

Review

Radiation-Assisted Synthesis of Polymer-Based Nanomaterials

Olgun Güven

Department of Chemistry, Hacettepe University, 06800 Beytepe, Turkey; guven@hacettepe.edu.tr;
Tel.: +90-312-297-7977

Abstract: Radiation technology has long been proven as a simple, rapid, green and sustainable technology with macroscale applications in healthcare, industry and environment. Its merits, however, have not been fully utilized in today's ever growing nanotechnology. Ionizing radiation has beneficial effects for the synthesis and modification of structure and properties of nanomaterials. This paper intends to update the application of ionizing radiation in the development of various nanomaterials under the categories: (i) carbon-based nanomaterials, (ii) metal-based nanomaterials, (iii) polymer-based nanomaterials, (iv) polymer nanocomposites and (v) nano-scale grafting for advanced membrane applications.

Keywords: nanomaterials; gamma radiation; electron beam; nanogels; quantum dots; nanoscale grafting; advanced functional membranes



Citation: Güven, O. Radiation-Assisted Synthesis of Polymer-Based Nanomaterials. *Appl. Sci.* **2021**, *11*, 7913. <https://doi.org/10.3390/app11177913>

Academic Editors: Dorota Swiatla-Wojcik, Yosuke Katsumura and Radosław A. Wach

Received: 4 August 2021

Accepted: 26 August 2021

Published: 27 August 2021

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1. Introduction

The Japanese scientist Norio Taniguchi of Tokyo University was the first to use the term “nano-technology” in a 1974 conference to describe semiconductor processes such as thin film deposition and ion-beam milling exhibiting characteristic control on the order of a nanometer. His definition was that “nano-technology” mainly consists of the processing of separation, consolidation and deformation of materials by one atom or one molecule [1].

Nanotechnology is the science and technology of making and using very small structures called nanomaterials. As the scales of the constructions become smaller, the conventional methods of making these structures—lithography, etching, micromolding—reach physical limits and it becomes extremely difficult to apply these top-down methods at nanoscale dimensions. To overcome the limitations and create smaller and ordered structures, a so-called “bottom-up” approach must be used. As the component size decreases in nanofabrication, the “bottom-up” approach is being increasingly used in the preparation of nanomaterials, which are materials with at least in one dimension less than 100 nm in size.

The ionizing radiations 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 generate free radicals homogeneously in the media they pass through. This allows irradiation of monomers or polymers in any state at—or if needed, below—room temperature. These unique properties make ionizing radiation a very useful tool for the preparation of nanomaterials [2,3].

Nanomaterials are currently categorized into four types:

1. Carbon-based nanomaterials;
2. Metal-based nanomaterials;
3. Polymer-based nanomaterials;
4. Composite nanomaterials.

Quantum dots can be considered as new-generation nano-systems with hybrid metalloid–polymer structures which can be included under metal-based nanomaterials. Materials prepared from graft copolymers with nanoscale graft chain lengths can also be considered as nanomaterials and will be discussed under a separate title.

Nanomaterials are synthesized by one of the three different approaches: chemical, physical or biological methods. Although various techniques are employed under one of these three approaches for the synthesis of nanomaterials, ionizing radiation is seldom mentioned as either a standalone technique or in combination with any conventional technique as a tool for the preparation of polymeric nanomaterials. The aim of this short review is meant to bring awareness of the advantages of using ionizing radiation for the synthesis of nanomaterials.

2. Carbon-Based Nanomaterials

The basic constituent of these nanomaterials is carbon in the form of carbon nanotubes (CNT), graphene and fullerenes. One of the major problems associated with this all-carbon nanomaterial family is their poor dispersion in aqueous and even organic media due to their hydrophobic and fused aromatic structures. The formation of agglomerates, clusters of these carbon-based nanomaterials limits their use for some applications such as in biomedical devices, drug delivery platforms, etc. CNTs, graphene and fullerenes are generally used as nanofiller for the preparation of polymer nanocomposites to achieve superior properties. However, their poor compatibility with commodity and engineering polymer matrices prevents these materials from achieving their full potential. To overcome these problems, surface modification of carbon nanomaterials by covalent and noncovalent functionalization has been elaborated [4]. Covalent functionalization of these fully aromatic compounds is best achieved via reactions to be initiated by irradiation with gamma rays or accelerated electrons.

Pre-irradiation of CNTs with gamma rays can be applied to disintegrate the agglomerates and disperse them into a polymer matrix and to maintain stable dispersions instead of using a dispersant or reducing agent [5]. Chemical functionalization and subsequent dispersion were better achieved for the irradiated CNTs as compared to pristine CNTs. Enhanced interaction between CNTs and polymer matrix help in uniform dispersion improving the electrical and mechanical properties of corresponding composites. Fullerene was shown to be functionalized with –OH groups by gamma irradiation in methanol solution for biosensor applications [6]. Water-soluble poly(acrylic acid) grafted multiwalled carbon nanotubes (MWCNTs) were prepared by two-step gamma irradiation [7]. Solution processable reduced graphene was prepared first by radiation-induced reduction of graphene oxide later grafted with poly(vinyl pyrrolidone) by pre-irradiation technique [8]. Green synthesis of water-dispersed graphene nanosheets was achieved by gamma irradiation and using natural capping agents [9]. The surface of CNTs was functionalized by radiation-induced grafting of acrylic acid, methacrylic acid, glycidyl methacrylate, maleic anhydride and 4-vinylphenylboronic acid [10]. The CNT/polymer nanocomposites were shown to be successfully prepared by radiation curing using epoxy resins [11]. These works and many other clearly show that ionizing radiation is a very useful tool to functionalize CNTs, graphene and fullerene to make them compatible with a variety of polymer matrices for the preparation of nanocomposites.

