

Conference paper

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Ionizing radiation: a versatile tool for nanostructuring of polymers

DOI 10.1515/pac-2016-0813

Abstract: Very high energies of particulate (accelerated electrons, swift heavy ions) or electromagnetic wave (γ , X-rays) radiation can be used to initiate free radical based reactions in solids, liquids or gases. Because of non-selectivity of absorption of X-rays, γ rays and accelerated electrons in matter free radicals are generated homogeneously in the bulk material. These free radicals on the polymers or monomers are used extensively in the synthesis and modification of polymeric materials. The unique properties of ionizing radiation make it a very useful tool in the top-down and bottom-up synthesis of nanomaterials. In this article the utilization of ionizing radiation in the form of swift heavy ions, accelerated electrons, X- and γ rays will be described for development of advanced materials by radiation-induced grafting in nanoscale, synthesis of polymeric nanoparticles, radiation-assisted synthesis of nanogels and nanocomposites. The properties difficult to be attained by other techniques will be described by giving examples for the cases of ion track-etched membranes, fuel cell membranes, sensors, detectors, cell culture media, polymer thin films embedded with metal nanoparticles, polymer/clay nanocomposites with a prospect for the future outlook.

Keywords: fuel cell membranes; ionizing radiation; ion-track membranes; nanocomposites; nanogels; nanostructured materials; POC-16.

Introduction

Irradiation of polymers with high energy radiation (γ rays, X-rays, accelerated electrons and swift heavy ions) leads to the formation of very reactive intermediates in the form of excited states, ions and free radicals. These intermediates are almost instantaneously used up in several reaction pathways which result in disproportionation, hydrogen abstraction arrangements or formation of new bonds, structures. The ultimate effects of these reactions are crosslinking and/or scissioning of main or side chains, formation of oxidized products and grafting if irradiation is carried out in air or in the presence of a vinyl monomer, respectively. The degree of dominance of these transformations depend on the nature of the polymer and the conditions of treatment before, during and after irradiation. Close control of these factors make the modification of polymers possible by radiation processing.

The unique properties of ionizing radiation are not well appreciated however, mostly due to historical reluctance of researchers to store, use and handle radioisotopic sources. In most countries access to ionizing radiation sources are restricted with the availability of such systems in the laboratories of national Atomic Energy Authorities. This image is slowly changing with the development and manufacturing of electron accelerators with wide ranges of energy and current that would replace radioisotopic sources such as Co-60 and Cs-137. When properly used commercial or laboratory scale radiation sources and radioactive materials pose no problems to people and environment. The International Atomic Energy Agency (IAEA) has been

Article note: A collection of invited papers based on presentations at the 16th International Conference on Polymers and Organic Chemistry (POC-16), Hersonissos (near Heraklion), Crete, Greece, 13–16 June 2016.

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instrumental in advancing the promotion and application of ionizing radiation in fields such as medicine, industry, agriculture and environmental research [1].

Polymers are generally classified as predominantly undergoing degradation or crosslinking when exposed to ionizing radiation. Since the inception of radiation processing by polymer industry its crosslinking effect has been widely utilized in the manufacturing of heat-shrinkables, wire and cable insulations, automobile tyres, PE foams, etc. [2]. In degrading type polymers rapid combination of broken chain ends is sterically hindered. Hence as a result of disproportionation polymer radicals are stabilized with the formation of two stable end groups resulting with reduced chain length, lower molecular weight polymers. The primary consequence of chain scission is the enhanced solubility of degraded polymers. The improvement in the solubility of a polymer upon radiation induced controlled degradation has long been utilized in lithography. Focused beam of energetic particles comprising electrons, ions and X-rays provide means for generating patterns in a proper resist material that can not be achieved by photolithography. These techniques have extremely high resolution capabilities because of their short wavelengths (< 0.1 nm) combined with a large depth of focus. A variety of materials have been demonstrated for use in electron beam lithography including polymers. Poly(methyl methacrylate) PMMA is a typical polymer that undergoes extensive chain scissioning when exposed to ionizing radiations. Due to its high sensitivity to radiation it has been the material of choice as the positive resist in lithography. The controlled degradation of polymers for lithographic applications can be considered as the first commercial application of ionizing radiation in nanotechnology. This subject has been recently elaborated in a thematic issue by Huth [3].

The ionizing radiations with well established applications in polymer industry possess properties that perfectly suit for the creation of new functional polymeric materials on nanoscale. By virtue of very high energies of γ photons (0.66–1.25 MeV) or accelerated electrons (several keV–10 MeV) and their ability to penetrate into solid materials, the precursors of chemicals reactions namely, free radicals are produced homogeneously in the media exposed to ionizing radiations. This allows irradiation of polymers or monomers in any state and at, above and below ambient temperatures. These unique properties make ionizing radiation a very useful tool for the preparation of materials with nanostructures [4].

