Chapter 9

# RADIATION-INDUCED GRAFTING

**Marta Walo**
*Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland*

## 1. INTRODUCTION

For many decades, radiation-induced grafting has been a way to functionalize the surfaces of existing polymer forms [1] so that they can be used in a variety of applications, such as biomedical, environmental and industrial uses [2]. Radiation grafting changes the surface of polymeric materials by chemically bonding polar or non-polar monomers having functional groups, such as –COOH, –OR, –OH, $–NH_2$, $–SO_3H$, –R and their derivatives, to affect surface properties without influence on the bulk material.

Ultraviolet radiation (UV), gamma rays and electron beam (EB) radiation can be used to generate active sites (free radicals) on a polymeric surface which can then react with vinyl monomers to form a graft copolymer.

A graft copolymer can be defined as branched copolymer composed of a main chain of a polymer backbone onto which side chain grafts (branches) are covalently attached. The polymer backbone may be a homopolymer or copolymer and differs in chemical structure and composition from the graft material [3].

A simplified structure of a graft copolymer composed of a backbone and graft side chains is presented in Fig.1.

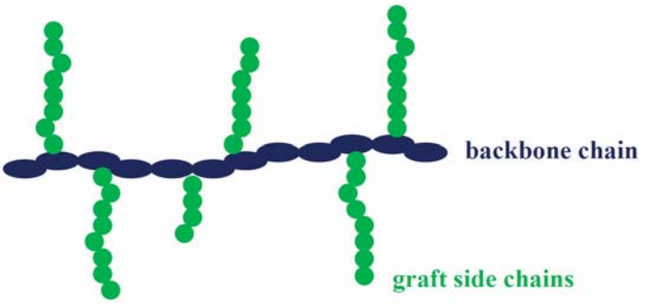



Fig.1. Simplified structure of graft copolymer.

The modification of polymer surfaces can be achieved by conventional grafting or by reversible addition-fragmentation chain transfer (RAFT)-mediated grafting methods. With conventional grafting methods, the molecular weight and polydispersity of grafted chains cannot be controlled. As a result the surface is covered with grafted chains of different lengths, as shown in Fig.2A. To obtain graft copolymers with predetermined graft molecular weight and very narrow chain length distribution, a novel method using a controlled radical polymerization (CRP) of reversible addition-fragmentation chain transfer polymerization grafting has been used [4, 5], as shown in Fig.2B.

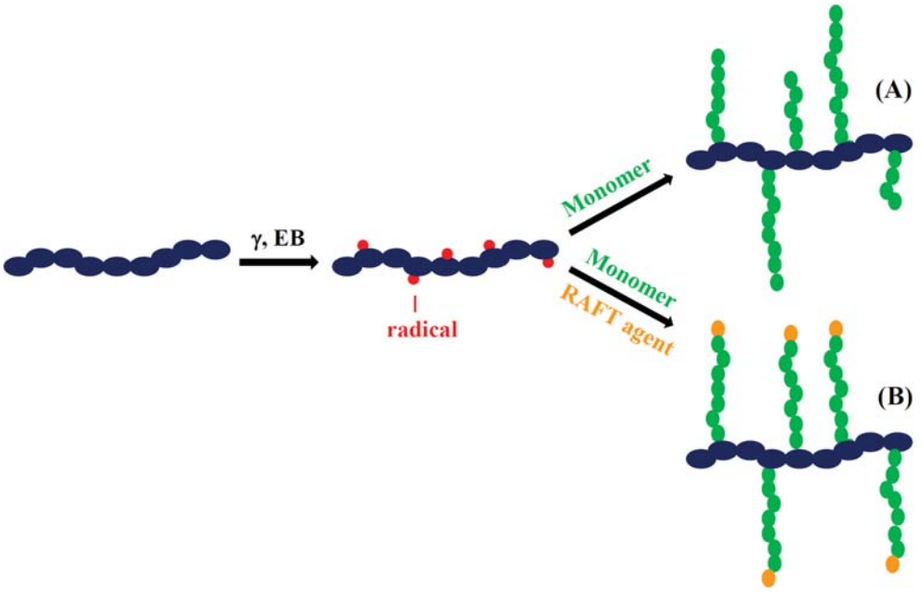



Fig.2. Radiation-induced grafting using (A) conventional and (B) RAFT-mediated polymerization initiated by ionizing radiation.

Surface modification by the conventional grafting method has several general advantages such as [6, 7]:

- It is a simple, relatively clean and repeatable process.
- Any polymer can be the modified surface which can be in the form of film, membrane, fiber, fabric, or powder and most free radical polymerizable monomers such as styrene, methacrylamides, acrylamides, methacrylates, acrylates, acrylonitrile, vinyl acetates, vinyl chlorides, acrylic acid, *N*-vinylpyrrolidone, can be grafted.
- The graft copolymer is very pure, with no initiator or related impurities remaining on the modified surface.
- The degree of grafting may be controlled by changes the reaction conditions (*e.g.* monomer concentration, reaction temperature, atmosphere, type of solvent, addition of suppressor of homopolymerization, addition of acid)

and the radiation exposure parameters (type of radiation, dose rate, irradiation time, dose).

- In comparison with chemical methods, radiation-induced grafting does not require heating of the system to initiate the graft polymerization reaction so that the polymer structure of the substrate is not changed and temperature sensitive monomers can be grafted.

Key strengths of RAFT-mediated grafting are [8-10]:

- The ability to control the molecular weight of grafted chains to have a narrow molecular weight distribution.
- Grafting can be done with a wide range of functional monomers: methacrylates, acrylates, acrylamides, acrylonitrile, styrene, dienes and vinyl monomers.
- Well-defined polymers with different topologies and molecular architecture can be synthesized (*e.g.* gradient, block, star, comb, or hyperbranched co-polymers).
- Macromolecule chain extension through the addition of other monomers is possible which can lead to the formation of block copolymers.

From an application perspective, graft surface modification of polymeric materials has many uses [2, 11, 12]:

- to improve or reduce polymer hydrophicility and/or hydrophobicity;
- to modify blood compatability of medical devices;
- to influence cell adhesion and growth on scaffolds used in tissue engineering;
- to improve the lubricity of implants;
- to facilitate the design of membranes used in batteries, fuel cells, chromatography;
- to prepare metal ion adsorbents.