3. Metal-Based Nanomaterials

Metal nanoparticles have a number of potential applications in many fields such as electronics, energy, medicine, magnetics, sensors, catalysis, optical devices, antibacterials and fungicide. A variety of metal nanoparticles were fabricated by top-down approaches such as mechanical milling, grinding, etching, sputtering, laser ablation, etc. These methods are generally costly, energy-intensive, with loss of starting materials or maybe harmful to the environment; therefore, more environment friendly procedures should be developed that will make the whole process greener [12].

Nano-sized materials have special characteristics that can be exploited for a number of advanced functional applications. However, difficulty in handling these very small objects has represented a strong limitation to their use. In addition, most of nano-sized metals are very instable. They can aggregate because of the high surface free energy and

can be oxidized by air, contaminated by surrounding atmosphere. Metal nanoparticles are generally utilized as embedded in an appropriate matrix. The embedding of nanoscopic metals into polymers is particularly interesting since they have a variety of characteristics. Polymer embedding is the easiest and most convenient way for the stabilization and use of nanometals. The universal method for the controlled synthesis of metal nanoparticles is by in situ reduction of metal ions.

3.1. Polymer–Nanometal Composites

A limited number of methods have been developed for the preparation of metal–polymer nanocomposites. Usually, such techniques can be classified as in situ and ex situ methods. In the ex situ processes, metal nanoparticles are chemically synthesized and their surface is organically passivated. The derivatized nanoparticles are dispersed into a polymer solution or liquid monomer that is then polymerized.

In the in situ methods, two steps are needed. First, the monomer is polymerized in solution with metal ions introduced before or after polymerization. Then, metal ions in the polymer matrix are reduced chemically, thermally or by radiation. The synthesis of metal nanoparticles from a diluted precursor involves several steps: reduction of metal ions by electron transfer, inducing nucleation and growth of the seeds into nanoparticles controlled by the stabilizers [13]. When aqueous solutions containing metal ions are exposed to ionizing radiation, the strongest reducing agent, namely in situ generated hydrated electron, $\{E^\circ [\text{H}_2\text{O}/e^-(\text{aq})]\} = -2.87 \text{ V}$, reduces any metal ions to their metallic state. The size and size distribution of metal nanoparticles can be controlled by the type (X-rays, gamma rays, accelerated electrons) of radiation, dose rate and metal ion/polymer ratio [14]. Polymer–nanometal composites with very unstable metal nanoparticles can be easily and safely prepared by this method by proper selection of polymers. One of these unstable metal nanoparticles, copper, when embedded in polymer films, was found to be stable for several months [15]. The stabilization of metal nanoparticles in polyelectrolyte matrices makes it possible to prevent their oxidation and aggregation. A wide variety of nano structures were synthesized because of the possibility of controlling the interaction between functional groups of polyanions and polycations with metal ions. The stability of metal nanoparticles can be achieved by using appropriate polymers or interpolymer complexes [16]. Bimetallic nanoparticles were synthesized in the films of interpolymer complexes. It was shown that radiation-induced reduction of (Cu/Ag) and Cu/Au) nanoparticles irradiated in the aqueous matrix of poly(ethylene imine)-poly(acrylic acid) complexes lead to the formation of bimetallic nanoparticles with narrow size distribution [17].

A recent review summarizes the radiation-induced synthesis of various nano-sized compounds including metals, metal alloys, core-shell systems, metal oxides, etc. [18].

3.2. Quantum Dots

Quantum Dots (QDs) are fluorescence type semiconductor nanosized particles which are composed of core material enclosed within a shell of another semiconductor material. They are made up of either heavy metal or inorganic materials with size range from 2 to 10 nm. Semiconductor materials in the outer shell of QDs facilitates the surface for bioconjugation. This provides effective surface area for binding of drugs with the target molecule. Functionalization and modification of the surface makes them suitable for applications in the pharmaceutical field, such as biomedical imaging, drug delivery and drug release studies. The semiconductor outer shell of QDs is made of heavy metals or inorganic materials such as cadmium, selenium, zinc oxide, silica, etc., which are coated with shell material. Figure 1 shows the ideal structure of a semiconductor quantum dot. Semiconductor QDs are synthesized through high temperature, gamma irradiation, and microwave and sol-gel techniques [19]. In the synthesis via gamma irradiation, the precursor is irradiated with γ -rays to different doses to form a colloidal product. This method is extensively used in the preparation of metal and metal oxide QDs as exemplified below.

