6. Advances in the development of functional polymers using radiation induced emulsion polymerization

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Abstract. In this chapter the latest progress in the preparation of functional polymers using radiation induced emulsion polymerization technique is presented. A brief encounter for basic fundamentals, advantages, methods and parameters of radiation-induced emulsion polymerization is presented. A number of potential applications of the obtained functional polymers such as ionic adsorbents, chelating agents, polymer catalysts and polymers with controlled biodegradability are reviewed with special attention given to fast emerging environmental applications.

1. Introduction

The interest in using emulsion polymerization is growing due to their widespread applications in the production of functional and specialty polymers.
Functional and specialty polymers are materials that possess advanced properties suitable for energy, biomedical and environmentally related areas such as stimuli-response, chelating adsorbents, polymer electrolytes, diagnostic tests, drug-delivery systems, synthetic rubbers, paints, and adhesives applications [1, 2]. This unique synthesis process which proceeds in a heterogeneous system was initially employed in industrial scale during World War II for fabricating synthetic rubbers from styrene and butadiene [3]. Currently emulsion polymerization accounts for the world production of more than $10^7$ tons of polymers per year [1, 4].

Emulsion polymerization is a general term, which covers several processes including conventional, inverse, mini-, micro-, and nano emulsion polymerizations [1, 5]. Normally, the conventional emulsion polymerization involves emulsification of the relatively hydrophobic monomer in water by proper emulsifier, followed by the initiation reaction either with chemical or radiation methods. Both water and oil soluble initiators (e.g. sodium persulfate and 2,2′-azobisisobutyronitrile (AIBN)) have been used to initiate the polymerization reactions [2]. The polymerization is initiated by activation of initiators (e.g. by increasing the temperature) and formation of radicals. Therefore, the required conditions for producing the radicals control the polymerization temperature and subsequently influence the polymer properties. In radiation induced emulsion polymerization (RIEP), the reaction can initiated by either ultrasonic irradiation [6, 7] or high energy radiation in form of electromagnetic waves such as $\gamma$-rays obtained from radioactive sources such as Co-60 or Cs-37 [8].

RIEP can be used to prepare variety of polymeric materials including homopolymers, copolymers, and graft copolymers as shown in the schematic diagram given in Fig. 1. Thus, RIEP involves homopolymerization,
copolymers or grafting copolymerization reactions depending on the starting reactants. Particularly, graft copolymerization of a monomer onto polymer substrates offers kinetic and technological advantages over conventional methods [9, 10]. The substitution of chemical initiators or catalysts with high energy radiation in RIEP simplifies the reaction and leaves no detrimental residues in polymer mixture. This makes the polymers synthesized by RIEP attractive for bio-related applications due to the absence of impurities [9]. RIEP can be also used to produce high molecular weight polymers at high reaction rates with better temperature control during polymerization due to the more rapid heat transfer in the emulsion.

Among RIEP reactions, graft copolymerization have attracted more attention recently due to its merits and potential in modifying the chemical and physical properties of preformed polymers without altering their inherent properties. Various combinations of functional and nonfunctional monomers together with commercial polymers in different forms (films, beads, fabrics and fibers) are available to serve as polymer substrates for functional copolymers [11]. Radiation induced emulsion graft copolymerization (RIEGC) has been found to provide means to control the composition of the obtained functional graft copolymer, reduce the monomer consumption, reduce irradiation dose and improve the economy of the reaction when compared with other grafting methods [12]. In addition, using water as a dispersion medium provides nonflammable, inexpensive, nontoxic and odorless systems.

There have been several review articles in various journals and chapters in books on radiation induced graft copolymerization of various monomer/polymer combinations and their applications. The coverage of such reviews was dedicated to graft copolymers obtained by RIGC in solvents and their various applications [8, 13-21]. The technological process for industrialization of RIEP was briefly reviewed with the focus on batch process for industrial-scale production and the advantages were described in comparison with chemically initiated process [22]. However, there are no review texts on the use of RIEP for preparation of functional polymers and the latest progress in their applications.