## 2. METHODS OF RADIATION-INDUCED GRAFTING

Radiation-induced grafting can be performed by two major methods: a mutual or simultaneous technique or a pre-irradiation technique [13]. Typically grafting is performed in solution or emulsion where the reaction medium is usually water with a small amount of surfactant (*e.g.* Tween 20) [2, 14].

The selection of either method depends on the polymer to be modified, the reactivity of monomer and the radiation source.

The pre-irradiation technique is particularly useful if access to a gamma source or an accelerator is limited. A polymer surface may be pre-irradiated (in air or in vacuum) and then even after some storage time can be used to initiate the graft polymerization.

## 2.1. MUTUAL OR SIMULTANEOUS METHOD

In this method, the polymeric material is immersed in the monomer solution (or in pure monomer) and exposed to ionizing radiation. Irradiation can be performed in air or in inert atmosphere (*e.g.* nitrogen) usually using gamma sources. This is the simplest and a common method chosen for polymeric material surface modification and is suitable for substrates that are sensitive to radiation.

The mechanism for this process is given in the following sequence of equations:

$$PH \xrightarrow{\gamma} P^{\bullet} + H^{\bullet} \quad (1)$$

$$P^{\bullet} + M \rightarrow PM^{\bullet} \quad (2)$$

$$PM^{\bullet} + nM \rightarrow PM_{n+1}^{\bullet} \quad (3)$$

Ionizing radiation forms in the polymeric substrate active sites, PH (Eq. (1)). The primary radicals of polymer backbone, $P^{\bullet}$, react with a molecule of the monomer, M, initiating the graft polymerization (Eq. (2)). After the initiation step, the propagation step takes place and the graft chain grows onto the polymer backbone and continues to occur after successive joining of the monomer to the macroradical centers (Eq. (3)).

Since the grafting mixture is exposed to ionizing radiation, active sites can be formed in polymer backbone, in the monomer and in the solvent. Side reactions can also take place which limit the degree of grafting due to the consumption of monomer by radicals other than in the polymeric backbone. In the mutual method, there is, in parallel with the grafting reaction, homopolymerization of monomers leading to the formation of a homopolymer (Eqs. (4)-(6)) [13].

$$M \xrightarrow{\gamma} M^{\bullet} \quad (4)$$

$$M^{\bullet} + nM \rightarrow M_{n+1}^{\bullet} \quad (5)$$

$$M_{n+1}^{\bullet} + M_m^{\bullet} \rightarrow M_{n+m+1}^{\bullet} \quad (6)$$

Homopolymerization suppresses the degree of grafting by increasing the viscosity when the homopolymer formed is soluble in the monomer or solvent used in grafting. The diffusion of monomer to the reactive sites on the polymer backbone becomes difficult. Moreover, due to the consumption of monomer in homopolymer formation, less monomer is available for the grafting reaction [15].

To reduce the formation of homopolymer, inorganic salts can be added to the grafting system when water or other media are the solvents.

## 2.2. PRE-IRRADIATION METHOD

The pre-irradiation method involves a sequence of the following steps:

- The polymer substrate is irradiated in air or in an inert atmosphere to generate active radical sites.
- Monomer reaction is initiated with the irradiated polymeric substrate.

- Heating is applied to support the propagation of the reaction when peroxides are involved.

$$PH \xrightarrow{\gamma} P^{\bullet} + H^{\bullet} \quad (7)$$

$$P^{\bullet} + O_2 \rightarrow POO^{\bullet} \quad (8)$$

$$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet} \quad (9)$$

$$POOH \xrightarrow{\Delta} PO^{\bullet} + {}^{\bullet}OH \quad (10)$$

$$PO^{\bullet} + M \rightarrow POM^{\bullet} \quad (11)$$

$$POM^{\bullet} + nM \rightarrow POM_{n+1}{}^{\bullet} \quad (12)$$

With polymeric substrates exposed to ionizing radiation in air, peroxide radicals are generated due to oxidation of alkyl radicals (Eqs. (7)-(8)). These products when in contact with the polymeric substrate convert into the hydroperoxides (Eq. (9)). The hydroperoxides decompose under heating to alkoxy radicals (Eq. (10)). Radicals obtained this way are capable of initiating the graft polymerization in the presence of monomers (Eqs. (11)-(12)).

In the case of this pre-irradiation method in the presence of oxygen, it is possible to carry out the graft modification of a substrate for some time after irradiation, due to the stability of the hydroperoxides, especially when the irradiated substrate is stored at 0°C or lower.

Another variation of the pre-irradiation method is to use non-oxidized reactive radical species generated by radiation. In this case, in order to obtain a high concentration of radicals, the polymer should be irradiated at high dose rates, *e.g.* by high energy electrons, under an inert atmosphere or in vacuum and the grafting carried out immediately after the irradiation exposure.

An important advantage of the pre-irradiation method is that less homopolymer is formed. However, hydroperoxide species can be formed by thermal decomposition to produce $^{\bullet}OH$ radicals which can be involved in homopolymerization [16].

An important parameter that should be taken into account before planning a grafting process using the mutual or simultaneous method is to compare the radiation chemical yield G-value of polymeric substrate and of the monomer. (The G-value is defined as the number of product molecules formed or initial molecules changed for every 100 eV of energy absorbed; the SI unit of radiation--chemical yield is μmol/J, 1 molecule/100 eV = $1.036 \times 10^{-7}$ mol/J = 0.1036 μmol/J). The reaction proceeds in the favor of graft polymerization when $G(R_P^{\bullet})$ of the irradiated polymer is much greater than for the monomer. In contrast to homopolymerization which is prevailed when $G(R_M^{\bullet})$ of the monomer is higher than for the polymeric substrate [13]. G-values for various polymers may be found in the literature [14, 17].

In pre-irradiation technique, monomer is not exposed to radiation. Radicals are generated only on the polymeric substrate. Therefore, this method is relatively free from homopolymer formation.

The most significant differences between the mutual and the pre-irradiation methods are summarized in Table 1 [13, 14].