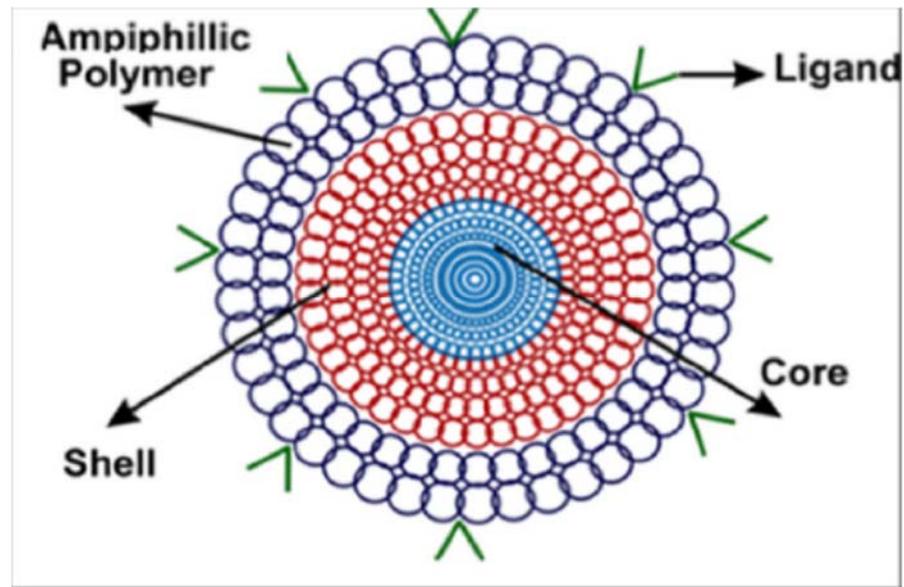


Figure 1. Semiconductor quantum dots. Reprinted with permission from Ref. [19]. Copyright 2021 Elsevier.

Cadmium selenide (CdSe) QDs are one of the most intensively studied among all QDs because of its wide applications as sensors, biomarkers, LEDs and photovoltaics. Radiation-chemical methods have been preferred among various routes of synthesis of CdSe QDs.

Chitosan-coated CdSe QDs were successfully synthesized in aqueous system through a gamma irradiation method at room temperature and ambient pressure. The diameter of the resulting QDs was about 4 nm with narrow size distribution [20].

Polymer films of poly (vinyl alcohol) containing CdSe QDs of various sizes from 3 to 5 nm have been synthesized by a radiation-chemical route using CdSO_4 and Na_2SeSO_3 as the starting materials under a reducing condition. The 2 MeV electron beam and γ -radiation were used for the synthesis. The sizes of QDs were found to be strongly dependent on the dose rate of radiation and initial precursor concentrations. The films containing these QDs were quite stable for months [21].

In a more recent work, CdSe QDs were synthesized in aqueous solutions using equimolar cadmium sulfate and sodium seleno sulfate through 7 MeV electron beam irradiation in the presence of different saccharides. Starch was found to have a better capping property, whereas glucose was found to reduce their cytotoxicity effect. The mechanism of radiolytic synthesis of these QDs was investigated by pulse radiolysis studies [22].

SnSe QDs have been mainly prepared by chemical vapor deposition, vacuum evaporation, electrodeposition and hydro- or solvo-thermal methods. In these methods, the growth temperatures are high and temperature gradient has to be carefully controlled in addition to the problem of using toxic organometallic precursors. A fast and easy method of ionizing radiation was exploited for the synthesis of SnSe QDs at room temperature with the aid of CTAB as the surfactant. The QDs obtained with an average diameter of 4 nm showed strong blue luminescence [23].

The synthesis of size-controlled, stable ZnSe QDs with narrow size distribution in aqueous environments by conventional chemical methods remains to be a challenge. Stable, monodisperse and luminescent ZnSe QDs capped with chelating ethylene diamine were synthesized under ambient conditions. The concentration of precursors, zinc salt, selenium source, ethylene diamine and absorbed dose (7–90 kGy) were optimized for obtaining good quality particles. Selective quenching of luminescence of as-synthesized QDs by Cu^{2+} ions showed a detection limit of cupric ions in nano-molar range [24].

CdS QDs of 1.3–5.6 nm have been synthesized in micellar solutions by gamma irradiation. It has been found that γ -irradiation reduces the size polydispersity and enhances the fluorescence of QDs. For the first time, the average fluorescence lifetime of single QD was observed to increase after γ -irradiation at an absorbed dose of 7.9 kGy [25].

Room temperature synthesis of graphene QDs via electron-beam irradiation has been achieved. A nitrated polycyclic aromatic hydrocarbon (PAH) namely, 1,3,6-trinitro pyrene in aqueous solution of hydrazine hydrate was e-beam irradiated to various doses. Graphene QDs obtained exhibited highly efficient fluorescence at 475 nm with a quantum yield of 32%. Their application as a safety fluorescent probe for cell imaging is demonstrated [26].

4. Polymer-Based Nanomaterials

The above mentioned conventional techniques and more sophisticated ones developed typically involve expensive chemicals, difficult processing techniques and specialized chemistry. However, treatment with ionizing radiation of monomers or polymers with the same aim has been shown to be a simple, rapid and so-called green technique operated at ambient conditions [3].

Polymer-based nanomaterials can be prepared by irradiating either polymers or monomers with ionizing radiation to comply with the two basic approaches of nanotechnology, namely top-down and bottom-up. The polymers predominantly degrading with radiation are suitable for lithographic applications and developing track-etched membranes, demonstrating typical top-down applications already matured to industrial level. However, there is more room in the preparation of polymer-based nanomaterials by the bottom-up approach. In the following examples, bottom-up synthesis of polymer-based nanomaterials by ionizing radiation is discussed.