The two fundamental approaches of nanotechnology namely, top-down and bottom-up can be easily applied for the preparation of nanomaterials by using ionizing radiation when polymers or monomers are used as the starting materials, respectively. The controlled degradation of polymers by X-rays or electron-beams in lithography, formation of ion track-etched membranes by swift heavy ion bombardments of polymer thin films are typical examples of top-down approach. The synthesis of polymeric nanoparticles or polymer films with embedded metallic nanoparticles, formation of nanogels, nanocomposites, grafting at nanoscale for tissue engineering applications can be mentioned where radiation has been used for bottom-up synthesis of nanomaterials. When the nanochannels generated in polymer thin films by heavy ion bombardment are functionalized by radiation-induced grafting, the advanced functional materials thus obtained are the results of combined application of radiation in top-down and bottom-up approaches. From the point of view of nano-sized end-products to be obtained by radiation processing it is possible to group them under the following titles: (a) radiation-induced grafting at nanoscale, (b) synthesis of nanoparticles, (c) synthesis of nanogels, (d) synthesis of nanocomposites. Basic principles involved in the preparation of above listed nanomaterials by using ionizing radiation and some typical applications will be described in the following paragraphs with some examples from the literature and author's laboratory.

Radiation-induced grafting at nanoscale

Ion track-etched membranes

Scissioning (controlled degradation) of polymer chains by high energy radiation is a typical case for top-down manufacturing process in nanostructuring of polymers. The most widely used application of controlled

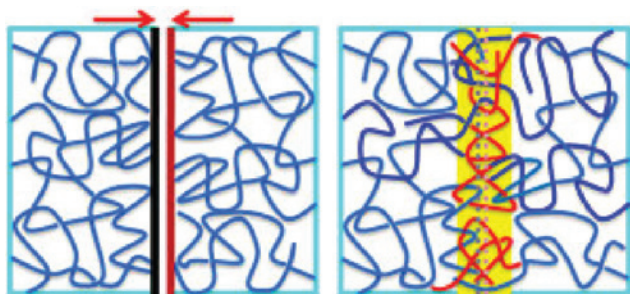


Fig. 1: Schematic presentation of formation of latent track (right) showing damaged zone upon heavy ion irradiation and cylindrical ion track pore after chemical etching of latent track.

degradation in lithography has already been mentioned briefly in the Introduction part. When polymeric thin films are irradiated with energetic heavy ions, zones of high density excitations and ionizations are created as they pass through the materials leaving a straight track of radiation damage. These damaged zones are called latent tracks and they can be converted into well defined cylindrical or conical ion track pores by chemical etching, as shown in Fig. 1.

The unirradiated parts of the polymer is chemically stable. During chemical etching the damaged zone is removed and transformed into a hollow cylindrical channel. Etching conditions and procedures determine the size and shape of the pores [5]. Polycarbonate, poly(ethylene terephthalate) and polyimides are the most preferred polymers whose films are used for the preparation of cylindrical ion-track pores with uniform sizes. Swift heavy ion beams in the 1–10 MeV/u energy range have been used. Ion-track membranes are precision bore films with very narrow pore-size distribution. The pore diameters can be from 10 nm to tens of microns and pore density can vary from 1 to $10^{10}/\text{cm}^2$. Track-etched membranes are commercially available for process filtration, cell culture and laboratory filtration. Purification of deionized water in microelectronics, filtration of beverages, separation and concentration of various suspensions can be listed as other so-called passive applications of these membranes [6]. The cylindrical nanochannels of ion track membranes are often used for the template synthesis of nanostructures [7].

The use of ion track membranes are further enhanced by grafting of pores with stimuli-responsive polymers thus converting passive membranes into responsive membranes [8]. While the flow through passive membranes is ruled by the applied pressure difference, the flow through responsive membranes is controlled by temperature, pH, chemical composition of the solution and electrical potential. When inside walls of the pores are grafted with polymers such as poly(N-isopropyl acrylamide) [9, 10] or poly(acryloil N-proline methyl ester) [11] the pores acquire temperature responsiveness whereas with poly(acrylic acid) pH responsiveness. The chains of former thermo-responsive polymers swell in water, expand and fill the pores below about 30 °C (near the lower critical solution temperature of grafted polymers) and collapse and open the gates above this temperature thus acting as on-off devices or valves. Changing the environmental factors controls the flow rate and the transmittance of small and large molecules through these membranes. It has been shown that opening and closing of pores can be cycled many times over long time periods by varying the temperature [9]. The recent progress in methods and applications of radiation-induced grafting inside the confined spaces of nanoporous materials has been outlined in a review article [12].

Fuel cell membranes

The use of radiation-induced grafting in preparation of proton-exchange membranes based on fluorine-containing polymers is an attractive technique that have received intensive research efforts [13]. This method allows introduction of graft chains carrying ionic groups to a preformed polymer film by grafting of a vinyl monomer and subsequent functionalization reaction [14]. Compared to conventional preparation methods of ionic membranes, radiation-induced grafting has the advantages of simplicity, low cost, close control over

reaction parameters and ability to tune the content as well as the distribution of the grafted chains in the membranes.

The pore-filled membranes prepared based on track-etched substrates have advantageous properties compared to corresponding membranes with substrates having random pores. The cylindrical pores in the track-etched membranes provide short pathways for the proton transfer. Grafting of polyelectrolytes from the inner surfaces of nanopores provides strong covalent bonding between the polymer base and grafted chains. This approach increases durability of the pore-filled membrane by eliminating the risk of leaching of physically trapped polyelectrolytes during application.

Ion track grafting has been shown to be a promising way of preparing highly conductive membranes for fuel cell applications. Proton conducting membranes were prepared in four steps by γ irradiation grafting of styrene onto Xe ion irradiated ETFE film by: (1) Xe ion irradiation to form the latent tracks and chemical etching, (2) γ -ray pre-irradiation to generate radicals, (3) styrene grafting from radical sites to introduce aromatic rings and (4) sulfonation of aromatic rings to introduce sulfonic acid groups [15]. These membranes showed high proton conductivity depending on the degree of grafting. A maximum proton conductivity of 0.1 S/cm was achieved at a degree of grafting of 50 % and water content of 40 %.

