). The H<sup>+</sup> atom interacts with H<sub>2</sub>O to form H<sub>3</sub>O<sup>+</sup> and <sup>-</sup>OH. This structure (H<sub>3</sub>O<sup>+</sup>) is to great extent, similar to H<sup>+</sup>. The production of hydrated electron (e<sub>hy</sub>) was detected surrounded with opposite charge of water molecules. This (e<sub>hy</sub>) hits one water molecule to produce two radicals (•H and •OH) leaves the surrounded water molecules as (H<sub>2</sub>O<sup>+</sup>). After finishing the exposure to ionizing radiation, the water molecule returns to the initial state. The equations of radical production by water ionization by (e<sub>hy</sub>) are as follows:

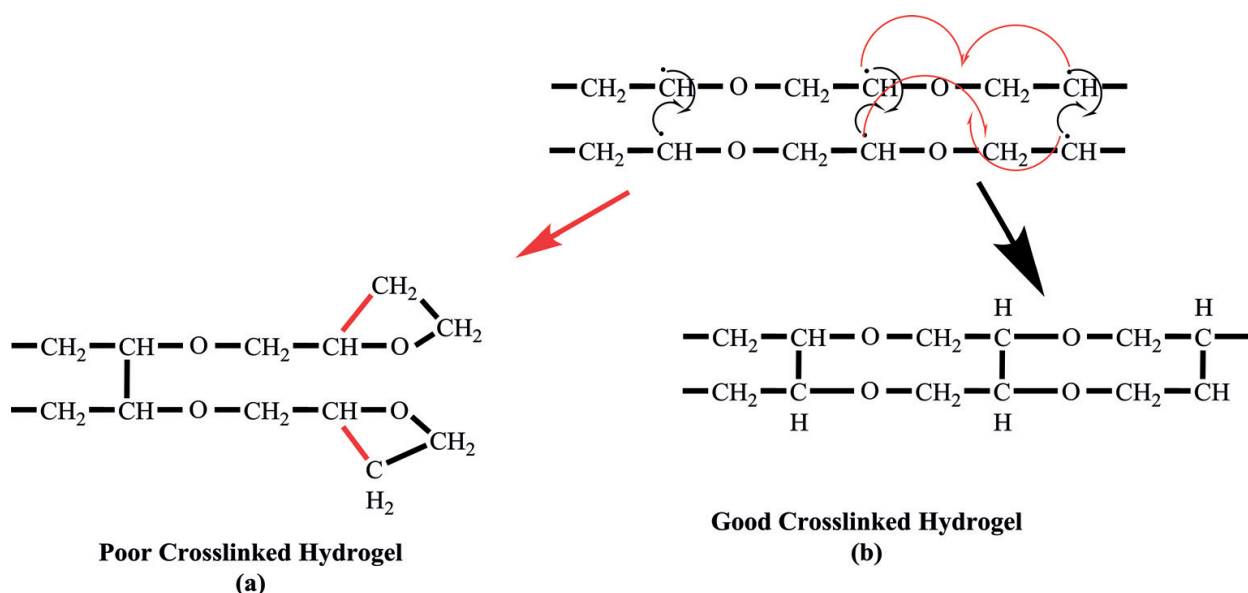


The polymerization reactions depend on several parameters: (1) chemical structure of the polymer (e.g., monomer containing aromatic rings has a much greater resistance to radiation crosslinking rather than the aliphatic monomer), (2) pH and temperature of the polymerization system, (3) kind and composition of the appropriate solvent, and (4) exposure time. The control of all of these parameters facilitates the modification of polymers by radiation

techniques. Polymerization reactions are generally classified as follows: (1) predominantly undergoing crosslinking that gives hydrogel when the polymer has hydrophilic character, (2) grafted film, (3) dimerization, and (4) oligomerization.