Radiation-induced grafting has been successfully used to functionalize track-etched membranes, improve properties of fuel cell membranes, make the surfaces of cell culture dishes thermoresponsive and develop specialty adsorbents and molecularly imprinted polymer matrices, just to name the most established applications. Irradiation of aqueous solutions of polymers leads to the formation of nanoparticles, nanogels, polymer–clay nanocomposites, and polymer–metal nanocomposites.

4.1. Polymer Nanoparticles

Emulsion polymerization has been known to be a conventional method for the preparation of polymer particles in the size range of 100–1000 nm. It has been shown that by applying mini- and micro-emulsion techniques, particles with size ranges of 50–200 and 20–50 nm, respectively, could be prepared. It is known that in micro-emulsion polymerization, a large amount of surfactant is needed to make nano-sized particles. However, the removal of surfactant from the resultant dispersion is extremely difficult. Emulsions are not thermodynamically stable systems and the stability of emulsion during the course of the irradiation period must be checked. The developments on radiation-induced emulsion polymerization have been discussed in a recent review by Wang et al. [27].

It has been suggested that block copolymers can self-assemble into nanoparticles in a selective solvent in which only one block is soluble [28]. Not only block copolymers but also ionomers have been shown to self-assemble in a selective solvent to form surfactant-free nanoparticles. The self-assembly can be induced by chemical reaction, polymer-polymer complexation and microphase inversion. In this respect, micro-wave radiation has been used to prepare uniform surfactant-free nanoparticles [29].

Using monomers as the building blocks, polymer nanoparticles can be directly synthesized by radiation-induced dispersion and emulsion polymerization techniques. Dispersion polymerization is a simple single-step process leading to the formation of micron to sub-micron size microbeads as shown in the case of synthesis of highly monodisperse PMMA particles by irradiation of MMA in aqueous alcohol solution [30]. One of the most interesting examples of preparation of polymer-based nanoparticles by radiation-induced dispersion polymerization is the synthesis of PTFE nanoparticles with ~200 nm. When

the dispersion of tetrafluoroethylene in acetone was gamma irradiated at $-78\text{ }^{\circ}\text{C}$, 100% conversion was achieved at 4 kGy with the formation highly monodisperse nanoparticles. The PTFE nanopowder obtained has excellent properties of friction and abrasion [31]. Chitosan nanoparticles with average size of 15 nm were synthesized by gamma irradiation of its dilute solutions. These particles were tested for their antioxidant properties as well as a reducing agent for the preparation of gold nanoparticles [32].

4.2. Protein-Based Nanoparticles

In medical applications, surface potential of nanoparticles significantly affects their accumulation in the cell. In addition to particle size and surface potential, the presence of amino acids in particle structure is an important factor for cell adhesion. This invoked interest in radiation modification of proteins. Protein-based drug carriers are promising alternatives to traditional polymeric drug delivery systems due to their intrinsic biocompatibility and biodegradability. Albumin nanoparticles are known for their effectiveness and safety as drug carriers. Numerous functions and properties of serum albumin have attracted the interest of scientists for the preparation of its nanoparticles. Classical methods of chemical crosslinking or thermal gelation may cause undesirable reactions and protein denaturation. Hence, as a room temperature process not requiring chemical crosslinking agents, ionizing radiation has been found to be quite advantageous for the preparation of albumin nanoparticles. It has been shown that gamma irradiation of ethanol solution of Bovine Serum Albumin (BSA) allowed the formation of nanoparticles within the size range of 20–40 nm [33]. The mechanism of radiation-induced formation of albumin nanoparticles has been elaborated and explained by a two-step process. First, protein molecules aggregate in the water/ethanol mixture. Changing the concentration of ethanol provides a certain level of size control of the aggregates prior to the second step of irradiation. Irradiation of albumin solution leads to the formation of corresponding nanoparticles via intramolecular crosslinking within the coil. The optimization of parameters of cosolvent concentration and irradiation dose allowed fine tuning of nanoparticle size from 7–70 nm [34]. Radiation-induced synthesis of other protein-based nanoparticles has been demonstrated also as a technique capable of inducing protein crosslinking and conferring controllable particle size at nanoscale, while preserving their biological properties. Papain nanoparticles of $7.7 \pm 0.9\text{ nm}$ and 85% residual proteolytic activity were synthesized using phosphate buffer and ethanol as cosolvent irradiated to 10 kGy dose [35]. Basically, the technique combines, as in the case of albumin, protein aggregation by means of protein desolvation and radiation-induced intramolecular crosslinking. This approach has been recently advanced by the same group to have a better understanding of crosslinking process and the possible contribution of tyrosine linkages and disulfide bridges on the formation of nanoparticle assembly. The feasibility of radiation sterilization of nanoparticles during their synthesis was also checked [35].

In order to establish a nanoparticle platform suitable for diagnostic and drug delivery applications, peptides composed of aromatic amino acid residues were designed and synthesized by means of radiation crosslinking mechanism of proteins. The peptide nanoparticles with particle size of $\sim 100\text{ nm}$ produced by γ -irradiation (5–15 kGy dose range) displayed a positive surface potential, maintained biodegradability and were stable in water and phosphate buffer solution during actual diagnosis [36].