The objective of this chapter is to provide an overview for the latest progress in the use of RIEP for preparation of functional polymers. A brief outline for basic fundamentals, advantages, methods and parameters are presented. A number of potential applications in different fields are reviewed with an attention given to fast emerging environmental applications.
2. Radiation induced emulsion polymerization

Radiation induced polymerization is a reaction that involves formation of polymer, copolymer or graft copolymer by exposure to high energy radiation, which generate radicals in the system that allow the reaction to proceed. This reaction can be performed in different media including bulk, solution, and emulsion as depicted in the schematic diagram shown in Fig. 2. Polymerization or grafting onto polymers in the emulsion media is a method for carrying out the reaction in a disperse system generally containing hydrophobic monomer and water as a dispersion medium. The stability of the emulsion system containing the monomer is maintained using a surfactant. The surfactant plays an important role in bringing monomers into contact with the substrate and generally acts as an emulsifier which stabilizes the emulsion medium during the reaction. In addition to forming the micelles to solubilize the water-insoluble monomers, the surfactant also decreases the surface tension at the monomer-water interface.

RIEP can also be carried out in an inverse emulsion polymerization with hydrophilic monomers [23, 24]. For example, aqueous solution of hydrophilic monomers such as N-isopropylacrylamide, acrylamide, acrylic acid, and salt of acrylic acid can be emulsified in nonpolar organic solvents such as xylene or paraffin. This method is commonly used in surface modification of films and preparation of polymeric microcapsules [23].

Emulsion polymerization reaction proceeds in three stages involving particle nucleation, particle growth, and termination [25, 26]. In particle nucleation, only one of 100-1000 micelles can capture the free radicals and

![Figure 2. Schematic representation of radiation induced polymerization in various media.](image-url)
becomes latex particle. The particle nucleation is followed by the polymerization reaction, which takes place in the micelles. Thus, the micelles can be regarded as living micro reactors, which facilitates the reaction. Based on the Smith-Ewart theory [26] the surfactant and initiator concentrations or irradiation dose (in RIEP) and time which controls the amounts of radicals are the most important factors that controls the number of latex particles nucleated per unit volume of water. One of the obvious advantages of RIEP over conventional polymerization methods is the independency of radical formation on the temperature. Such independency allows the polymerization initiation at low temperature and in viscous media.

When the emulsion is used to obtain a homopolymer, the emulsion mixture containing monomer, water and surfactant is irradiated by γ-rays leading to formation of radicals such as H• and OH• in the water phase in addition to monomer radicals all of which can participate in initiation of polymerization of monomers migrated inside the micelles. Unlikely, when irradiated polymer is incorporated in water emulsifier mixture, the reaction takes place in surface of the polymer and proceeds inward forming side chain grafts on polymer substrate.

In the growth step, the chains inside the micelles continue to grow until monomer supply or free radical is exhausted. According to the Smith-Ewart theory, at constant temperature, polymerization rate depends on the type and concentrations of surfactant and monomer and dose rate. The following equation is widely used to determine the rate of polymerization (R_p):

\[
R_p = k_p [M]_p \left( \frac{NN_p}{N_A} \right)
\]

where, \(k_p\) is the rate constant of the propagation step, \([M]_p\) is the monomer concentration in the particles, \(n\) is free radicals average number in particle, \(N_p\) is number of latex particles nucleated per unit volume of water and \(N_A\) is the Avogadro number. More details on the kinetics and mechanisms can be found elsewhere [2, 27, 28].

2.1. Homo- and copolymerization

Emulsion polymerization is among the most important methods for obtaining variety of commercialized homo- and copolymers. This method produces high molecular weight polymers by using the minimum amount of volatile organic compounds in safe and environmental friendly process [29]. Most of the produced water born polymers by emulsion are industrially important mainly in the producing synthetic rubbers, paints, adhesives, coatings, nonwoven tissues, biomaterials and high-tech products. Industrially,
vinyl acetate (VAc) based homo- and copolymers are account for more than 28% of the total waterborne synthetic latex, which are mainly used as low cost and durable component in coatings and adhesives [30, 31].

As discussed earlier, producing these materials by irradiation-induced method bring additional advantages including the yield, purity and control over polymer properties such as molecular weight. For example, the comparison between conversion percentage of poly(vinyl acetate) prepared by RIEP and bulk revealed that the conversion percentage in emulsion is almost four times higher than in bulk [32]. In addition, the polymer obtained by emulsion shows considerable higher molecular weight and glass transition temperature.