### 5.1. Radical polymerization induced by gamma irradiation

Radical initiation is an easy and a suitable method for the synthesis of hydrogels. When vinyl monomers are exposed to ionizing radiation in aqueous media (e.g., water), the radiolysis of water leads to formation of radicals that are responsible for initiating the polymerization reactions. In the propagation steps, the rapid recombination of two monomers takes place [47–49]. **Figure 9** shows the proposed mechanism of ionizing radiation-induced hydrogel formation. An example for this is hydrophilic crosslinked hydrogel. When the irradiated polymer and/or monomer is dissolved in aqueous solution, reactive radicals on C<sup>•</sup> atom are formed [50]. The main reactive species generated in water by irradiation are hydroxyl radicals <sup>•</sup>OH, hydrated electrons (*e<sub>hy</sub>*), and hydrogen radicals <sup>•</sup>H. The hydrated electron (*e<sub>hy</sub>*) reacts with water molecules to produce <sup>•</sup>OH and <sup>•</sup>H radicals (**Figure 1**). The direct action of *e<sub>hy</sub>* is very weak [51]. However, two <sup>•</sup>H radicals combine fast to form H<sub>2</sub> gas. **Figure 9** demonstrates the proposed mechanism of PEO (poly ethylene oxide) radical polymerization. The main reactive species (<sup>•</sup>OH radical) are responsible for the polymerization process. In general, the number of radicals generated in water is higher than that in polymer and/or monomer itself. Therefore, the description in **Figure 9** below will only refer to the indirect mechanism. Hydroxyl (<sup>•</sup>OH)/abstract hydrogen atoms from C–H in polymer molecules leads to form macroradical (C<sup>•</sup>). Thus, macroradical (polymer radicals) causes 3D crosslinked polymer. The rate constant of the polymerization reactions is proportional to the number of radical's production. Details are shown in **Figure 9** for only polyethylene oxide, all the hydrogen atoms are equivalent in the polymer molecule, so that the only one type of macroradicals C<sup>•</sup> can be

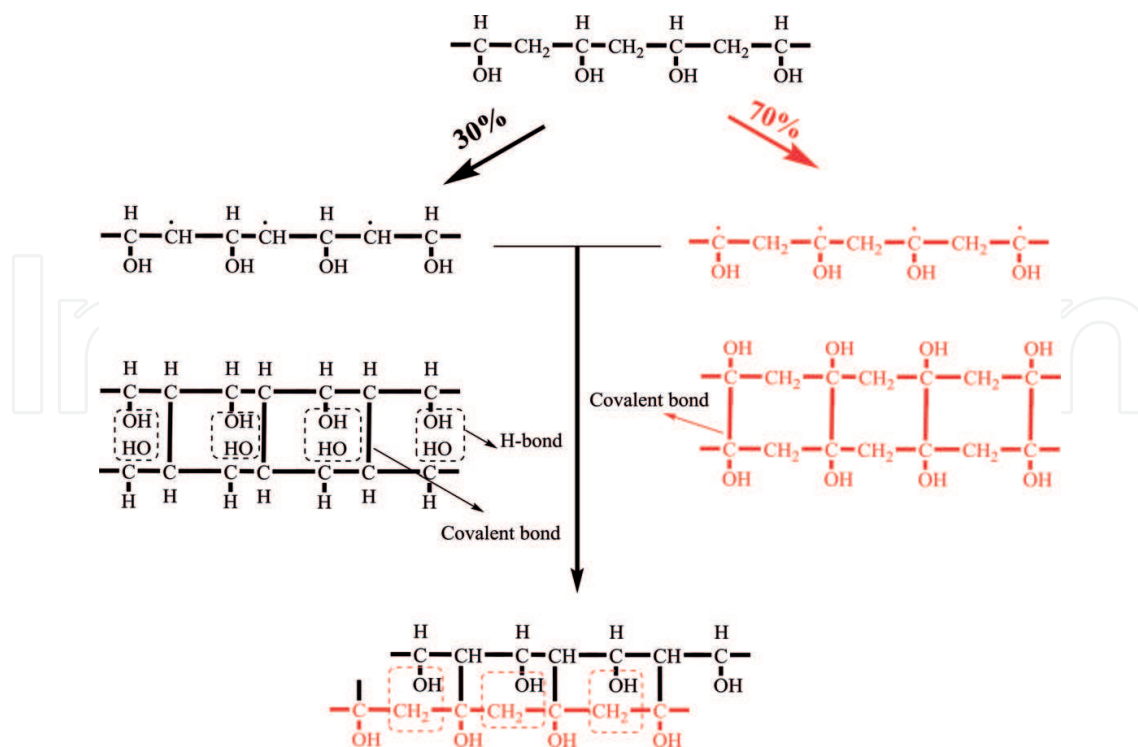


**Figure 9.** Proposed macroradicals formation induced by ionizing irradiation of water-soluble PEO in aqueous solution.



formed by  $\cdot\text{OH}$  radicals abstraction of hydrogen. While in non-equivalent H atoms positions in polymer backbone, hydroxyl radical abstract hydrogen atoms from various attitudes (randomly) lead to the formation of different kinds of macroradicals of different polymer structure.