Table 1. Comparison of mutual and pre-irradiation methods of radiation-induced grafting [13, 14].

| Parameter | Mutual method | Pre-irradiation method |
|---|---|---|
| Type of radiation | Gamma, EB | EB, gamma |
| Absorbed dose | Low (10 kGy or less) | High (100 kGy and more) |
| Dose rate | Low [kGy/h] | High [kGy/s] |
| Irradiation time | Long [h] | Short [min] or [s] |
| Atmosphere | Inert gas | Air/inert gas/vacuum |
| Side reactions: homopolymerization | High | Low |
| Temperature | Ambient | Irradiation: ambient/low temperature, graft polymerization: high (peroxide decomposition) |

## 2.3. RAFT-MEDIATED GRAFTING

Research has been carried out in the field of controlled radical polymerization, *i.e.* atom transfer radical polymerization (ATRP) [18, 19], nitroxide mediated polymerization (NMP) [20, 21] and reversible addition-fragmentation chain transfer (RAFT) polymerization [22, 23]. Each of these methods enables the synthesis of well-defined graft copolymers with narrow molecular weight distribution (polydispersity) of the grafted chains. However, only the RAFT polymerization process can be initiated by gamma or electron beam radiation. Radiation generates active sites (free radicals) in polymeric substrate which can further react with monomers in the presence of a RAFT agent to form grafted coatings. In other methods, heat or a photoinitiator must be used to generate a free radical on an initiator and then the active center is transferred to the monomer/polymer backbone.

RAFT-mediated grafting initiated by ionizing radiation can be performed by the mutual and the pre-irradiation methods as well. The difference compared to conventional method of grafting lies in the presence of the RAFT agent in the grafting system. RAFT agents are commercially available thiocarbonylthio compounds [ZC(=S)SR] such as dithioesters, dithiocarbamates, trithiocarbonates, xanthates [24]. The general structure of a RAFT agent is presented in Fig.3.

Z group modifies addition and fragmentation rates in polymerization whereas R group can be detached easily to form $R^{\bullet}$ (must also be able to reinitiate polymerization) [24]. The success of RAFT-mediated grafting depends on appropriate selection of RAFT agent for monomer. In literature, data on diverse RAFT agents working appropriately with various monomers is available (*e.g.* [24-27]).

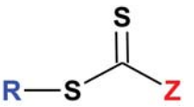
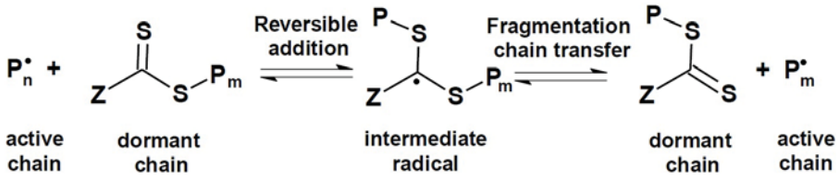



Fig.3. The general structure of RAFT agent [24].

The key step in RAFT polymerization is chain equilibrium reaction between the active radicals and dormant propagating polymer chains (Eq. (13)). A rapid equilibrium between the active propagating radicals ($P_n^{\bullet}$ and $P_m^{\bullet}$) and the dormant thiocarbonyl thio-capped chains provides equal probability for all chains grow and allows the synthesis of low polydispersity polymers [9, 10, 28, 29].




(13)

To obtain graft copolymer with predetermined molecular weight, $M_n$, preparation of a solution with appropriate RAFT agent and monomer concentration is necessary.

The theoretical number average molecular weight, $M_n$, of grafted polymer chains can be calculated according to the Eq. (14) [30]:

$$M_n = M_{RAFT} + \frac{n\,M}{n_{RAFT}}k \tag{14}$$

where: $M_{RAFT}$ – molecular weight of the RAFT agent, n – number of moles of the monomer initially present in the system, $n_{RAFT}$ – number of moles of RAFT agent, M – molecular weight of monomer, k – conversion.

In RAFT-mediated grafting, the determination of the molecular weight of grafted chains onto a polymer surface is done by size exclusion chromatography (SEC). The assumption is made that in the RAFT polymerization process, the graft chain growth is in a dynamic equilibrium with the free polymer chains in solution. Therefore, analysis of the free polymer precipitated from the solution provides information on the molecular weight and polydispersity of grafted polymer [31].

## 3. PARAMETERS AFFECTING THE RADIATION-INDUCED GRAFTING

The degree of grafting depends on many factors, such as the type of polymer and monomer, monomer concentration, type of radiation, temperature, reaction

atmosphere, concentration of homopolymerization suppressor and type of solvent [13, 32, 33]. Therefore, the efficiency of the process can be controlled by the selection of these reaction parameters.

The following discusses the factors that control the radiation-induced grafting.

## 3.1. TYPE OF POLYMER

Radiation-induced grafting can be used for surface modification of all commercially available synthetic and natural polymers. Materials for grafting have to meet certain requirements since the chemical structure and morphology significantly affect the degree of grafting and the final properties of grafted materials. For radiation degradable polymers, high irradiation dose used usually in the pre-irradiation method is not recommended. In contrast, radiation resistant materials may be modified by both grafting methods.

The degree of grafting strongly depends on the amount of radicals in the irradiated polymeric substrate. Electron paramagnetic resonance (EPR) spectroscopy can be used to monitor the radicals in the sample and to identify and track the conversion of radiation generated paramagnetic species to their subsequent products. This method allows for the comparison of radical amounts in polymers and is helpful in predicting their behavior in radiation-induced grafting. For example, for polystyrene (PS), polypropylene (PP) and polyethylene (PE) irradiated at the same dose by ionizing radiation, the concentration of radicals stable at room temperature and the radiation yields of radicals ($G(R_p^{\bullet})$) is in following order: PS < PP < PE. Under comparable conditions, the same relationship was found for the degree of radiation-induced grafting of acrylic acid on these polymers using the mutual method [34].

Among many polymers, whose surfaces were modified by radiation grafting, the largest group are polyolefins: polyethylene and polypropylene, often in the form of filters, films, brushes or powders (*e.g.* [35-40]). However, there are many examples of surface modification which were successfully carried out onto polyamide (PA) (*e.g.* [41, 42]), poly(ethylene terephthalate) (PET) (*e.g.* [43, 44]), polyurethane (PUR) (*e.g.* [45, 46]), silicon (*e.g.* [47, 48]), cellulose (*e.g.* [49, 50]), poly(tertafluoroethylene) (PTFE) (*e.g.* [51, 52]) or poly(vinylidene fluoride) (PVDF) (*e.g.* [53, 54]).