4.3. Nanogels

Polymeric nanogels are nanosized hydrogel particles prepared by physical or chemical crosslinking of hydrophilic or amphiphilic polymers which can be ionic or nonionic. The size of nanogels ranges from 20–200 nm. Nanogels can be prepared by one of these methods [37]: (1) physical self-assembly of interactive hydrophilic polymers, (2) polymerization of monomers in micro or nano environment, (3) crosslinking of preformed polymers or (4) template assisted fabrication of nanoparticles. Covalent crosslinking of preformed polymers exposed to ionizing radiation was first proposed by Rosiak [38] and elaborated

by Rosiak and Ulanski in the years to follow in many publications that laid the foundations of radiation synthesis of nanogels [39]. This method provides unique opportunities, as the synthesized nanogels would be free from residual monomers, crosslinking agents or surfactants, thus eliminating tedious purification steps. By working with dilute polymer solutions, the formation of intermolecular crosslinks between polymer coils can be reduced in favor of intramolecular crosslinks within a single coil with resultant nanogels. Crosslinks are formed by combination of polymer-bound radicals generated either by the direct action of radiation or via the OH radical attacks abstracting hydrogen from polymer chains abundantly produced by the radiolysis of water. In order to avoid formation of intermolecular crosslinks, concentration of polymer chains must be kept at minimum, which results with the absorption of radiation by the water of the medium. OH radicals abundantly generated in water will attack polymer chains with possible reactions depicted schematically in Figure 2. By taking the necessary precautions, most of these reactions can be suppressed in favor of the desired one.

In fact, non-radiation methods such as electrochemistry [40] and Fenton reactions [41] can also be used in the generation of OH radicals in aqueous environment to abstract hydrogen atoms from polymer backbones to initiate intramolecular crosslinking for the synthesis of nanogels. The conditions for the radiation synthesis of nanogels are fulfilled when working in very low polymer concentrations and using high dose rates [38]. The control of particle size of nanogels is of great importance as they affect the blood circulation time, viscosity and drug loading capacity. Particles with diameters ranging from 70–200 nm are known to show the maximum bioavailability [42]. The molecular weight and concentration of polymer and total dose and dose rate are the factors affecting size of nanogels. The prospect of radiation synthesis of nanogels from aqueous polymer solution was elaborated in a very recent review [43]. Current techniques used in designing nanogels with a future outlook was the focus of another review highlighting the upgrades in the methodologies, microfluidics and 3D printing [44]. In the following two sections, radiation formation of PVP and PAA nanogels is discussed, as these are the water-soluble polymers most frequently studied by different groups.

- PVP nanogels

The synthesis of PVP nanogels by radiation has been widely investigated as PVP is an FDA-approved polymer for medical applications. Formation of intramolecular crosslinks within a PVP coil by using ionizing radiation was first proposed by Rosiak [38], who also developed the idea of radiation synthesis of PVP-based hydrogel wound dressings. A review published in 2014 collects results of the early studies on radiation synthesis of PVP nanogels [45]. During the past decade, the groups led by Dispenza from Italy and Abd El-Rehim from Egypt intensified their research on various aspects of radiation synthesis and applications of PVP nanogels. The formation of primary amino groups and carboxyl groups useful for bioconjugation were followed as a function of dose [46]. By working with both N_2O and air-saturated conditions, the impact of oxygen with the consequences of H_2O_2 formation on nanogel properties was investigated. A very simple and effective method to quantitatively measure formation of double bonds on PVP was also proposed [47]. Although PVP is not a thermosensitive polymer, at relatively high temperature, the coils start to shrink due to loss of water of hydration with eventual collapse into tight coils. When thermally collapsed PVP coils are irradiated at relatively high temperatures intrachain crosslinks form leading to the formation of corresponding nanogels [48]. The results of a recent detailed parametric study give the guidelines for the radiation synthesis of poly(vinyl pyrrolidone) (PVP) nanogels in the size range of 30–200 nm, which is the range most suitable for biomedical applications by using either gamma rays or accelerated electrons. Various parameters—polymer-based; molecular weight, concentration and radiation source-based; Co-60 vs. E-beam, dose rate and absorbed dose—were investigated systematically [49].