As seen in **Figure 9**, macroradicals may undergo *intra*-molecular crosslinking giving PEO hydrogel network with randomly covalent bonds beside H bonds. The inter-molecular crosslinking is the most important reaction by “recombination” of macroradicals localized on two different chains, at this condition, the yield of crosslinked hydrogel will increase [52] (**Figure 9b**). Furthermore, inter-molecular “disproportionation” involves either linked radical or scission in the same chain. This process does not lead to hydrogel formation [53] (**Figure 9a**). There is a competition between *inter*- and *intra*-molecular crosslinking fully recognized in using ionizing radiation. Energetic photon could increase the yield of inter-molecular crosslinks (Gx), defined as the number of crosslinks formed in the system upon absorption of 1 J of ionizing radiation energy [54]. So the formation of hydrogel network depends on the energy of interchain bonds formation. The radicals combine by various ways that can be estimated in a number of routes. **Figure 10** presents various proposed routes of crosslinked formation of PVA. As illustrated in the figure, the hydrogen bond formation between chains increases the chance of polymerization mechanism to undergo intra-molecular “recombination” crosslinking rather than inter-molecular “disproportionation.” However, in the case of oxygen gas, “disproportionation” reactions will be predominantly leading to the formation of carbonyl groups. In the presence of oxygen, the PVA radicals are converted into the corresponding ( $\text{HOO}\cdot$ ) peroxy radicals leading to strand breakage [55]. It is well-known that the hydrogel formation is of high yields in oxygen-free systems.



**Figure 10.** Proposed macroradicals formation induced by ionizing irradiation of water-soluble PVA in aqueous solution.

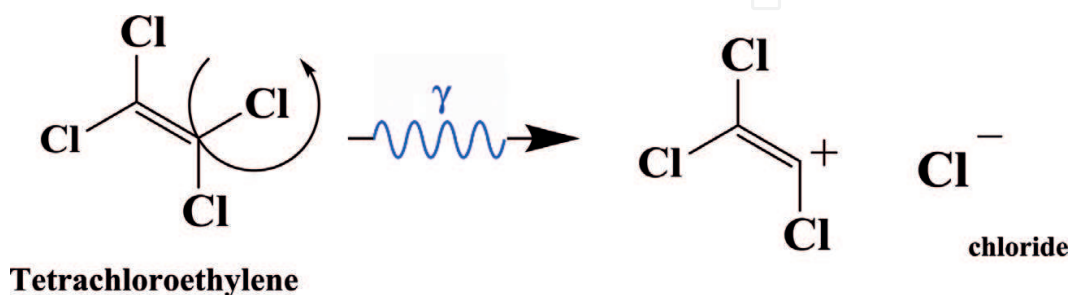
## 5.2. Ionic polymerization: anionic and cationic polymerization

Cationic and anionic polymerization induced by ionizing radiation are more complicated than radical polymerization mechanism, where cationic and anionic polymerization require some conditions and additives that act as Lewis acid and base, respectively. Gamma irradiation is very useful to obtain these additives by solvent radiolysis. Before formulating the main steps of the ionic polymerization mechanisms in radiation initiation, this section will consider the main concepts forcing an ionizing radiation-induced ionic polymerization. First, the nature of chemical structure of monomers, e.g., for cationic mechanism is vinyl ethers, isobutylene,  $\beta$ -pinene, and cyclopentadiene, and for anionic mechanism is vinylidene cyanide and nitroethylene. Second, it is necessary to use the radiation tool for formation and stabilization of  $C^+$  (*Carbonium*) in cationic and  $C^-$  (*Carbanion*) in anionic mechanisms. Third, choosing appropriate halogenated solvents for cationic polymerization, e.g., methylene chloride, ethyl chloride, tetrafluoromethane, difluorodichloromethane, perchloroethylene, etc. These solvents generally undergo radiolysis to yield Lewis acid (electron acceptor) from a Lewis base (polymer) and to form “*adduct*.” Solvent for anionic polymerization, e.g., triethylamine, dimethyl formamide, tetrahydrofuran, isopropylamine, ethylpropyl ketone, acetone, pyridine, etc. These solvents that generally undergo radiolysis to yield Lewis base (electron donating) are suitable for anionic mechanism.

Some compounds such as solid additives, catalyze the radiation-induced cationic polymerization, e.g., calcium, zinc, silica gel, and magnesium oxides [56, 57]. Even the monomer can be polymerized by combining the two mechanisms (radical/anionic or radical/cationic), then by changing the conditions (temperature and solvent).