## 3.2. TYPE OF MONOMER

The degree of radiation grafting (gravimetrically determined by the percentage of mass increase) is a function of the reactivity of the consumed monomer. Monomer reactivity depends on the polarity, the energy of bonds,

and the chemical structure, *etc*. The degree of grafting is also influenced by the monomer concentration and the type of solvent used for grafting. The reactivity of a monomer depends not only on the kinetics of the process but also on the diffusion of the reactant to the polymer surface, which affects the rate and efficiency of grafting [13]. Generally, with increasing monomer concentration, the degree of grafting increases. However, using too high concentration of monomer may enhance homopolymerization and decrease the degree of grafting [55]. For every grafting system, the monomer concentration should be adjusted to avoid this undesired homopolymerization of the monomer.

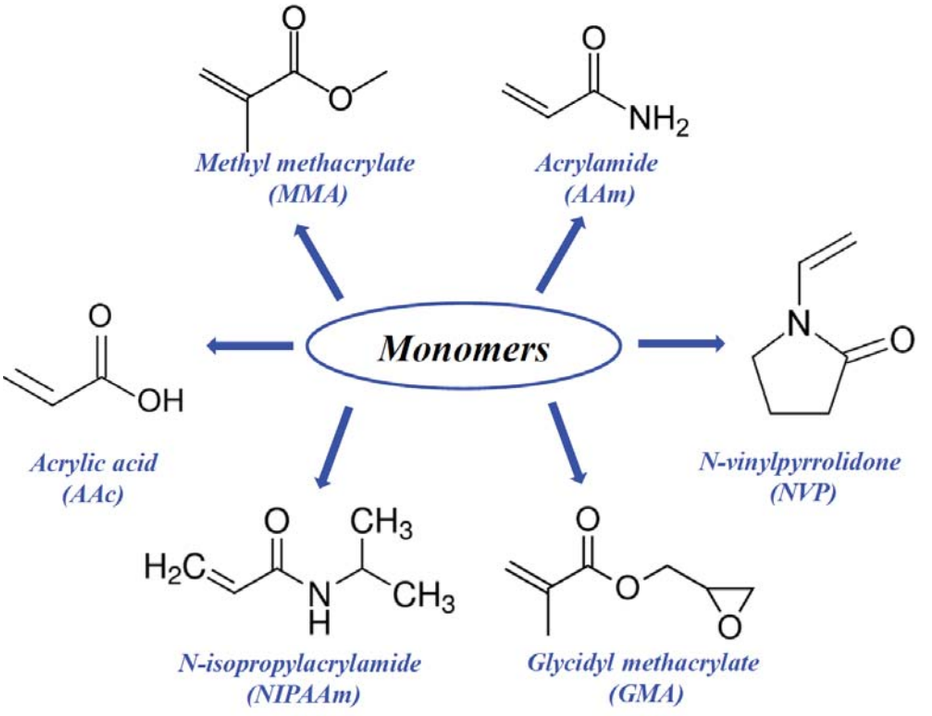



Fig.4. Chemical structure of the most frequently used monomers in radiation-induced grafting.

The most frequently used monomers in graft polymerization are vinyl monomers such as: methyl methacrylate (MMA), glycidyl methacrylate (GMA), acrylamide (AAm), acrylic acid (AAc), *N*-vinylpyrrolidone (NVP), *N*-isopropylacrylamide (NIPAAm).

The chemical structure of some of the monomers used in radiation-induced grafting is presented in Fig.4.

### 3.3. TYPE OF SOLVENT

Depending on the solvent, its properties and behavior during the grafting process, the degree of grafting for the same monomer, dose, atmosphere reaction, temperature, *etc.* can differ significantly. The type of solvent affects not only the grafting efficiency but also the homogeneity of the grafted chains, which can be obtained using good swelling solvents [13]. Water and alcohols are widely used for grafting of hydrophilic monomers. However for every grafting system, the solvent should be selected experimentally, especially for the RAFT-mediated grafting processes.

### 3.4. TYPE OF RADIATION (DOSE, DOSE RATE)

Radiation-induced grafting may be carried out using gamma radiation ($^{60}$Co, $^{137}$Cs) and EB radiation as well. Grafting by the mutual method is usually performed using a gamma source, as compared to the pre-irradiation method, where the preferred radiation is an electron beam [13, 56]. The main difference in these two types of radiation is the dose rate defined as dose delivered in a specific unit of time. In the case of isotope sources, the dose rate is relatively low (kGy/h), while for electron beams it is high (kGy/s). Consequently, the irradiation time in a gamma source is much longer (h) than when using a high energy electron beam (min or s). This factor significantly affects the degree of grafting. The higher the dose, the greater the amount of radicals are generated in the polymeric material, which has a direct impact on the degree of grafting. The dose rate effects the concentration and lifetime of radicals, the oxidation and time after that the termination of the growth graft chains occurs. In mutual or simultaneous grafting, for the same dose, increase in the dose rate results in lower efficiency of grafting, because the high concentration of radicals increases their recombination leading to a rapid termination process and to more homopolymerization.

### 3.5. TEMPERATURE

Irradiation temperature and grafting temperature are important parameters influencing the process of radiation-induced grafting.

#### 3.5.1. Irradiation temperature

In the pre-irradiation method, the polymeric substrate might be irradiated at sub-ambient temperatures (0°C and lower) in order to restrain the combination of radicals generated during irradiation. Then, even after storage, the trapped radicals may be used to initiate graft polymerization.

During mutual grafting, irradiation temperature also affects the degree of grafting. If irradiation is performed above the glass transition temperature of polymer, $T_g$, due to enhanced mobility of chain segments, the active sites can migrate to the surface increasing population of the radicals involved in grafting. On the other hand, below the $T_g$ irradiated polymers are rigid and thus monomers have access to the active centers produced *via* irradiation on the external layer of material. Thus, selection of irradiation temperature determines the final effect of the grafting process. Thermal conditions influence also diffusion of monomers in solution.

### 3.5.2. Grafting temperature

In general, the rate of grafting increases with the increase of the reaction temperature. The grafting process is also controlled by diffusion, so this effect could be significant. In the solution there are many competing reactions which reduce the concentration of radicals and accelerate their termination. Typically, increasing the temperature is to (i) enhance the process of grafting by changing the kinetics of the reaction or (ii) decompose peroxides leading to the formation of active centers that initiate monomers and chain propagation polymerization in the process.