Radiation-initiation is a complex procedure which the consequence of ionization and excitation depends on the physical state and composition of material and type of radiation source [33]. Upon irradiation, some primary products formed due to the breaking of indiscriminate chemical bond. These primary products may either react with other materials or recombine to produce even more secondary products [33]. In initiation of RIEP, water is a very important component. Pure water molecules undergo radiolysis to yield solvated electrons (e\textsubscript{\text{aq}}), protons and hydroxyl radicals [34]. The undergoing reactions in the radiolysis of water are shown below [33]:

\[
\begin{align*}
\text{H}_2\text{O} + \gamma &\rightarrow \text{e}^- + \text{H}_2\text{O}^+ \\
\text{H}_2\text{O} + \gamma &\rightarrow \text{H}_2\text{O}\textsuperscript* 
\end{align*}
\]

\(\text{H}_2\text{O}^+\) rapidly react with water (~10\textsuperscript{-14} s) to produce hydroniums and hydroxyl radicals.

\[
\begin{align*}
\text{H}_2\text{O}^+ &\rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \\
\text{H}_2\text{O}\textsuperscript* &\rightarrow \text{e}^- + \text{H}_2\text{O}^{++}
\end{align*}
\]

The exact nature of the water in the excited state (\(\text{H}_2\text{O}\textsuperscript{*}\)) remains uncertain but it seems likely that radicals will be produced on decomposition of excited state within 10\textsuperscript{-14}-10\textsuperscript{-13} s.

\[
\begin{align*}
\text{H}_2\text{O}^* &\rightarrow \text{OH}^- + \text{H}^+ \\
\text{H}_2\text{O}^* &\rightarrow \text{e}^- + \text{H}_2\text{O}^{++}
\end{align*}
\]

In the absence of reactive species electrons are rapidly (~10\textsuperscript{-11} s) solvated:

\[
\text{e}^- + \text{nH}_2\text{O} \rightarrow \text{e\textsubscript{\text{aq}}}
\]

Solvated electrons, which are strongly reducing species, are rapidly react with protons at any reasonable pH:

\[
\text{e\textsubscript{\text{aq}}} + \text{H}^+ \rightarrow \text{H}^-
\]
Advances in the development of functional polymers using radiation induced emulsion polymerization

In the presence of monomers, hydroxyl radicals and free electrons can add to the \( \pi \)-electrons of double bonds and start the free radical polymerization reaction.

\[
\begin{align*}
\text{OH}^+ + \text{CH}_2=\text{CRX} & \rightarrow \text{CH}_2\text{OH}^\cdot \text{CRX} \\
\text{e}^- + \text{CH}_2=\text{CRX} + \text{H}^+ & \rightarrow \text{CH}_3^\cdot \text{CRX}
\end{align*}
\]

RIEP has been applied in obtaining various polymers such as poly(vinylacetate) [32], polystyrene [35-39], poly(vinylpyrrolidone) [24, 40], poly(butylacrylate) [41] and poly(methyImethacrylate) [42]. It has been also used to prepare copolymers with improved properties including divinylbenzene crosslinked polystyrene [43], butylacrylate/acylonitrile [44], and 2-methacryloyloxyethyl) trimethyl ammonium chloride/acrylamide [45] starting from their corresponding monomers in water using gamma rays in presence of various surfactants. Table 1 shows a summary of some previous studies on the use of radiation induced emulsion polymerization to prepare polymers and copolymers.

Table 1. Previous studies on preparation of polymers and copolymers by radiation induced emulsion polymerization.

<table>
<thead>
<tr>
<th>Starting monomer(s)</th>
<th>Source</th>
<th>Surfactant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylacetate</td>
<td>( \gamma )rays</td>
<td>Sodium lauryl sulphate</td>
<td>[45]</td>
</tr>
<tr>
<td>Styrene</td>
<td>( \gamma )rays</td>
<td>Sodium 4-(8-(methacryloxy)octyl)benzenesulfonate</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methacryloxyoctyltrimethylammonium bromide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sodium isodecanoate</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(vinyl pyrrolimine)</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkali soluble polymeric surfactant</td>
<td>[39]</td>
</tr>
<tr>
<td>N-vinylpyrrolidone</td>
<td>( \gamma )rays</td>
<td>Isoparaffinic hydrocarbon</td>
<td>[24, 40]</td>
</tr>
<tr>
<td>Butyl acrylate</td>
<td>( \gamma )rays</td>
<td>Sodium 12-butinoxyo-9-octadecenat</td>
<td>[41]</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>( \gamma )rays</td>
<td>12-acryloxy-9-octadecenoic acid/sodium dodecyl sulf</td>
<td>[42]</td>
</tr>
<tr>
<td>Styrene/divinyl benzene</td>
<td>( \gamma )rays</td>
<td>Nonionic surfactant</td>
<td>[43]</td>
</tr>
<tr>
<td>Butylacrylate/acylonitrile</td>
<td>( \gamma )rays</td>
<td>Sodium alkylsulphonate</td>
<td>[44]</td>
</tr>
<tr>
<td>(2-ethacryloyloxyethyl) trimethyl ammonium chloride/acrylamide</td>
<td>( \gamma )rays</td>
<td>Span 80/ OP10</td>
<td>[45]</td>
</tr>
</tbody>
</table>