By a similar approach proton conducting individual channels have been created in poly(vinylidene fluoride) PVDF films using ion track grafting technique [16]. Polystyrene was radiation grafted and later sulfonated leading to formation of poly(styrene sulfonate) chains inside the tracks. The cylindrical pores filled with conductive polymers allow proton conduction when used in fuel cells. The optimum degree of grafting has been shown to be 140 %. These membranes assembled in fuel cells showed conductivities between 50 and 80 mS/cm depending on the operating conditions which are values close to that of Nafion used under similar conditions.

Radiation-induced grafting method was also employed for the preparation of micro-patterned proton-exchange membranes. It is known that mechanical properties of a graft polymer film may deteriorate, limiting the use of resultant membranes in fuel cells. One of the approaches used to overcome this problem is partial grafting of a substrate only in defined areas of the film. Patterning with lateral dimensions as small as 100 nm can be achieved by means of either electron beam or lithographic X-ray exposures by using masks [17, 18]. Subsequently, an irradiated substrate is exposed to a monomer solution to initiate graft polymerization. During grafting, growth of the polymer occurs only on the irradiated area and the polymer chains form “brush-like” structures on the surface of the substrate. As a final step, sulfonation is carried out to introduce functionality to the membrane. Consequently, the grafted areas can provide the required ionic conductivity while the remaining non-irradiated areas maintain the mechanical stability of pristine film.

The amount and distribution of proton conducting sulfonic acid groups are among the most critical factors affecting the performance of PEMs. In radiation-induced grafting method these parameters are directly related with the graft characteristics, e.g. lengths of the grafted chains, their distributions, uniformities, etc. By conventional radiation-induced grafting technique, controlling/tailoring of such properties is not achievable. The grafting is totally a random process in conventional radiation-induced grafting and neither the molecular weight nor its distribution can be controlled. The control over free radical polymerization has been achieved during last two decades by reversible activation–deactivation of polymerization kinetics [19]. One of these techniques applicable under irradiation conditions is called reversible addition-fragmentation chain transfer (RAFT) polymerization. The control of chain growth has been made possible by employing special chain transfer agents of thionyl thio compounds [20].

Novel membranes based on ethylene-tetrafluoroethylene (ETFE) copolymer for fuel cell applications have been synthesized by RAFT-mediated radiation-induced graft polymerization of styrene followed by sulfonation as depicted in Fig. 2 [21]. Frontal development of grafting process across the membrane thickness resulted with homogeneous distribution of graft chains with uniform chain lengths hence increasing the compactness of the membranes. The introduction of RAFT-mediated graft polymerization enhanced the structural uniformity and showed a significant increase in terms of proton conductivity compared to conventional grafting.

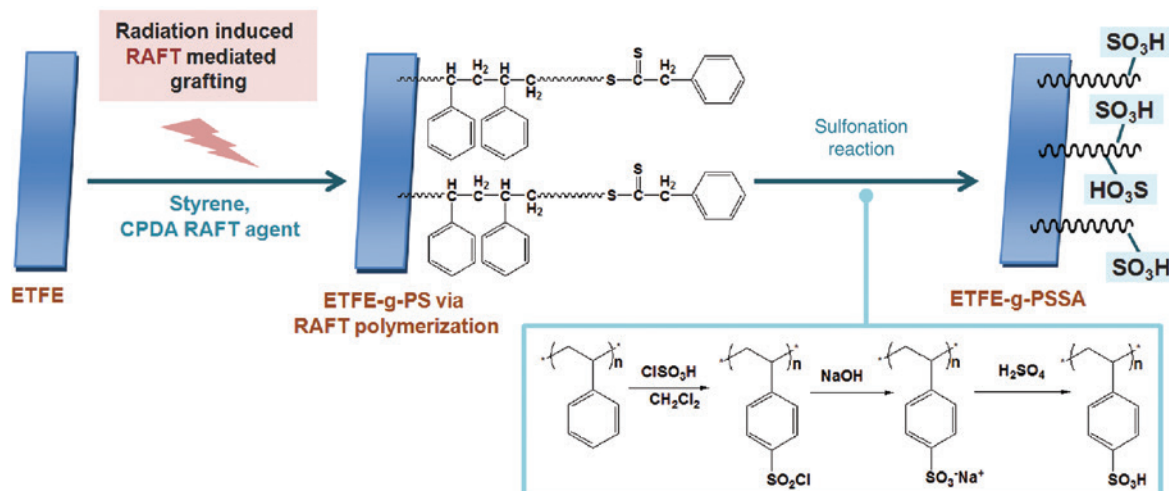


Fig. 2: General procedure of radiation-induced RAFT-mediated controlled grafting of styrene from ETFE films and sulfonation for preparing fuel cell membranes [21].