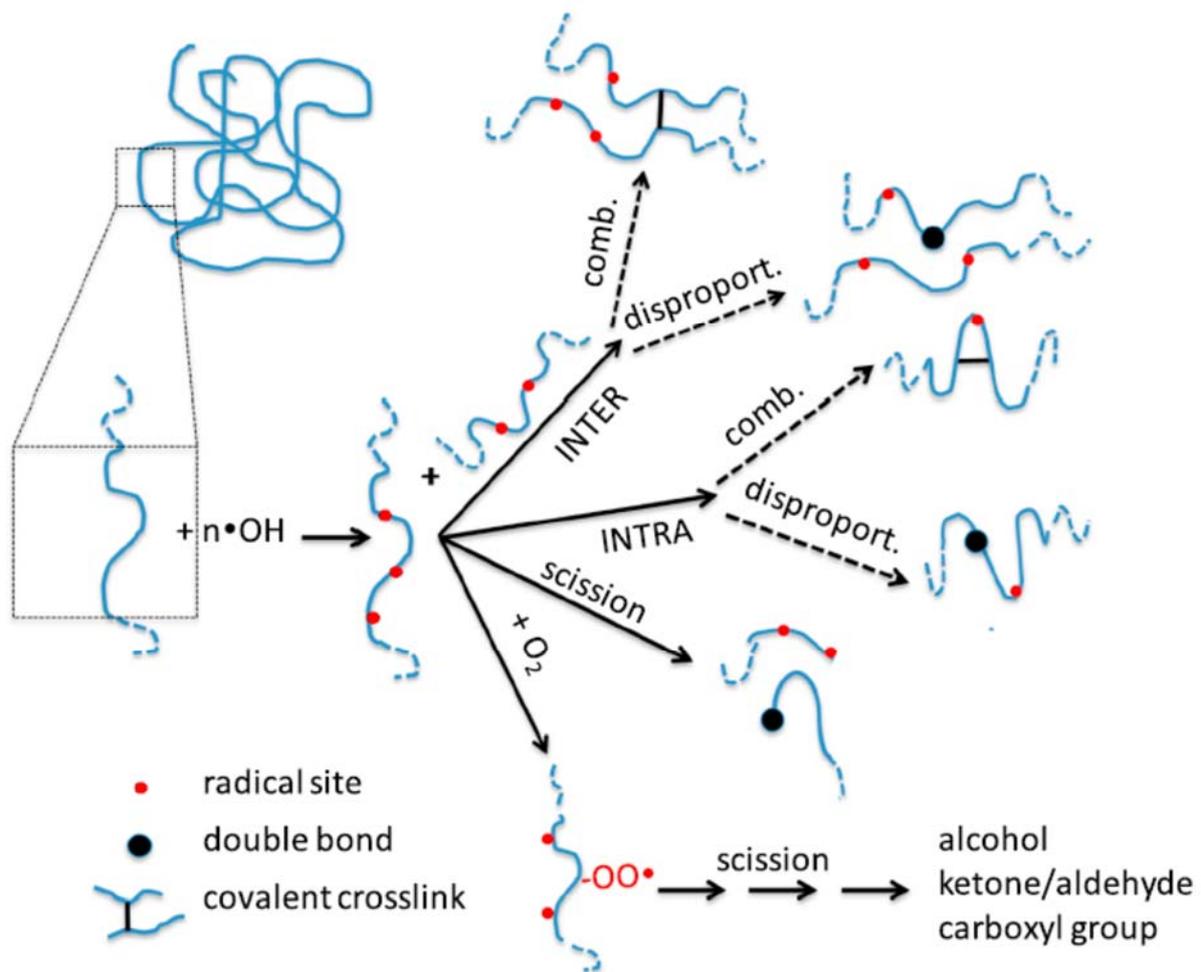


Figure 2. The fate of polymer-bound radicals generated by OH radical attack in aqueous systems. Reprinted with permission from Ref. [47]. Copyright 2021 Elsevier.

- PAA nanogels

Poly(acrylic acid) is another water-soluble polymer approved by the FDA as biocompatible. Because of its polyelectrolyte nature, PAA has been shown to undergo predominantly chain scission over a broad pH range. Only in dilute solutions below $\text{pH} = 3$, where carboxylic acid groups are protonated, does crosslinking start to dominate. In other words, in order to synthesize PAA nanogels by radiation, one should work in dilute solutions at low pH under high dose rate irradiations. Hence, PAA nanogels were synthesized by pulse irradiation of deoxygenated PAA solutions with 6 MeV electrons [50,51]. In another work from the same group, PAA nanogels with hydrodynamic radii of 25–44 nm were synthesized by irradiating various concentrations of air-saturated PAA solutions with e-beam. When the same solutions were irradiated with gamma rays in the same dose range, the hydrodynamic radii of nanogels were found to be between 50–250 nm. One can control the dimensions of PAA nanogels by adjusting the concentration of polymer, pH of the solutions and absorbed dose and dose rate [52].

pH-sensitive nanogels of narrow size distribution were directly prepared by gamma irradiation of acrylic acid in aqueous solution of PVP as a template polymer. Once the radiation-formed PAA reached the proper length for complex formation with PVP, further irradiation allowed the formation of intra-particle crosslinks and hence, the development of nanogels. Hydrogen bonding between PVP and radiation polymerized PAA during the course of irradiation has facilitated crosslinking with the formation of nanogels. The size control of PAA-rich nanogels was achieved by controlling the feed concentration,

composition and absorbed dose [53]. Very similar PAA-based nanogels prepared from acrylic acid rich feed solutions at 20 kGy by the same group were tested as low-viscosity biomimetic fluid tears [54].

- Synthesis of nanogels from interpolymer complexes

When complex formation between two different polymers in their aqueous solutions is favored, either due to hydrogen bonding or electrostatic or hydrophobic interactions, irradiation of these binary systems results with intra-coil crosslinks leading to the formation of nanogels composed of two polymers with different functionalities. This is an easy, straightforward method for the synthesis of multifunctional nanogels instead of using copolymeric precursors. Naturally, the two most frequently studied water-soluble polymers, namely PVP and PAA, form a good pair for the radiation synthesis of PVP/PAA nanogels in combined form. Detailed studies on the radiation formation of PVP/PAA nanogels from their hydrogen bonded complexes were performed by Henke et al. [55]. A comprehensive analysis was made by using high molecular weight PVP and oligomeric PAA to obtain interpolymer complexes in the pH around 4.0. Irradiation of these complex structures by pulsed electrons in dilute, deoxygenated solutions induced intercomplex crosslinking evidenced by decrease in viscosity and radius of gyration, leading to the formation of permanent PVP/PAA nanogels.