2.2. Graft copolymerization

Graft copolymerization is a process in which side chain grafts originated from a monomer are attached to the main chain of a polymer backbone by covalent bonds to form a branched copolymer. A graft copolymer can be represented as follows:

\[
\begin{array}{cccccccccc}
\text{B}_n & & & & & & & & & \text{B}_m
\end{array}
\]
where, $B_n$ and $B_m$ are the side chain grafts originated from the monomer $B$ onto the main polymer chain. The extent of polymerization in $B_n$ and $B_m$ grafts is called the degree of grafting ($DG$) and can be gravimetrically determined through the weight increase. The grafting reaction takes place as a result of formation of active sites on the polymer backbone, which can be initiated by various means including chemical initiator [46], thermomechanical initiation (melt grafting) [47], plasma treatment [48], ultraviolet light radiation [49], and high energy radiation [11]. Unlike plasma and photoinitiated grafting, RIGC is capable of achieving bulk modification and has been widely investigated for preparation of various ion exchange and adsorbent polymers [8].

RIGC is an effective method for modifying the properties of a pre-existing polymer by imparting new functionalities without compromising the desired properties of the parent polymer [14]. This method is used to introduce polar groups to the bulk or surface of non-polar polymers of various morphologies (fiber, film, fabrics and beads) to bring about modification in wettability, adhesion, printability, metallization, anti-fog properties, anti-statics properties, and biocompatibility. Thus, it has been used to develop various forms of functional polymers suitable for medical, biological, environmental, chemical and solid state applications [8] [15].

In the RIGC method, the reaction usually follows free radical polymerization mechanism and can be initiated with various high energy radiation in form of electromagnetic waves such γ-rays obtained from

![Diagram](image)

**Figure 3.** Schematic representation of radiation induced graft copolymerization methods.
radioactive sources such as Co-60 or Cs-37. However, Co-60 is more advantageous and has been widely used due to higher energy emission (1.25 MeV compared to 0.66 MeV for Cs-137), easier preparation, lower cost and shorter half-life (5.27 year) [50]. Particulate radiation such as electron beam (EB) can be also used to initiate grafting but at a shorter time (few minutes) and lower penetration levels compared to γ-rays [51].

RIGC can be performed using two main methods as shown in the schematic representation in Fig. 3. This includes (i) direct (simultaneous) irradiation and (ii) preirradiation. In the direct irradiation, both the polymer and the monomer are irradiated together after the grafting solution is flushed with N₂ or evacuated using freeze thaw cycles. An inhibitor is often added to the solution to suppress the homopolymerization in the liquid phase when the reactive monomer is grafted. Alternatively, in the preirradiation method, the polymer is irradiated first in the absence of monomer and then brought into contact with a monomer solution to initiate the reaction. As can be seen in Fig. 3, this irradiation can be either in an inert atmosphere or in the presence of air. In the irradiation in oxygen or air atmosphere, which usually refer as a peroxidation grafting method, peroxide and hydroperoxide radicals formed upon irradiation. Grafting reaction is then initiated by thermal decomposition of the trapped radicals in the polymer backbone in presence of monomer units under controlled conditions.