Sensors/detectors

Another interesting field of application of ion track membranes is in the development of sensors and detectors. Ion tracks are particularly suitable in biosensing applications because they have nanoscale dimensions. Ion tracks can confine chemical reactions in well-defined pre-determined locations ensuring the high enrichment of reaction products locally. If membranes containing such etched, modified tracks are placed in the path of current flows in a vessel, the ions would be forced to pass through the nanopores. The changes occurring in the electrical resistance of the pores would help sensing of chemical reactions. The advantages of using conically etched tracks were shown by Siwy et al. [22, 23] where conically etched tracks were developed by etching the polymer foil from one side only. In a recent work, temperature dependent ionic transport through the nanochannels functionalized by amine-terminated poly(*N*-isopropylacrylamide) brushes has been achieved. The effective pore diameter is tuned by manipulating the temperature via swelling/shrinking behavior of brushes grafted to the nanopore walls, controlling the ionic transport across the membrane [24].

The controlled grafting on wall surfaces of cylindrical nanochannels in track-etched membranes imparts almost endless properties and consequent applications of these membranes. One such recent development is the preparation of polymer thin film electrodes based on radiation modification of poly(vinylidene fluoride) (PVDF) membranes. Poly(acrylic acid) was grafted inside the cylindrical nanopores of track-etched PVDF membranes with 75 nm diameters in a controlled manner by RAFT polymerization [25]. It was observed that the pore diameter decreased steadily with the degree of grafting and pores started to be filled by PAA graft chains beyond ~40 % grafting as determined from AFM measurements. These membranes were transformed into very sensitive polymer thin film electrodes by gold sputtering onto both surfaces of the membrane. These polymer thin film electrodes were found to be very sensitive to sub-ppb concentrations of Pb^{2+} ions in square-wave anodic stripping voltammetry measurements [26]. Controlling of graft chain lengths by RAFT mechanism was found to increase the sensitivity of membrane electrodes almost three times compared to grafting by conventional free radical polymerization in sub-ppb concentrations of Pb^{2+} . Figure 3 shows schematically the formation of graft polymers inside the cylindrical nanochannels of PVDF track-etched membranes and cross-sectional view of a nanopore with grafted PAA capturing lead ions.

The track-etched poly(ethylene terephthalate) (PET) membranes can be used as templates for effective radiochemical synthesis of metallic nanoparticles in the interior of cylindrical nanochannels of the membrane. Radiation-induced synthesis of copper nanoparticles was achieved first by functionalization of interior surface of the nanochannels through successive oxidation and graft polymerization of acrylic acid [27],

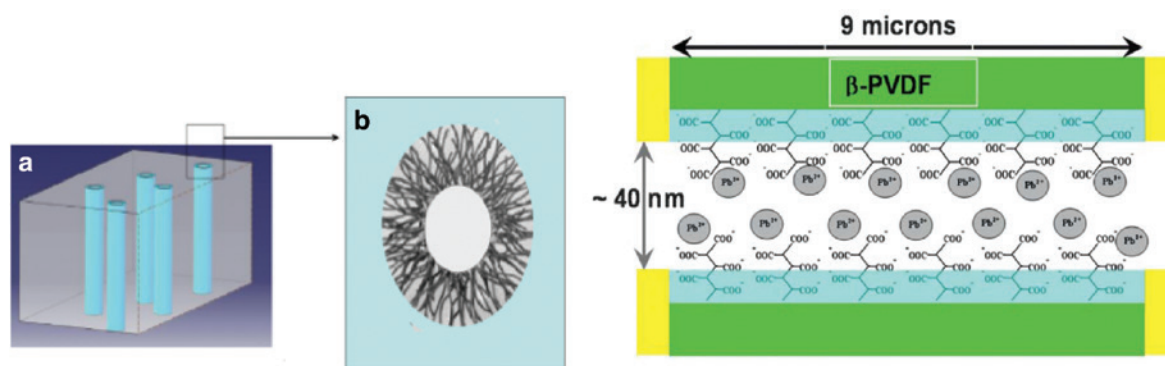
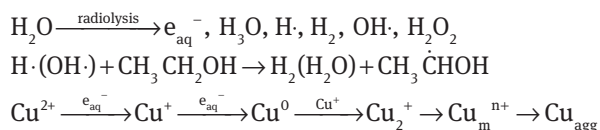


Fig. 3: Diagram showing controlled radiografting of polymer chains on pore walls by RAFT polymerization (a and b) and a single pore from a gold coated 9 micron thick PAA grafted track-etched PVDF membrane with lead ions absorbed from water [25, 26].

which allowed the capture of Cu^{2+} ions by the carboxylate groups and at the same time stabilizing the nanoparticles on the surface and inside the pores of PET membranes. The conversion of Cu^{2+} ions into metallic copper was straightforward by the reaction of extremely reactive hydrated electrons generated in the aqueous irradiation medium. The reaction scheme is shown below [28]:



In the radiolysis of water mainly hydrated electrons, and OH radicals are generated and with equal efficiency. Although hydrated electrons are the strongest reducing agents in aqueous systems, OH radicals on the other hand are the strongest oxidizing species in water. In order to eliminate possible oxidation of radiation synthesized metallic copper nanoparticles to corresponding oxides, OH radical scavengers like ethyl alcohol is added to reaction medium converting the oxidizing species to strong reducing agents like ethyl alcohol radicals thus providing an all reducing reaction medium [29].

The results showed an almost complete reduction of copper ions at a dose of 250 kGy to form metallic copper nanoparticles with an average size of 70 nm [28]. Electron microscopy revealed a good distribution of nanoparticles throughout the length of the nanochannels, as seen from Fig. 4. Track-etched PET membranes with nanometallic copper loaded nanochannels showed promising results for catalytic and sensor applications.