## 3.6. ATMOSPHERE OF RADIATION GRAFTING

Radiation-induced grafting may be carried out under an inert atmosphere (*e.g.* nitrogen), in vacuum or in the presence of air. The use of an anaerobic atmosphere prevents reactions of alkyl radicals with oxygen and the formation of peroxide radicals, which in consecutive reactions convert to the stable oxidation products. The absence of oxygen reduces the radicals involved in the grafting process. The presence of oxygen can lead to oxidative degradation of the irradiated polymeric material, which impairs its physicochemical properties. Moreover, oxygenated degradation products can be toxic and can affect the biological tolerance, which is particularly undesirable in materials to be used in biomedical applications [57]. In pre-irradiation method, the irradiation can be carried out in the presence of oxygen, to form peroxides and hydroperoxides which, after thermal decomposition, initiate graft polymerization.

## 3.7. SUPRESSION OF HOMOPOLYMER FORMATION

The use of homopolymerization suppressors is an important element in the process of radiation grafting in aqueous systems. During exposure to ionizing radiation, active centers can be formed in polymeric materials and in the monomer. If the monomer concentration is high and the reactivity of the radicals is

high as well, the dominant reaction is homopolymer formation. This is undesirable since surface modification will not be achieved. Research in this field has showed reduction and, in some cases, elimination of the homopolymerization process by adding to the irradiation system a small amount of a suppressor (usually of a few millimoles). For this purpose, inorganic metal salts are used, *e.g.* iron (II) chloride ($FeCl_2$), copper (II) chloride ($CuCl_2$), copper (II) sulfate ($CuSO_4$), ammonium iron (II) sulfate ($Fe(NH_4)_2(SO_4)_2(6H_2O)$) (Mohr's salt) [13, 14]. These additives are used in aqueous solutions of monomers and after dissolving they become hydroxyl radical scavengers, reducing homopolymerization. There is a threshold concentration of these salts to prevent homopolymerization, above which there is no formation of a homopolymer. Further increasing the concentration of such an inhibitor affects very little of the degree of grafting. There are a few studies which confirm that the copper and iron salts not only inhibit the homopolymerization process, but also help to increase the efficiency of grafting. Such an effect was observed by Dworjanyn *et al.* [58] when grafting styrene onto cellulose or polyolefin substrates.

To understand the mechanism of the action of metal ions in aqueous systems, water radiolysis products are formed during irradiation (Eq. (15)). In the mutual or simultaneous grafting method, among radical products of water radiolysis there are some uncontrolled effects resulting from hydroxyl radicals that are capable of initiating homopolymer chain growth. Also, in the case of the mutual method in the presence of oxygen, hydroperoxides are formed in the polymeric substrate, and their degradation at elevated temperatures leads to the formation of active radicals $^{\bullet}OH$ (Eq. (16)). Therefore, the metal ions are added to the system to deactivate hydroxyl radicals to inactive $OH^-$ anions (Eq. (17)) [59, 60]. Metal ions play a role as hydroxyl radical scavengers.

$$H_2O \xrightarrow{\gamma,\, e^-} {}^{\bullet}OH,\ H^{\bullet},\ e^-_{aq},\ O_2,\ H_2O_2 \tag{15}$$

$$POOH \rightarrow PO^{\bullet} + {}^{\bullet}OH \tag{16}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{17}$$

In the literature [61], it was noted that in aqueous systems in which grafting process is carried out by the mutual method in the presence of $Cu^{2+}$ ions, the mechanism of suppression of the homopolymerization process can be illustrated by the following equations:

$$Cu^{2+} + {-}CH_2{-}C^{\bullet}H{-}R \rightarrow Cu^{+} + H^{+} + {-}CH{=}CH{-}R \tag{18}$$

$$Cu^{+} + H^{+} + {-}CH_2{-}C^{\bullet}H{-}R \rightarrow Cu^{2+} + {-}CH_2{-}CH_2{-}R \tag{19}$$

$$Cu^{+} + {}^{\bullet}OH \rightarrow Cu^{2+} + OH^- \tag{20}$$

$Cu^{2+}$ ions are involved directly in the deactivation of homopolymer radicals according to (Eq. (18)). $Cu^+$ ions in solution are then oxidized to $Cu^{2+}$ ions and again participate in the process of inhibiting the homopolymer chain growth (Eq. (19)). $Cu^+$ ions can also deactivate $^{\bullet}OH$ radicals as expressed by (Eq. (20)).

### 3.8. ROLE OF ADDITIVES

The addition of mineral acid (*e.g.* hydrochloric acid, sulfuric acid) to the aqueoues solution of a monomer enhances the degree of grafting [13, 62]. Under such conditions (low pH), hydrated electrons generated during water radiolysis are trapped by protons and converted into hydrogen atoms. The ability of the species to abstract hydrogen from polymeric material is higher than their pecursors, *i.e.* electrons. Therefore, the yield of radicals formed in polymeric chains incerases, which results in the enhancement of active sites initiating grafting. Also, the addition of polyfunctional monomers (*e.g.* divinyl benzene, multifunctional acrylates in amount of about 1% v/v) can accelerate the grafting process and such action is recommended when improved properties of the finished product is desired, especially in radiation-grafted fuel cell membranes [63].

## 4. CHARACTERIZATION OF RADIATION-GRAFTED COPOLYMERS

Upon completion of the graft polymerization process, prior to the characterization of grafted substrate, samples should be extracted by suitable solvents in order to remove unreacted monomers, free polymer, and additives. Then the product can be dried to a constant weight. The degree of grafting, DG (wt%) can be determined gravimetrically using the following equation:

$$DG = (W - W_0)/W_0 \times 100\% \quad (21)$$

where W and $W_0$ are the weights of the grafted and non-grafted polymer, respectively.

There are a number of analytical techniques which can be used to provide information about the polymer surface, ranging from the micron to the nanometer scale. A comparative analysis of non-grafted and grafted samples can confirm the effects of the grafting process by using several methods: attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), contact angle (CA) measurements.

Monitoring structural and morphological changes induced by radiation grafting can be performed as well as by: differential scanning calorimetry (DSC), thermogravimetry (TGA), dynamic mechanical analysis (DMA), X-ray diffraction (XRD) and others.