A recipe for preparing multifunctional nanogels with double amphiphilic properties using PVP and PAA was developed. Interpolymer complexes of these two polymers with coil size range of 40–300 nm were prepared under different experimental conditions of polymer molecular weight, concentration, mixing ratios, pH and temperature and irradiated with gamma rays. At relatively low absorbed doses of 5 and 10 kGy, nanogels with size range of 30–250 nm, zeta potential of -12 to -28 mV and polydispersities lower than 0.17 were obtained. The PVP/PAA complex nanogels obtained were found to show high colloidal stability [56].

Multifunctional poly(ethylene oxide)-poly(acrylic acid), PEO/PAA nanogels were also obtained from their interpolymer complexes by radiation-induced intramolecular crosslinking. PEO is a water-soluble nonionic polymer showing very high biocompatibility. Its complex with another biocompatible polymer, PAA, makes their nanogels very promising nanobiomaterials for biomedical applications. Prior to irradiation, the size of interpolymer complexes were reduced by using acetone, which is a non-solvent for both polymers. The effect of acetone on the contraction of coils was carefully investigated by dynamic light scattering technique before the formation of corresponding nanogels by gamma irradiation. A wide range of surface charge values of the nanogels prepared with equimolar stoichiometric ratio of polymer repeating units was achieved between -5.31 mV (pH = 2) and -45.00 mV (pH = 11). The size of the nanogels in the swollen state was between 100 and 240 nm. PEO/PAA nanogels synthesized in 25% acetone solution exhibited size stability over a period of 2 months. It was concluded that this simple method of preparing nanogels from polymer pairs avoids the synthesis of corresponding block copolymers as precursors of functional nanogels [57].

PAA at pH 3.5 was complexed with poly(acrylamide) in their aqueous solutions and irradiated with gamma rays up to 7 kGy dose. Biocompatibility of submicron gels were assessed by MTT assay [58]. Nanosilver embedded antimicrobial poly(acrylamide) bioactive nanogels were prepared by solution polymerization of monomer/AgNO₃ in nanoemulsion using gamma radiation. PAAm/Ag nanogel matrix with the size range of 10–50 nm was achieved. Bactericidal action of nanogels was found to be suitable for developing antimicrobial surfaces in surgical devices and synthetic implants [59].

More sophisticated nanogels were prepared by e-beam irradiation of micelle forming graft copolymers of thermosensitive poly(*N*-isopropylacrylamide) backbone and poly(2-ethyl 2-oxazoline) hydrophilic graft chains for specific compositions above the transition temperature of the backbone ~ 32 °C. A low number of side chains (3 mol% graft sites) and a degree of polymerization of at least 100 for the polyoxazoline chains were found to be necessary to keep the thermoresponsive behavior of the backbone and to stabilize the

micelles with the hydrophilic side chains to avoid formation of large aggregates. These graft copolymers were used to form core/shell type nanogel with thermo-reversible swelling and deswelling by electron beam crosslinking in the micellar state at 38 °C. The crosslinking occurred mainly in the collapsed hydrophobic core, allowing further stabilization by the polyoxazoline chains. Thus, stable thermoresponsive nanogels of about 30 nm in the collapsed state were achieved. The reversibility of the volume change of the nanogels were verified eight times by dynamic light scattering [60].

Multifunctional nanogels with carefully controlled chemistry, size, surface charge and other properties can carry drugs and bioactive substances, providing a safer and effective therapy than conventional chemotherapy. Increasing appearance of review articles on radiation synthesis of nanogels during the past couple of years is a proof of this growing scientific interest. A recent review covers and compares the research and development works of the past twenty years on the synthesis of nanogels from the aqueous solutions of precursor polymers using ionizing radiation with an outlook towards the potential medical applications [61]. A short review by Sabatino et al. discusses the features of PVP-based radiation-synthesized nanogels decorated with various biologically active molecules. The review includes UV-radiation-induced synthesis of nanogels in addition to gamma and e-beam [62]. The most recent review by Sütekin et al. considers the factors affecting the formation of nanogels their sizes, the degree of crosslinking by controlling the polymer solution properties and/or operational parameters of radiation engineering. The most recent examples of the radiation synthesis of nanogels from polymers, copolymers and interpolymer complexes are given in this review [43].