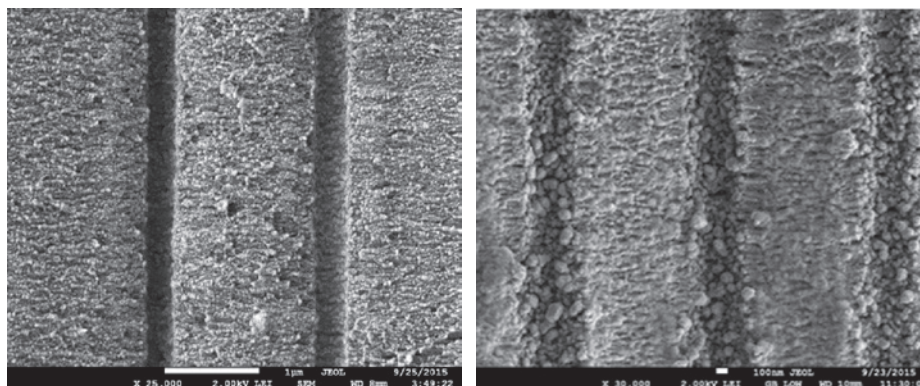


Fig. 4: SEM microphotographs of cross-sectional view of PAA-g-PET nanochannels with (right) and without (left) Cu nanoparticles deposited after γ -irradiation to a dose 98 kGy [28].

Cell culture dishes

When tissue engineering was first proposed in the 1980s the key materials used were biodegradable polymeric scaffolds. By combining preformed polymeric scaffolds and specific cell types, various tissues have been reconstructed. After transplantation of tissue-engineered constructs into hosts the scaffolds degrade over weeks or months. The space formerly occupied by the scaffolds is filled with proliferated cells and deposited extracellular matrix (ECM) such as collagen. However, ECM deposition in tissues often results in fibrosis and some properties of the scaffolds can be undesired in some tissues. This gave rise to the development of Cell Sheet Engineering in order to find solutions to avoid these limitations.

In tissue reconstruction cell sheets are used not single cells. Cell sheets are prepared by using temperature responsive culture dishes. Imparting thermoresponsive properties to the surfaces of culture dishes is best achieved by radiation-induced grafting of a thermoresponsive polymer called poly(*N*-isopropylacrylamide) (PNiPAAm) on the surfaces where cells will be grown. For cell culturing commercially available polystyrene dishes are usually used for grafting of PNiPAAm. Okano and his group for the first time prepared PNiPAAm grafted cell culture dish surfaces by electron beam irradiation [30]. The cell sheets grown at 37 °C with the graft polymer in fully hydrophobic state are detached simply and easily by lowering the temperature below 32 °C with polymer transformed into hydrophilic state as described schematically in Fig. 5 [31]. Very thin layer of radiation-grafted PNiPAAm offers non-invasive control of cell attachment and detachment.

The thickness of the PNiPAAm layer is a key factor affecting the hydration features and hence the cell sheet recovery characteristics. For a PNiPAAm layer with a thickness higher than the desired level, poor hydrophobicity and a non-cell adhesive character are reported as the dehydration promoted by the PNiPAAm chains at the substrate interface cannot efficiently reach the PNiPAAm chains at the outermost surfaces. The optimum thickness of PNiPAAm layer has been found to be 20–30 nm [32]. Fine controlling of the thickness of PNiPAAm within the desired limits is best possible by controlling the free-radical graft polymerization of PNiPAAm from PS petri dish via reversible addition fragmentation chain transfer (RAFT) polymerization already mentioned in Fuel Cell Membranes section. By using this technique in surface initiated grafting it is possible to prepare polymer brushes with well defined, predetermined molecular weights, thus bringing a full control over the thickness of the thermoresponsive graft layer [33].

A rapid cell sheet recovery is desirable for clinical applications. To accelerate the cell-sheet detachment process, hydration of PNiPAAm chains should occur in a relatively short time. In order to facilitate the hydration of PNiPAAm layer, grafting a layer of hydrophilic poly(acrylamide) (PAAm) prior to modification of cell culture dishes with PNiPAAm functionalities enhances the cell recovery features [34]. In an ongoing study

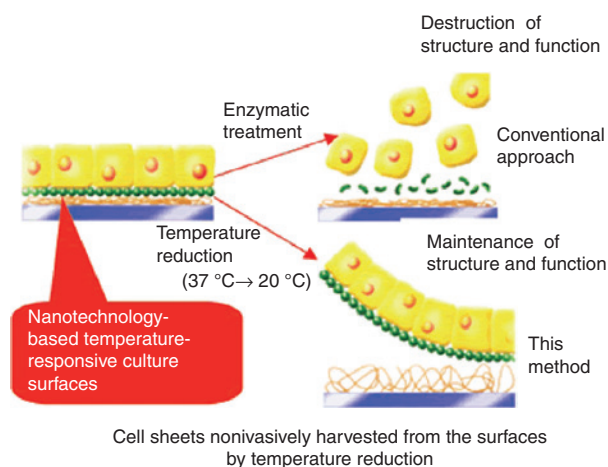


Fig. 5: Cell sheet harvesting from PNiPAAm grafted PS surfaces. Cell sheets grown on hydrophobic surface at 37 °C (shown on the left) can be detached at temperatures below 32 °C from the hydrophilic surface (lower right). Enzymatic treatment would destroy the cell-cell connections as well as deposited ECM [31].

from author's lab PAAm component as a model hydrophilic polymer has been grafted from electron beam (EB) irradiated surface of PS petri dishes via RAFT polymerization. PAAm grafts were further extended by PNIPAAm chains based on the living features provided by the RAFT chain-end moieties of PAAm.