### 5.2.1. Cationic polymerization

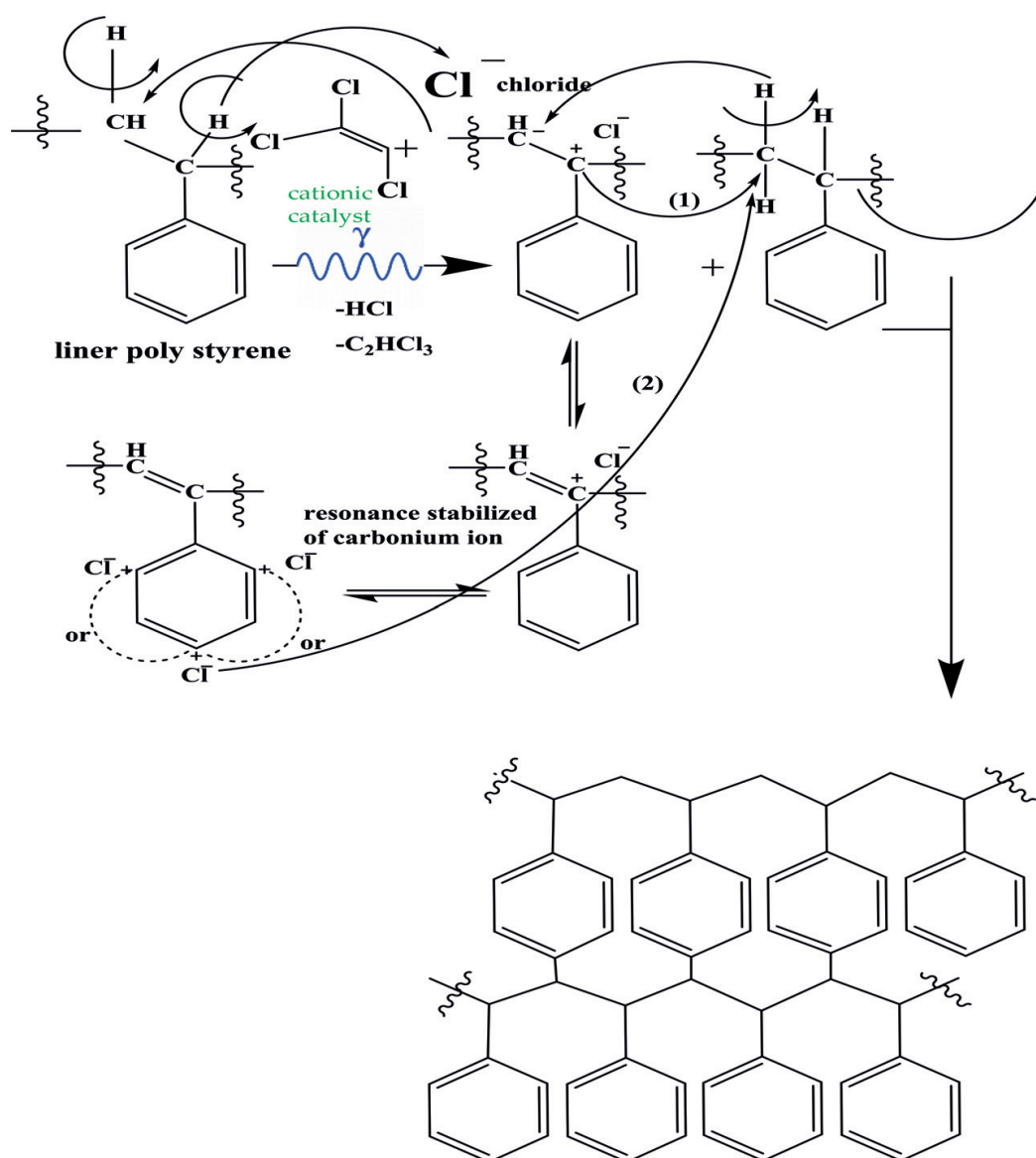
The rate of polymerization by cationic mechanism depends on the stability of carbonium ions in the macromolecules. This can be achieved if the center of the charged ion is strongly solvated by opposite charge and the distance between solvated ions is far. For the carbonium ion to be sufficiently stable and have enough lifetimes, it is preferred to choose a monomer that has a sufficient nucleophilic character. Examples of active monomers that can undergo cationic polymerization by gamma radiation are styrene monomer. In this monomer, the combination of a carbonium with an electron donating (Lewis acid) leads to



**Figure 11.** The essential step is the formation of Lewis acid by solvent radiolysis.

cationic polymerization reaction. **Figure 11** shows the essential step of the formation of Lewis acid by solvent radiolysis. For that tetrachloroethylene, a chlorinated hydrocarbon solvent, could be used as effective reaction media to promote the cationic polymerization of styrene [58].