2.2.1. Radiation induced emulsion graft copolymerization

RIEGC is a chemical reaction similar in principles with RIGC but differs in the components of the grafting mixture. Particularly, the monomer in RIEGC is diluted with water as a dispersion medium and emulsified by the addition of a small amount of a surfactant. Although the use of solvent in RIGC facilitates the swelling of the base polymer and monomer diffusion leading to high levels of grafting, the stronger demand for environmentally friendly procedures where water is used as an alternative solvent makes RIEGC more appealing and sustainable [52]. Compared to RIGC in solvents, RIEGC have the advantage of: 1) high efficiency, 2) low absorbed dose, 3) using water as dispersion medium which allows easily recycling in industrial scales, 4) possibility to use green surfactants, and 5) high sustainability and environmental friendly. In addition, under properly chosen conditions of emulsion, the low viscosity of the emulsion along with the lower possibility of termination step allows higher polymerization rates and high molecular weight polymers which is not readily accessible in solution or bulk polymerization reactions [12, 53]. Besides these advantages, the products synthesized by irradiation are beneficial to bio-application because
contamination with chemical initiators is avoided and the final products are sterilized [9].

A comparison between radiation induced graft copolymerization in a solvent and that in emulsion is presented in Table 2.

**Table 2.** Comparison between RIGCs in solvent and that in emulsion.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Radiation grafting in solvent</th>
<th>Radiation grafting in emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafting medium</td>
<td>Solvent</td>
<td>Water</td>
</tr>
<tr>
<td>Surfactant</td>
<td>No surfactant</td>
<td>Surfactant is added</td>
</tr>
<tr>
<td>Irradiation dose</td>
<td>High dose</td>
<td>Low dose</td>
</tr>
<tr>
<td>Monomer concentration</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Residue/waste</td>
<td>Waste production</td>
<td>Waste can be recycled easily</td>
</tr>
</tbody>
</table>

**Figure 4.** Reaction mechanisms for preparation of various ionic copolymers by RIEGP of GMA followed by variety of chemical treatments.

A typical example to highlight the advantages of RIEGC is the grafting of glycidylmethacrylate (GMA) onto various polymer substrates to produce grafted precursors that can be converted to variety of functional materials suitable for wide spectrum of applications. In RIEGC reaction, GMA is diluted with water and is emulsified by adding a small amount of surfactant such as Tween 20 in presence of polymers substrates such as PE fibers or fabrics [54, 55]. This method provides interesting advantages in terms of elimination of solvents, irradiation dose reduction and less monomer consumption leading to an improvement in the economy of the process.
Fig. 4 depicts mechanisms for preparation of various ionic copolymers by RIEGP of GMA and subsequent possible functionalization reactions.

The use of RIEGC in preparation of graft copolymers allows imparting favourable properties by modification of existing natural and synthetic polymers. In that regard, various grafting systems such as styrene/butadiene latex [56], 4-chloromethylstyrene/kenaf fiber [57], methyl methacrylate/jute fibers [58, 59], GMA/polyethylene (PE) fibers [53, 60], GMA/nonwoven cotton fabrics [61], various vinyl monomers/polyurethane [62], methylmethacrylic acid/waterborne polyurethane [63], styrene/waterborne polyurethane [64], vinylacetate/poly(3-hydroxybutyrate) film [55], N-vinyl pyrrolidone/polystyrene [9], GMA/poly(vinylidine fluoride) [65], octafluoropentyl acrylate/silk fibers [66], GMA/PE beads [12], acrylonitril/PE non-woven fabric [67], and 4-chloromethylstyrene [68] have been reported in literature. In addition, grafting onto nonwoven fabric material composed of both natural and synthetic polymers [69] as well as co-grafting of monomer mixtures have been considered [70].

2.2.2. Factors affecting radiation induced emulsion graft copolymerization

There are many parameters which strongly affect RIEGC process. Variation of these parameters affects the degree of grafting in the resulting copolymers and this provides means to closely control the compositions and the properties of the functional copolymers. A combination of optimum parameters has to be adapted to achieve successful grafting reactions towards obtaining desired composition [57, 71].

Reaction parameters that have to be controlled can be classified into: 1) those directly related to irradiation source and 2) others related to the grafting mixture [8]. The former include nature of radiation, dose and dose rates whereas the latter includes monomer type and concentration, storage time, grafting atmosphere, temperature, radical storage time and reaction time. The influence of these parameters on the radiation-induced grafting has been the subject of detailed investigations in various groups [18, 72]. In addition, emulsion related parameters including the type (anionic, cationic, nonionic and amphoteric) and concentration of surfactant, stability of emulsion mixture, and micelle size were found to play important role on grafting. For instance in the radiation-induced emulsion graft polymerization of 4-chloromethylstyrene on kenaf fiber, it was observed that the (i) micelle diameter gradually change upon changing both temperature and storage time, (ii) reducing the micelles size from 500 nm to 250 nm leading to the emulsion stability, and (iii) the larger the micelle size results in higher degree
of grafting [57]. The effects of these parameters on the degree of grafting could be cumulative and interdependent [58]. More details on the effect of each one of these parameters on the degree of grafting in a variety of grafting system were reported in various occasions [8].