In case of RAFT-mediated grafting, size exclusion chromatography (SEC) is a key method to evaluate the molecular weight of grafted chains.

## REFERENCES


[1]. Chapiro, A. (1962). *Radiation chemistry of polymeric systems*. New York: John Wiley & Sons.

[2]. Nasef, M.M., & Güven, O. (2012). Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions. *Prog. Polym. Sci.*, *37*(12), 1597-1656. DOI: 10.1016/j.progpolymsci.2012.07.004.

[3]. Herman, F.M. (2007). Graft copolymers. In *Encyclopedia of polymer science and technology. Concise* (3rd ed., p. 526). New Jersey: Wiley.

[4]. Moad, G., Chong, Y.K., Postma, A., Rizzardo, E., & Thang, S.H. (2005). Advances in RAFT polymerization: The synthesis of polymers with defined end--groups. *Polymer*, *46*(19), 8458-8468. DOI: 10.1016/j.polymer.2004.12.061.

[5]. Moad, G., & Thang, S.H. (2008). Radical addition–fragmentation chemistry in polymer synthesis. *Polymer*, *49*(5), 1079-1131. DOI: 10.1016/j.polymer.2007.11.020.

[6]. Choi, J.H., Jung, C.H , Kim, D.K., & Ganesan, R. (2008). Radiation-induced grafting of inorganic particles onto polymer backbone: A new method to design polymer-based nanocomposite. *Nucl. Instrum. Meth. B*, *266*(1), 203-206. DOI: 10.1016/j.nimb.2007.11.012.

[7]. Güven, O., & Sen, M. (1991). Preparation and characterization of poly(N-vinyl 2-pyrrolidone) hydrogels. *Polymer*, *32*(13), 2491-2495. DOI: 10.1016/0032-3861 (91)90093-X.

[8]. Moad, G., Chiefari, J., Chong, Y.K., Krstina, J., Mayadunne, R.T.A., Postma, A., Rizzardo, E., & Thang, S.H. (2000). Living free radical polymerization with reversible addition – fragmentation chain transfer (the life of RAFT). *Polym. Int.*, *49*, 993-1001. DOI: 10.1002/1097-0126(200009)49:9<993::AID-PI506>3.0.CO;2-6.

[9]. Moad, G., Rizzardo, E., & Thang, S.H. (2006). Living radical polymerization by the RAFT process – A first update. *Aust. J. Chem.*, *59*(10), 669-692. DOI: 10.1071/CH06250.

[10]. Barner-Kowollik, C., Blinco, J.P., Destarac, M., Thurecht, K.J., & Perrier, S. (2012). Reversible addition fragmentation chain transfer (RAFT) polymerization: Mechanism, process and applications. In *Encyclopedia of radicals in chemistry, biology and materials* (Vol. 4, pp.1895-1929). Chichester: John Wiley & Sons, Ltd.

[11]. Ratner, B.D., & Hoffman, A.S. (2004). Physicochemical surface modification of materials used in medicine. In B.D. Ratner, A.S. Hoffman, F.J. Schoen & J.E. Lemons (Eds.), *Biomaterials science: An introduction to materials in medicine* (2nd ed., pp. 201-218). USA: Elsevier Academic Press.

[12]. Hoffman, A.S. (1995). Surface modification of polymers. *Chinese J. Polym. Sci.*, *13*(3), 195-203.

[13]. Nasef, M.M., & Hegazy, E.S.A. (2004). Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. *Prog. Polym. Sci.*, *29*(6), 499-561. DOI: 10.1016/j.progpolymsci.2004.01.003.

[14]. Makuuchi, K., & Cheng, S. (2012). *Radiation processing of polymer materials and its industrial applications* (1st ed.). USA: John Wiley & Sons, Inc.

[15]. Kumar, V., Bhardwaj, Y.K., Rawat, K.P., & Sabharwal, S. (2005). Radiation-induced grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton

fabric and study of its anti-bacterial activities. *Radiat. Phys. Chem.*, *73*(3), 175-182. DOI: 10.1016/j.radphyschem.2004.08.011.

[16]. Choi, S.H., & Nho, Y.C. (2000). Radiation-induced graft copolymerization of binary monomer mixture containing acrylonitrile onto polyethylene films. *Radiat. Phys. Chem.*, *58*(2), 157-168. DOI: 10.1016/S0969-806X(99)00367-9.

[17]. Charlesby, A. (1960). *Atomic radiation and polymers*. England: Pergamon Press Limited.

[18]. Kato, M., Kamigaito, M., Sawamoto, M., & Higashimura, T. (1995). Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine)ruthenium(II)/methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system: Possibility of living radical polymerization. *Macromolecules*, *28*(5), 1721-1723. DOI: 10.1021/ma00109a056.

[19]. Wang, J.S., & Matyjaszewski, K. (1995). Controlled/"living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes. *J. Am. Chem. Soc.*, *117*(20), 5614-5615. DOI: 10.1021/ja00125a035.

[20]. Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., & Hamer, G.K. (1993). Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules*, *26*(11), 2987-2988. DOI: 10.1021/ma00063a054.

[21]. Hawker, C.J, Bosman, A.W., & Harth, E. (2001). New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.*, *101*(12), 3661-3688. DOI: 10.1021/cr990119u.

[22]. Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E., & Thang, S.H. (1998). Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process. *Macromolecules*, *31*(16), 5559-5562. DOI: 10.1021/ma9804951.

[23]. Destarac, M., Charmot, D., Franck, X., & Zard, S.Z. (2000). Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents. *Macromol. Rapid Commun.*, *21(15)*, 1035-1039. DOI: 10.1002/15213927(20001001)21:15< 1035::AID-MARC1035>3.0.CO;2-5.

[24]. Moad, G., Rizzardo, E., & Thang, S.H. (2005). Living radical polymerization by the RAFT process. *Aust. J. Chem.*, *58*(6), 379-410. DOI: 10.1071/CH05072.

[25]. Barsbay, M., & Güven, O. (2013). RAFT mediated grafting of poly(acrylic acid) (PAA) from polyethylene/polypropylene (PE/PP) nonwoven fabric via preirradiation. *Polymer*, *54*(18), 4838-4848. DOI: 10.1016/j.polymer.2013.06.059.