The gamma radiolysis ( $\gamma$ -rays) of tetrachloroethylene liberates: (i) chloride ions ( $\text{Cl}^-$ ), (ii) carbonium species ( $\text{C}^+$ ) that act as Lewis acid species [59], and/or (iii) combined cation radical species ( $\text{C}^{+\bullet}$ ) [60–62], which can induce PS linear chain recombination (crosslinking). The proposed mechanism, illustrated in **Figure 12**, of radiation-induced cationic polymerization of linear polystyrene in tetrachloroethylene gave rather good reproducibility and shows a good agreement with the results of Ueno et al. [63]. Also, in the polymerization of styrene in methylene chloride, Tsuda [64] has suggested that hydrogen chloride produced by the irradiation of chlorinated hydrocarbons causing initiation of cationic polymerization of styrene. It is



**Figure 12.** The proposed mechanism of styrene radical polymerization induced by gamma irradiation.

well-known that in chlorinated solvent, the polymerization of styrene proceeds well by cationic polymerization. This proposed mechanism is in a good agreement with studies carried out by Sigwalt and Moreau [65]. As shown in **Figure 12**, the initiation starts by the formation of  $\text{Cl}^-$  due to solvent radiolysis which is released as  $\text{HCl}$  giving a carbon cation on styrene units. Propagation step is formed by head-to-tail addition in carbocation polymerization.  $\beta$ -Hydrogen atoms of the propagating carbonium cation are quite acidic, owing to the delocalization of the positive charge [66] belonging to the phenyl ring. The transfer of positive charge in the phenyl ring gives a chance of addition on the phenyl ring causing the formation of 3D crosslinked polymer. Still cationic polymerization may be one of the most challenging areas of future research [67]. The final structure as seen in an ideal shape (head-to-tail), sometimes, the propagating chain may rearrange randomly.

## 6. Advantages of ionizing radiation-induced polymerization

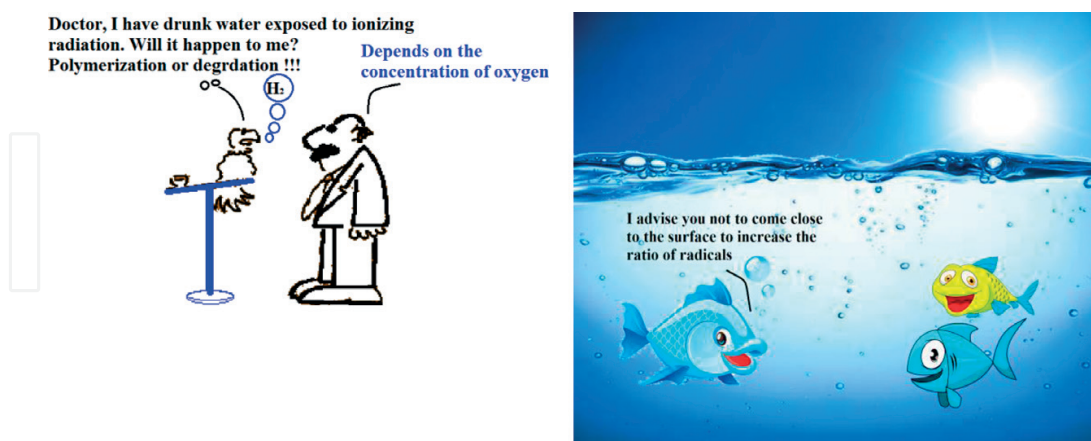
The advantages are:

1. Easy process of polymerizing a wide range of monomers which are resistant to polymerization reaction by conventional methods [68].
2. Very safe, in case of polymerization involving hazardous compounds (e.g., Organo chlorine) that can be decomposed by radiation [69, 70].
3. Polymerization reaction in the solid state could be carried out [71, 72].
4. Increased purity of polymer obtained without by product; while in conventional methods, it needs complicated purification steps [73, 74].

## 7. Concluding remarks

This chapter presents a very brief introduction of the interactions between high energy photons with water molecules, and the subsequent physico-chemical stage of water radiolysis based on previous literatures. Some proposed mechanisms in radiation polymerization were also outlined in this chapter. The main reactive species ( $(e_{hy})$  hydrated electron,  $\bullet\text{OH}$  radicals, and  $\text{H}^\bullet$  radicals) generated from water radiolysis are presented. The ionized species of water molecules involving them are ultrafast, occurring on femtosecond. The reason to focus on water radiolysis is the reactivity of radicals and hydrated electron, which are the initiators of polymerization reactions. Irradiation can be very useful in the processing of polymer blends, which often undergo physical phase separation of components due to incompatibility of materials. In a number of blend systems, irradiation has been used to induce crosslinking of one or more of the components and/or formation of crosslinking between the different phases, resulting in improvement of physical properties.

## 8. Image gently advocates on the safety of radiation uses



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