3. Applications of polymers obtained by radiation induced emulsion graft polymerization

Like their counterparts prepared by conventional radiation grafting, graft copolymers obtained by RIEGC are proposed for various applications with advantages of being prepared using less monomer consumption and low irradiation doses i.e. they are more economical. The diversity of functionalities that can be incorporated in the grafted polymers rendered them suitable for a variety of applications. However, separation applications remain the main field with functional graft copolymers. Particularly, decontamination of the waste water from pollutants is in the heart of separation applications of such materials.

3.1. Removal of pollutants from waste water

Amine-type adsorbents prepared by RIEGP of GMA onto PE fibers followed amination with three chemical agent; diethyltriamine (DETA), triethyltriamine (TETA) and ethylenediamine (EDA) were tested for adsorption of Pb$^{2+}$ and Ni$^{2+}$ from waste water. The distribution coefficient of Pb$^{2+}$ was found to be $10^4$ in all amine-type adsorbents and that of Ni$^{2+}$ decreased in the order of DETA-type, EDA-type and TETA-type. The EDA-type adsorbent also showed the highest selectivity against U ion and the distribution coefficient was $2.0 \times 10^6$ [53].

Another amine-containing adsorbent for heavy metal adsorption was prepared by radiation emulsion grafting of 4-hydroxybutyl acrylate glycidylether (4-HB) onto polyethylene/polypropylene nonwoven fabric followed by amination with EDA. A typical adsorbent has a $DG$ of 135% and amine group density of 2.8 mmol/g. The adsorbents showed adsorption metal ions in the order of Cu$^{2+}$ > Pb$^{2+}$ > Zn$^{2+}$ > Ni$^{2+}$ > Li$^+$. It also exhibited not only better mechanical property but also higher adsorption capacity of Cu$^{2+}$ and Pb$^{2+}$ compared to similar amine-type adsorbent based on grafted GMA [73]. Column and batch mode studies were performed for 4-HB and GMA grafted onto PE absorbents functionalized with various amine derivatives of diethylamine, EDA, DETA, and TETA [74]. By using EDA-based adsorbent, good and similar sorption behaviour for Cu$^{2+}$ and Pb$^{2+}$ was observed for individual ions. However very low selectivity was resulted for mixed ions.
Upon irradiation-induced crosslinking of amine functionalized adsorbent, higher sorption capacity for Cu\(^{2+}\) and almost no capacity for Pb\(^{2+}\) was obtained. By changing the anion in the solution, similar results were found which indicates the independency of the selectivity improvement from the anion in the solution. This increases in selectivity upon crosslinking can be explained by the decreases in the distance of the chelating groups after crosslinking. Since the Pb\(^{2+}\) radius (0.120 nm) is much larger than Cu\(^{2+}\) (0.072 nm), reducing the distances between the chelating groups make the materials more favourable for chelating smaller ions.

METOLATE\textsuperscript{®} is a recently commercialized heavy metal adsorbent based on the RIEGP of GMA onto PE nonwoven fabric followed by amination \cite{75}. This high performance fibrous absorbent was designed for the removal of Ni and Cu ions from strongly corrosive alkaline solution which used in the etching process of the surface of Si wafer. Due to the corrosive nature of medium, other commercially available absorbent resins are not proper for this application and usually shrink in such strong alkaline solutions. The absorbent with the \textit{DG} of 120\% remove Ni ions from the concentration of 100 ppb in 48 wt\% NaOH solution to less than 1 ppb. In the case of Cu ions with the concentration of 10 ppb in 48 wt\% KOH, less than 0.5 ppb remains after treatment with absorbent which are satisfied for the requirement. In addition, 30 higher lifetimes and possibility to use in almost 20 times higher flow rate than commercial resin was reported.