The application of cell sheet technology based on thermosensitive polymer grafting has been extended to include corneal epithelial, esophageal ulceration, cardiac tissue, periodontal tissue, sealing of lung air leak, pancreatic islet tissues [35].

Radiation induced synthesis of nanoparticles

Polymer nanoparticles can be prepared either from preformed polymers or by direct polymerization of monomers using by one of the well known polymerization techniques. Irradiation of polymers in their dilute aqueous solutions would lead to the formation of so-called nanogels which will be discussed in detail under a separate heading. In order to prepare polymeric nanoparticles by irradiating monomers one should make use of either dispersion polymerization or emulsion polymerization techniques. Radiation-induced dispersion polymerization was used to make monodisperse polymer nanoparticles with narrow particle size distribution from monomers such as acrylamide [36], and methyl methacrylate [37].

One of the most interesting applications of radiation-induced dispersion polymerization is the synthesis of monodisperse poly(tetrafluoroethylene) (PTFE) particles with ~ 200 nm as shown in Fig. 6. PTFE was obtained by radiation-induced polymerization of tetrafluoroethylene in acetone at -78°C . The average size of PTFE particles was very small compared to commercially available ones. 100 % conversion was reached at 4 kGy absorbed dose. The abrasion resistance of the new product was excellent [38].

The nanoparticles of chitosan with average size of 15 nm obtained by irradiating aqueous chitosan solutions have been used as a water based antioxidant and a reducing agent for the preparation of gold nanoparticles [39].

In the conventional emulsion polymerization the ingredients are comprised of water, water-insoluble monomer, water soluble initiator and a surfactant. In radiation-induced emulsion polymerization there is no need to use initiators since monomer molecules are transformed into initiating radicals by direct or indirect absorption of γ radiation. Phase separation and formation of solid polymeric particles take place during the polymerization reaction. Recently emulsified monomers are used in radiation-induced grafting of monomers onto polymeric substrates to ensure the formation of very thin, nanoscale graft layers. The additional advantage of emulsion grafting is working at low doses. To achieve the same degree of grafting, dose requirement is reduced minimum 10 times when grafting is performed in emulsion state rather than direct grafting from monomer solution [40].

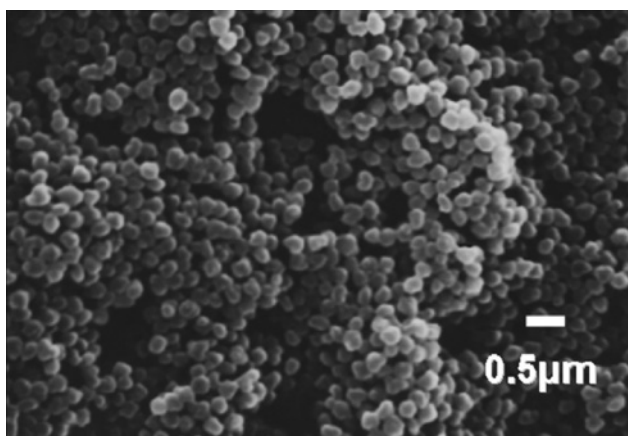


Fig. 6: SEM photograph of dried PTFE nanoparticles obtained by γ irradiation of TFE in acetone solution [38].

Nanogels

Intramolecularly crosslinked coils of hydrophilic or amphiphilic polymers or copolymers swollen in water are termed as nanogels. They are versatile nanoscopic drug delivery systems, carriers of pharmaceuticals because of their high loading capacity, high stability, and response to environmental stimuli [41]. The chemical structures of nanogels allow them to swell in aqueous environments and respond to stimuli such as temperature, pH, electrical field and ionic strength of the medium [42]. The loading of medical and pharmaceutical agents is usually achieved through electrostatic, hydrogen bonding and hydrophobic interactions between the agent and polymer matrix.

Currently nanogels are prepared by one of the following approaches: (1) physical self-assembly of inter-active hydrophilic polymers, (2) polymerization of monomers in micro or nano heterogeneous environment, (3) crosslinking of preformed polymers and (4) template assisted fabrication of nanoparticles [43]. Among the four methods mentioned above covalent crosslinking of preformed polymer chains provides unique opportunities especially when ionizing radiation is used as the tool to induce crosslinking where the synthesized nanogel would be free from monomer, crosslinking agents or surfactants thus eliminating the purification step. The free radicals are generated on the polymer chains upon direct absorption of radiation or via abstraction of hydrogen by the attack of OH radicals generated abundantly by the radiolysis of water. These polymer-bound radicals combine intra-molecularly to form covalent bonds within a single coil in dilute aqueous solutions. Figure 7 below shows the use of low dose rate γ irradiation and high dose rate electron beams for the synthesis of nanogels with different sizes.

This versatile, reproducible and low-cost method has been used in recent years after the first report published on radiation formation of polymeric nanogels where the requirements for the formation of nanogels and prevention of macro-gelation were elaborated [46]. The conditions for the formation of nanogels are met when the polymer coils are well separated from each other and when high numbers of radicals are generated on a single coil. These requirements can be smoothly fulfilled when working in very low polymer concentrations and processing with high dose rate [47].