[26]. Kodama, Y., Barsbay, M., & Güven, O. (2014). Poly(2-hydroxyethyl methacrylate) (PHEMA) grafted polyethylene/polypropylene (PE/PP) nonwoven fabric by γ-initiation: Synthesis, characterization and benefits of RAFT mediation. *Radiat. Phys. Chem.*, *105*, 31-38. DOI: 10.1016/j.radphyschem.2014.05.023.

[27]. Walo, M., Przybytniak, G., Męczyńska-Wielgosz, S., & Kruszewski, M. (2015). Improvement of poly(ester-urethane) surface properties by RAFT mediated grafting initiated by gamma radiation. *Eur. Polym. J.*, *68*, 398-408. DOI: 10.1016/j.eurpolymj.2015.05.019.

[28]. Barsbay, M., & Güven, O. (2009). A short review of radiation-induced raft-mediated graft copolymerization: A powerful combination for modifying the surface

properties of polymers in a controlled manner. *Radiat. Phys. Chem.*, *78*(12), 1054-1059. DOI: 10.1016/j.radphyschem.2009.06.022.

[29]. Chong, Y.K., Le, T.P.T., Moad, G., Rizzardo, E., & Thang, S.H. (1999). A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: The RAFT process. *Macromolecules*, *32*, 2071-2074. DOI: 10.1021/ma981472p.

[30]. Barsbay, M., Guven, O., Davis, T.P., Barner-Kowollik, C., & Barner, L. (2009). RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via γ-radiation. *Polymer*, *50*(4), 973-982. DOI: 10.1016/j.polymer.2008.12.027.

[31]. Barsbay, M., Guven, G., Stenzel, M.H., Davis, T.P., Barner-Kowollik, C., & Barner, L. (2007). Verification of controlled grafting of styrene from cellulose via radiation-induced RAFT polymerization. *Macromolecules*, *40*(20), 7140-7147. DOI: 10.1021/ma070825u.

[32]. Gupta, B., Jain, R., Anjum, N., & Singh, H. (2006). Preirradiation grafting of acrylonitrile onto polypropylene monofilament for biomedical applications: I. Influence of synthesis conditions. *Radiat. Phys. Chem.*, *75*(1), 161-167. DOI: 10.1016/j.radphyschem.2005.04.003.

[33]. Binh, D., & Huy, H.T. (1998). The effect of concentration of acrylic acid, dose rates and temperature on preirradiated graft of natural rubber-based thermoplastic elastomer. *Radiat. Phys. Chem.*, *53*(2), 177-180. DOI: 10.1016/S0969-806X(98)00009-7.

[34]. Przybytniak, G., Kornacka, E.M., Mirkowski, K., Walo, M., & Zimek, Z. (2008). Functionalization of polymer surfaces by radiation-induced grafting. *Nukleonika*, *53(*3), 89-95.

[35]. Catarí, E., Albano, C., Karam, A., Perera, R., Silva, P., & González, J. (2005). Grafting of a LLDPE using gamma irradiation. *Nucl. Instrum. Meth. B*, *236*(1-4), 338-342. DOI: 10.1016/j.nimb.2005.03.273.

[36]. Bucio, E., & Burillo, G. (1996). Radiation-grafting of 2-bromoethylacrylate onto polyethylene film by preirradiation metod. *Radiat. Phys. Chem.*, *48* (6), 805-810. DOI: 10.1016/S0969-806X(96)00066-7.

[37]. Hegazy, E.-S.A., AbdEl-Rehim, H.A., Kamal, H., & Kandeel, K.A. (2001). Advances in radiation grafting. *Nucl. Instrum. Meth. B*, *185*(1-4), 235-240. DOI: 10.1016/S0168-583X(01)00834-5.

[38]. Barsbay, M., Kavaklı, P.A., & Güven, O. (2010). Removal of phosphate using copper-loaded polymeric ligand exchanger prepared by radiation grafting of polypropylene/polyethylene (PP/PE) nonwoven fabric. *Radiat. Phys. Chem.*, *79*(3), 227-232. DOI: 10.1016/j.radphyschem.2009.09.003.

[39]. Desai, S.M. Solanky, S.S., Mandale, A.B., Rathore, K. & Singh, R.P. (2003). Controlled grafting of *N*-isoproply acrylamide brushes onto self-standing isotactic polypropylene thin films: surface initiated atom transfer radical polymerization. *Polymer*, *44*(25), 7645-7649. DOI: 10.1016/j.polymer.2003.09.060.

[40]. Sherazi, T., Ahmad, S., Kashmiri, M., Kim, D., & Guiver, M.D. (2009). Radiation-induced grafting of styrene onto ultra-high molecular weight polyethylene powder for polymer electrolyte fuel cell application: II. Sulfonation and characterization. *J. Membrane Sci.*, *333*(1-2), 59-67. DOI: 10.1016/j.memsci.2009.01.052.

[41]. Makhlouf, C., Marais, S., & Roudesli, S. (2007). Graft copolymerization of acrylic acid onto polyamide fibers. *Appl. Surf. Sci.*, *253*(12), 5521-5528. DOI: 10.1016/j.apsusc.2006.12.086.

[42]. Nasr, H.I., Haggag, K.M., & El Kharadly, E.A. (1980). Polyamides with improved moisture regain via γ-rays. *Radiat. Phys. Chem.*, *16*(6), 447-449. DOI: 10.1016/0146-5724(80)90190-9.

[43]. Chumakov, M.K., Shahamat, L., Weaver, A., LeBlanc, J., Chaychian, M., Silverman, J., Richter, J.K., Weiss, D., & Al-Sheikhly, M. (2011). Electron beam induced grafting of N-isopropylacrylamide to a poly(ethylene-terephthalate) membrane for rapid cell sheet detachment. *Radiat. Phys. Chem.*, *80*(2), 182-189. DOI: 10.1016/j.radphyschem.2010.07.030.

[44]. Zhitariuk, N.I., & Shtanko, N.I. (1990). Influence of some factors on radiation grafting of styrene on poly(ethylene terephthalate) nuclear membranes. *Eur. Polym. J.*, *26*(8), 847-851. DOI: 10.1016/0014-3057(90)90156-X.