A chelating adsorbent for removal of boron was prepared with RIEGP of GMA onto PE fibers followed by treatment with \textit{N}-glucamine. The obtained absorbent showed 4 times higher breakthrough capacity and almost 10 times faster boron adsorption than conventional commercial glucamine resin \cite{76}. Similar adsorbent precursors were prepared by grafting of GMA onto poly(vinylidene fluoride) powder and acrylonitrile and GMA onto PE nonwoven fabric using preirradiation-induced emulsion graft polymerization \cite{65,67,77}. Grafted GMA onto PE non-woven fabric functionalized with aminated compounds such EDA, DETA, TETA and tetraethylenepentamine were tested for the removal of copper and uranium ions from solution. For the contaminated water with concentration up to 1000 ppb, at least 90\% of copper and 60\% of uranium was removed by such absorbents \cite{77}.

Similar amine adsorbent with biodegradable nature was prepared by grafting of GMA onto nonwoven cotton fabric followed by treatment with EDA or DETA and tested for Hg\(^{2+}\) adsorption. The resulting amine-type adsorbents showed distribution coefficients of Hg of \(1.9 \times 10^{5}\) and \(1.0 \times 10^{5}\) for EDA-and DETA-type adsorbents, respectively, on batch basis. The EDA-type adsorbent removed mercury ion from 1.8 ppm Hg\(^{2+}\) solution at a space velocity of 100h\(^{-1}\), which corresponds to 16,000 times the volume of
the packed adsorbent when tested on column basis. The adsorbed Hg$^{2+}$ on the EDA-type adsorbent could be completely eluted by 1 M HCl solution. A microbial oxidative degradation test revealed that the EDA-type adsorbent is biodegradable. This suggest that the obtained adsorbent is a potential environment friendly candidate for Hg$^{2+}$ adsorption [61].

Arsenic adsorbent was prepared by RIEGP of 2-hydroxyethyl methacrylate phosphoric acid monomer onto a nonwoven cotton fabric followed with chemical modification by zirconium Zr(IV) solution [78]. The phosphorous o xoacid derivatives have strong affinity against Zr(IV) to form a complex of phosphate-Zr at a high concentration of nitric acid and this complex displays great adsorption capacity of As(V). In a pilot scale, the adsorbent was successfully prepared with a DG of 118% at a monomer concentration of 5% for 1 h at 40 °C. In the batch mode adsorption studies with 1 ppm of As(V), the adsorption capacity of 0.02 mmol/g-adsorbent was achieved.

In the most recent study, metal ion adsorbent for removal of the Cu$^{2+}$ and Ni$^{2+}$ ions in aqueous solutions was developed based on nonwoven fabric material composed of both natural and synthetic polymers [69]. A preirradiated mixture of abaca, which is a product of some farming regions in the Philippines, and polyester nonwoven fabric was grafted with GMA using emulsion grafting technique and finally modified by reaction with EDA. An absorbent with the DG of 150% and an amine group density of 2.7 mmol/g showed almost 4 times higher adsorption capacity for Cu$^{2+}$ than Ni$^{2+}$. In a comparison with a commercial Diaion WA20 resin, which is also an amine functional material, this adsorbent showed greater Ni$^{2+}$ and Cu$^{2+}$ adsorption capacity and rate.

3.2. Controlled biodegradability

Polymeric substances with a good combination of durability and degradability are highly interesting especially for packaging and disposable applications [79]. In this regard, RIEGC was used to achieve the stability of biodegradable polymers. For instance, VAc was grafted onto biodegradable poly(3-hydroxybutyrate) (PHB) film. Grafting reactions were carried out in VAc/water/surfactant emulsion, VAc/water, and VAc/methanol systems. For emulsion grafting, Nonion L-4 was found to be the optimum surfactant with respect to the stability of a single emulsion layer. The emulsion with a 10:1 (w/w) ratio of VAc to surfactant yielded the highest DG: 230%. The grafting efficiency in the emulsion and the water and methanol solvents were evaluated. The results indicated that the grafting efficiency of the emulsion was 100 times more than that of VAc/methanol when the same 2 wt % VAc
was used in the grafting reaction [55]. The biodegradation of PHB is depressed by grafting of VAc and upon disposal it could be easily recover by hydrolysis (treatment with NaOH).