The particle size of nanogels is of great practical importance, and becomes the controlling factor especially for drug and vaccine delivery applications. Particle size affects the blood circulation time, viscosity and drug loading capacity [48]. Particles with diameters ranging from 70 to 200 nm demonstrate the most prolonged circulation times hence maximum bioavailability [49]. Therefore tuning the size and size distributions of nanogels is highly important for their *in vivo* biodistribution. A detailed parametric study [44, 45] gives the guidelines for the radiation synthesis of nanogels within a size range of 30–200 nm which is the range most suitable for biomedical applications. For a given water soluble polymer this range of nanogels can be synthesized by changing the molecular weight, concentration of the polymer as well as the total absorbed dose and dose rate

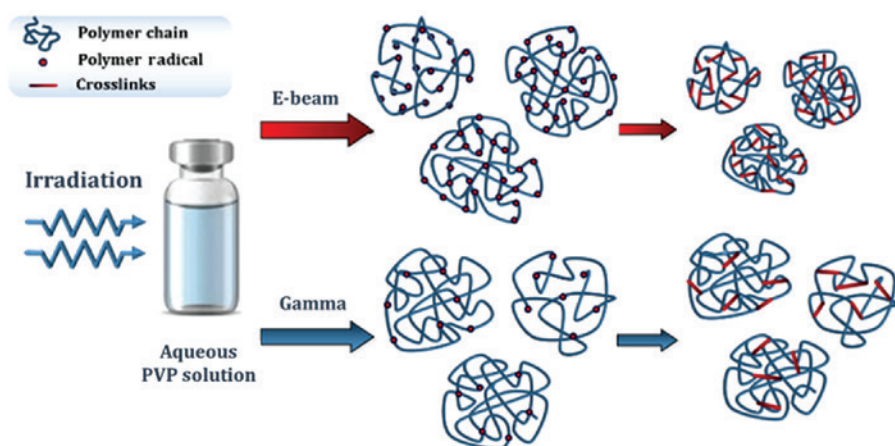


Fig. 7: Scheme showing the formation of nanogels with different sizes by high dose rate e-beam and low dose rate γ irradiation [44, 45].

of radiation. The two most important parameters to be considered are the concentration of polymer solution and the dose rate of radiation. Radiation-induced synthesis of nanogels have been used in the preparation of poly(N-vinyl pyrrolidone) [50], amine-functionalized poly(N-vinyl pyrrolidone) [51], poly(acrylic acid) [52] nanogels. Nanogels with various chemical functionalities can be easily prepared by irradiation of dilute solutions of interpolymer complexes obtained from different binary polymer combinations [53, 54]. Interpolymer complexes can be prepared from non-ionic, polycationic, polyanionic or amphiphilic polymer or copolymers.

Radiation-assisted synthesis of nanocomposites

Polymer thin films containing metal nanoparticles

Polymer films embedded with metal nanoparticles have shown great potential in various applications and industries such as, electronics, catalysis, chemical sensors/detectors, semiconductors and antibacterial surfaces. The size of the metal nanoparticles and the distance between them in a polymer matrix are known to have great influence on their electronic, magnetic and optical properties. Therefore control over size, dispersion, shape and homogeneity is very important for developing new devices with advanced capabilities [55].

Metal nanoparticles stabilized in a host polymer matrix can be synthesized by various routes all based on the reduction of precursor metal ions. The reduction of metal ions into their metallic state with the formation of nanoclusters can be achieved by; (a) using different chemical reducing agents, (b) photoreduction, (c) sonochemical, and (d) using ionizing radiation [56]. The unique advantage of radiolytic synthesis lies in the fact that the strongest reducing agent in aqueous environment namely, hydrated electron $\{E^\circ [\text{H}_2\text{O}/\text{e}^-(\text{aq})] = -2.87 \text{ V}\}$ is generated in-situ in de-aerated solutions with very high efficiency. This enables reduction of any metal ion including noble metals to their zero valence. The metal nanoparticles thus obtained are pure and very stable. γ irradiation of aqueous metal salt solutions for the synthesis of metal nanoparticles offers unequaled advantages of simplicity, reproducibility, absence of impurities and application at room temperature. By using X-rays or accelerated electrons with a range of dose rates it is also possible to have a control on the size and size distribution of metal nanoparticles. The higher the dose rate the higher will be the concentration of hydrated electrons hence increased nucleation rates of particle formation leading to the formation of nanoparticles with smaller sizes [29].

The stability of synthesized metal nanoparticles has been achieved by using proper capping agents or polymers appropriate for the specific metal ions. Radiation synthesized noble metal nanoparticles have been found to be relatively stable while stability of copper nanoparticles has been a challenge due to their easy oxidation [57]. It has been shown that when copper ions complexed with interpolyelectrolyte complexes of poly(acrylic acid) and poly(allyl amine), copper nanoparticles with very high stability can be obtained by γ or x-ray irradiations of films in the presence of water. The mechanism of reduction of Cu^{2+} under irradiation in aqueous environment has already been explained in the subsection titled Sensors before. It was shown that nanoparticles having sizes in the range of 3–4 nm and 5–10 nm were obtained when X-ray and γ irradiation were used, respectively. Controlling of nanoparticle sizes was achieved by using different radiation source, radiation dose and polymer/metal ion ratio. The metallic copper nanoclusters were observed to be stable when imbedded in polymer films for several months [58]. Figure 8 shows the TEM images of copper nanoparticles embedded in polymer blend films together with their electron diffraction patterns. The stability of copper nanoparticles thus synthesized against oxidation showed a good prospect for their use as sensors and catalysts.