[45]. Walo, M., Przybytniak, G., Kavaklı, P.A., & Güven, O. (2013). Radiation-induced graft polymerization of N-vinylpyrrolidone onto segmented polyurethane based on isophorone diisocyanate. *Radiat. Phys. Chem.*, *84*, 85-90. DOI: 10.1016/j.radphyschem.2012.06.039.

[46]. Alves, P., Coelho, J.F.J., Haack, J., Rota, A., Bruinink, A., & Gil, M.H. (2009). Surface modification and characterization of thermoplastic polyurethane. *Eur. Polym. J.*, *45*(5), 1412-1419. DOI: 10.1016/j.eurpolymj.2009.02.011.

[47]. Meléndez-Ortiz, H.I., Alvarez-Lorenzo, C., Burillo, G., Magariños, B., Concheiro, A., & Bucio, E. (2015). Radiation-grafting of N-vinylimidazole onto silicone rubber for antimicrobial properties. *Radiat. Phys. Chem.*, *110*, 59-66. DOI: 10.1016/j.radphyschem.2015.01.025.

[48]. Gonzalez-Perez, G., Burillo, G., Ogawa, T., & Avalos-Borja, M. (2012). Grafting of styrene and 2-vinylnaphthalene onto silicone rubber to improve radiation resistance. *Polym. Degrad. Stabil.*, *97*(8), 1495-1503. DOI: 10.1016/j.polymdegradstab.2012.05.003.

[49]. Madrid, J.F., & Abad, L.V. (2015). Modification of microcrystalline cellulose by gamma radiation-induced grafting. *Radiat. Phys. Chem.*, *115*, 143-147. DOI: 10.1016/j.radphyschem.2015.06.025.

[50]. Wojnárovits, L., Földváry, Cs.M., & Takács, E. (2010). Radiation-induced grafting of cellulose for adsorption of hazardous water pollutants: A review. *Radiat. Phys. Chem.*, *79*(8), 848-862. DOI: 10.1016/j.radphyschem.2010.02.006.

[51]. Gubler, L., Gürsel, S.A., & Scherer, G.G. (2005). Radiation grafted membranes for polymer electrolyte fuel cells. *Fuel Cells*, *5*(3), 317-335. DOI: 10.1002/fuce.200400078.

[52]. Qiu, J., Ni, J., Maolin, Z., & Wei, G. (2007). Radiation grafting of styrene and maleic anhydride onto PTFE membranes and sequent sulfonation for applications of vanadium redox battery. *Radiat. Phys. Chem.*, *76*(11-12), 1703-1707. DOI: 10.1016/j.radphyschem.2007.01.012.

[53]. Estrada-Villegas, G.M., & Bucio, E. (2013).Comparative study of grafting a polyampholyte in a fluoropolymer membrane by gamma radiation in one or two-steps. *Radiat. Phys. Chem.*, *92*, 61-65. DOI: 10.1016/j.radphyschem.2013.07.015.

[54]. Ferreira, H.P., Parra, D.F., & Lugao, A.B. (2012). Radiation-induced grafting of styrene into poly(vinylidene fluoride) film by simultaneous method with two different solvents. *Radiat. Phys. Chem.*, *81*(9), 1341-1344, DOI: 10.1016/j.radphyschem.2012.01.047.

[55]. Taher, N.H., Dessouki, A.M., & El-Arnaouty, M.B. (1998). Radiation initiated graft copolymerization of N-vinylpyrrolidone and acrylamide onto low density polyethylene films by individual and binary system. *Radiat. Phys. Chem.*, *53*(4), 437-444. DOI: 10.1016/S0969-806X(98)00008-5.

[56]. Gupta, B., Büchi, F.N., & Scherer, G.G. (1994). Cation-exchange membranes by preirradation grafting of styrene into FEP films. 1. Influence of synthesis conditions. *J. Polym. Sci. Pol. Chem.*, *32*(10), 1931-1938. DOI: 10.1002/pola.1994.080321016.

[57]. Chapiro, A. (1995). Radiation chemistry in the field of biomaterials. *Radiat. Phys. Chem.*, *46*(2), 159-160. DOI: 10.1016/0969-806X(95)00006-J.

[58]. Dworjanyn, P.A., Garnett, J.L., Long, M.A., Nho, Y.C., & Khan, M.A. (1993). Role of homopolymer suppressors in UV and radiation grafting in the presence of novel additives – Significance of processes in analogous curing reactions. In E. Reichmanis, C.W. Curtis & J.H. O'Donnell (Eds.), *Irradiation of polymeric materials: processes, mechanisms, and applications* (pp. 103-117). American Chemical Society. (ACS Symposium Series, Vol. 527).

[59]. Gargan, K., & Lovell, K.V. (1990). Preirradation grafting of hydrophilic monomers onto polyethylene.1. The influence of homopolymerization inhibitors. *Int. J. Radiat. Appl. Instrum. C: Radiat. Phys. Chem.*, *36*(6), 757-761. DOI: 10.1016/1359-0197(90)90174-G.

[60]. Goel, N.K., Rao, M.S., Kumar, V., Bhardwaj, Y.K., Chaudhari, C.V., Dubey, K.A., & Sabharwal, S. (2009). Synthesis of antibacterial cotton fabric by radiation--induced grafting of [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (MAETC) onto cotton. *Radiat. Phys. Chem.*, *78*(6), 399-406. DOI: 10.1016/j.radphyschem.2009.03.011.

[61]. Lin, Z., Tongwen, X., & Zhang, L. (2006). Radiation-induced grafting of N-isopropylacrylamide onto the brominated poly(2,6-dimethyl-1,4-phenylene oxide) membranes. *Radiat. Phys. Chem.*, *75*(4), 532-540. DOI: 10.1016/j.radphyschem.2005.10.018.

[62]. Viengkhou, V., Ng, L.-T., & Garnett, J.L. (1997). The effect of additives on the enhancement of methyl methacrylate grafting to cellulose in the presence of UV and ionising radiation. *Radiat. Phys. Chem.*, *49*(5), 595-602. DOI: 10.1016/S0969-806X(97)00001-7.

[63]. Dworjanyn, P.A., & Garnett, J.L. (1989). Role of multifunctional acrylates in radiation grafting and curing reactions. *Int. J. Radiat. Appl. Instrum. C: Radiat. Phys. Chem.*, *33*(5), 429-436. DOI: 10.1016/1359-0197(89)90107-0.