3.3. Biodiesel production

A polymer catalyst for converting Triolein to biodiesel by transesterification reaction was prepared by RIEGP of 4-chloromethylstyrene onto PE nonwoven fabric. The monomer emulsion containing Tween 20 and deionized water was reacted with PE irradiated at 100 kGy under inert atmosphere at 40 °C. Quaternary ammonium groups were introduced to the grafted PE fabric by a treatment with 0.5 M trimethylamine (TMA) at 50 °C followed by a treatment with 1 M NaOH to replace Cl⁻ with OH⁻. Grafting levels up to 340% and 3.6 mmol-TMA/g-catalyst were reached. The obtained catalyst achieved a conversion of 95% when used for transesterification of triglycerides and ethanol after 4 h at 50 °C. The catalyst demonstrates strong potential in the acceleration of biodiesel production [68].

3.4. Other applications

Modification of Silk fibers with octafluoropentyl acrylate through the vinyl bonds of acryloyloxyethyl isocyanate is reported to improve the fibers quality [66]. The thermal stability of the modified silk fibers was improved due to the introduction of fluoroacrylate. The fibers also displayed water repellence compared to pristine silk fibers.

PU synthesis by polycondensation reaction in emulsion were used to prepare PU-g-polyvinyl copolymer by an in-situ graft copolymerization with various vinyl monomers induced by γ-ray radiation [62]. Such hybrid materials can be potentially used in various industries, especially in the coating and paint productions. In comparison to simply mixing the PU and vinyl polymer, more homogeneity and better film quality was results by RIEGC.

4. Applications of some polymers and copolymers obtained by radiation induced emulsion polymerization

Polymeric nanocapsules from polar monomers; N-vinylpyrrolidone (NVP), styrene (St) and SDS surfactant with a liquid core of dodecane were prepared by γ-ray initiated miniemulsion polymerization. The grafting reaction between polystyrene and poly(N-vinylpyrrolidone) increases the hydrophilicity of the polymer and reduces the interfacial tension between
polymer and water, which leads to successful synthesis of nanocapsules. The increase in NVP/St ratios, SDS amount and dodecane/monomer ratios is favourable to obtain nanocapsules with a liquid core. The type of the surfactant shows a great influence on the particle morphology. The release study indicates good permeability of the synthesized nanoparticles [9].

Ag-loaded polystyrene (PS-Ag) composite nanoparticles were prepared by two different approaches (two step and single step processes). In the two step process, the PS nano-particles were synthesized by RIEP of styrene followed by loading Ag nanoparticles while in the one step method, Ag-PS nanoparticles were synthesized in a single step. The two-step method results in loading of Ag particles on the surface of the PS particles, while the one-step method distributes the Ag particles within the PS particles. When coated on a cloth, the PS-Ag nanoparticles produced by the one-step method showed an excellent antimicrobial activity. A cloth coated with those particles shows a high antimicrobial efficiency of 99.9% against two bacteria, Staphylococcus Aureus and Klebsiella Pneumoniase [38].

The developments of coatings which do not require any organic solvent have been in demand for social needs. The emulsion made by RIEP is considered to meet possibly this requirement, but it has not been utilized well in the application to water paint. Obviously, the technology used for the preparation of emulsion-type paint should be improved to meet the recent requirements either in the performance characteristics or in the environmental field. Although the emulsion-type paints have been developed and sold commercially; however, their antipollution and water-resistance properties are far from satisfactory [80].

5. Concluding remarks

RIEP is an advantageous technique for preparation of various functional copolymers, graft copolymers and homopolymers with a flexibility to control the composition of the obtained materials. Particularly, RIEP provides a considerable reduction in monomer consumption and irradiation dose in addition of using water as an alternative green solvent when compared with conventional methods. Functional graft copolymers obtained by RIEGC have been used in various applications including ionic adsorbents, chelating agents, catalysts and polymers with controlled biodegradability mainly for environmental remedy. In this regard, the ability of RIEGC to conduct graft copolymerization at low dose allows the modification of natural polymers and fine structure such as nano-fibers and converting them to cheap and highly selective adsorbents. Copolymers and homopolymers obtained by RIEP can be used for various applications such as making core-shell
structures, encapsulated materials, paints and antibacterial polymers. Intensive work is needed to develop new functional materials and to bring more researched materials from laboratories to industrial scale application.

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References


50. V.S. Ivanov, Radiation chemistry of polymer, VSP, Utrecht, the Netherlands, 1992.