Polymer/clay nanocomposites

Polymer/Clay Nanocomposites were first developed in 1985 in Toyota Central Research Laboratories and commercially applied to passenger cars in 1989 [59]. When a few percent of silicate layers of clay are randomly and homogeneously dispersed in polymer matrix superior mechanical, thermal and barrier properties are

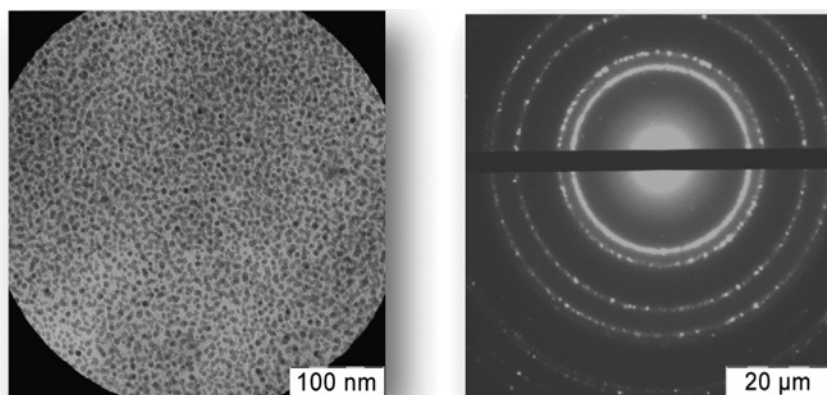


Fig. 8: TEM images of blend films composed of Poly(acrylic acid)/Poly(allyl amine)/Cu(II) in 2/2/1 molar ratio irradiated to 140 kGy dose at pH = 8.6. The average particle sizes of copper nanoparticles are 6 nm [58].

imparted to host polymers. Commodity or engineering polymers have long been reinforced with particulate or fibrous fillers such as talc, calcium carbonate, carbon black, glass or carbon fibers, typical content of a filler being usually between 20 and 40 %. Polymers and filler are not mixed homogeneously on a microscopic level limiting the interaction between the matrix and the filler. If mixing could be achieved on molecular level, the interface would be increased and interaction much improved.

According to the International Union of Pure and Applied Chemistry, a nanocomposite is a composite in which at least one of the phase domains has at least one dimension in the order of 1–100 nm [60]. Montmorillonite (MMT), one of the most abundant clay minerals has been shown to be a very good nanofiller since the layered silicates are 1 nm thick and have a cross-sectional area of 100 nm². Polymer/Clay nanocomposites can be prepared either by polymerizing a monomer in the presence of a clay or by solution or melt mixing of a polymer with the clay. Since clays are hydrophilic substances and most of the matrix polymers hydrophobic, either the clay or the polymer should be rendered more compatible with each other. This problem has been solved to a great extent by using commercially available organo-modified montmorillonites. Nylon6, polyimides, polypropylene, polyethylene, ethylene-vinyl acetate copolymers and rubber have been extensively investigated as the matrix polymers for polymer/clay nanocomposites. Ionizing radiation can be used in different ways for the preparation of polymer/clay nanocomposites. It can be used to initiate in-situ free radical polymerization inside the clay structure and depending on the chemical structure of monomer, simultaneous crosslinking of liquid vinyl monomers mixed with 1–5 % clay mineral thus forming the nanocomposite. Electron-beam induced reactive in-situ modification of unmodified MMT in polypropylene has been achieved. The effect of different electron-beam parameters such as electron energy and absorbed dose on intercalation/exfoliation of MMT in PP was investigated [61]. Recently RAFT-mediated grafting of polystyrene from the radicals confined on the surface of clay was investigated [62]. Polyolefines can be irradiated in air to control radiation-induced oxidation to impart polar and hydrophilic properties to enhance their compatibility with the clay. γ irradiated polypropylene was used as a compatibilizer in the preparation of short carbon fiber reinforced polypropylene composites. Strong compatibilizing effect of irradiated PP (radiation degraded and oxidized) on the mechanical properties of the composite was observed [63]. Another approach can be irradiation of compounded polymer/clay system to introduce crosslinks within the matrix to enhance mechanical and barrier properties.

Conclusions

The possibility of using particulate or electromagnetic wave based ionizing radiations in giving polymers nanosizes and shapes is almost endless. Only some of the examples exclusively based on radiation-induced

grafting on nanoscale were mentioned in this paper. In conjunction with the developments in controlled free radical polymerization, radiation-induced RAFT mediated grafting will have great potential in developing new materials in the near future. Ionizing and penetration ability of high energy radiations will benefit easy and rapid preparation of nanomaterials such as nanogels, nanocomposites, nanoparticles for a variety of applications ranging from drug delivery to tissue engineering, from sensors/detectors to specialty membranes. The increasing role of ionizing radiation in nanotechnology applications has been emphasized in a compilation of patents based on the use of radiation in nanotechnology [64]. The prospect of using ionizing radiation in nanotechnology is not limited to the applications mentioned in this review but will diversify to include the preparation of monoliths [65] for chromatographic applications, controlling of cavity size in molecularly imprinted polymer matrices [66], etc. There is also room to use ionizing radiation to impart compatibility to otherwise incompatible systems by radiation-induced admiscellar polymerization [67] hence deposition of very thin polymer films on hydrophobic or hydrophilic surfaces.

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