5. Composite Nanomaterials, Polymer Nanocomposites

Polymer nanocomposites consist of a polymer or copolymer having nanoparticles or nanofillers with at least one dimension in the range of 1–100 nm dispersed in a polymer matrix; therefore, they are composed of almost 95% polymers. One of the most interesting aspects of the use of nanofillers is the low concentration that needs to be added to the polymer system to obtain desired property improvements. These systems combine the best properties of each component through synergistic effect. The addition of low content nanofillers can lead to improvements in their mechanical, thermal, electrical, barrier and flammability properties without adversely affecting their processability. Among the most frequently used nanofillers, carbon nanotubes, graphene, nanoclays, nano-oxides, nanocellulose and metallic nanoparticles can be mentioned. In the previous sections, nanomaterials prepared by using CNTs, graphene and metal nanoparticles are were discussed. Among nano-oxides, TiO₂ and SiO₂ are the most frequently used nanofillers. Clays received particular attention as nanofillers due to their natural abundance, variety of types and ease of modification and processing. Montmorillonite (MMT) has been shown to be a very good nanofiller as the silicate layers are 1 nm thick with cross-sectional area of 100 nm². Clays are hydrophilic and incompatible with most commodity and engineering polymers, which are hydrophobic and nonpolar. To make these binary systems compatible, either clay particles must be rendered organophilic or polymers should be chemically modified (e.g., by incorporating maleic anhydride) to impart hydrophilicity or polarity. Ionizing radiation can be used in different ways for the preparation of polymer–clay nanocomposites. Gamma radiation can be used to initiate in situ polymerization of vinyl monomers in the presence of dispersed clay particles. Electron beam-induced reactive in situ modification of pristine MMT in polypropylene has been achieved by investigating the effect of electron energy and absorbed dose on the final structure of nanocomposites [63]. In a recent study, natural MMT was modified by first intercalating with a charged monomer and then radiation-induced in situ polymerization of monomer in between the silicate layers. Radiation modified clay was successfully used in the preparation of EVA-MMT nanocomposites [64]. Gamma-irradiated polypropylene was used as a compatibilizer in the preparation of short carbon fiber reinforced polypropylene composites. Shortened PP chains due to radiation degradation and simultaneous oxidation by air irradiation

enhanced the interactions between the carbon fiber and pristine PP with the formation of the nanocomposite [65]. The mechanical and barrier properties of some polymer–clay nanocomposites can be improved by radiation-induced crosslinking of polymer matrix. A critical review recently published provides an overview of the preparation, properties and uses of polymer nanocomposites by using basically three major types of nanofillers [66].

6. Controlling Radiation-Induced Grafting on Nanoscale

Radiation-induced grafting is one of the most promising applications of radiation processing as it allows control of the surface properties of polymers and inorganic particles. Since the introduction of the idea of using ionizing radiation for the generation of polymer-bound radicals to initiate copolymerization of a different monomer by the leading polymer scientists Chapiro and Stannett, this technique has been widely used for the modification of polymers [67]. Until quite recently, controlling of grafting frequency and graft chain length were not possible due to random and irreversible character of free radical polymerization. With the introduction of controlled free radical polymerization techniques, especially Atom Transfer Radical Polymerization and Reversible Addition-Fragmentation Chain Transfer Polymerization, grafting of polymers has taken a new and unprecedented dimension. However, only the latter can be applied under the radiation conditions which make RAFT grafting possible using ionizing radiation. This technique allows the synthesis of polymers with precise, predetermined molecular weights with very narrow dispersity. In a recent paper, nanostructuring of polymers by controlling ionizing radiation-induced free radical polymerization, copolymerization, grafting and crosslinking by the RAFT mechanism has been discussed [68]. In this section, the unique advantage of controlling of radiation-induced grafting in nanoscale is discussed considering functionalization of track-etched membranes, modification of fuel cell membranes and synthesis of polymer brushes for cell sheet harvesting.

6.1. Advanced Functional Track-Etched Membranes

When polymer thin films are irradiated with swift heavy ions, straight tracks of damaged zones are created. These damaged zones are converted into hollow cylindrical channels by chemical etching. The pore diameters may range from 10 nm to tens of microns with densities varying from 1 to 10^{10} /cm² [69]. When a thin film is irradiated with heavy ions, radicals are formed in the damaged zones, some of which are removed by etching. The residual carbon-centered radicals and peroxy radicals formed on the walls of nanopores by the strong oxidizing agents of the etching solution can be used to initiate grafting of vinyl monomers. In the presence of RAFT agents, the grafting process can be controlled to yield graft chain lengths with predetermined length and architecture and narrow dispersity. Radiation grafting of responsive polymers into the pores of track-etched membranes (TEMs) change their permeation properties in response to external stimuli such as pH or temperature [70].

Poly(acrylic acid), PAA, was grafted inside the nanochannel walls of track-etched PVDF membrane in a controlled manner by RAFT polymerization via the residual radicals remaining after the etching process. Various degrees of grafting from 5% to 63% were achieved, accompanied by a steady decrease in the pore diameter. The synthesized nanoporous membranes were later transformed into highly sensitive membrane electrodes by deposition of a thin gold layer on both sides without blocking the nanochannels. The membrane electrodes synthesized were found to be sensitive to sub-ppb concentrations of Pb²⁺ in square-wave anodic stripping voltammetry measurements [71].

Using a radiation-induced grafting technique, track-etched nanoporous PVDF membranes were functionalized with mercury sensitive poly(4-vinyl pyridine). Coating of these membranes with a very thin layer of gold results in an electrochemical sensor that is very selective and sensitive for mercury. A P4VP-functionalized PVDF membrane was found to be insensitive to pH variations (pH: 3–9), high salt concentrations and the presence of other heavy metal ions in the same solution [72].

PET TeMs with average pore size of 400 nm were photografted with poly(acrylic acid) using benzophenone immobilized on the inner walls of nanochannels. Cupric ions electrostatically attached to the carboxylate groups of dangling graft PAA chains were converted into metallic copper nanoparticles by radiation-induced reduction in aqueous alcohol solution using gamma rays. Copper nanoparticles ~70 nm in diameter were deposited in cylindrical nanochannels as potential nanosensors [73].

Gold nanoparticles were generated in the nanochannels of poly(acrylic acid) grafted poly(ethylene terephthalate) TeMs by radiation-induced reduction in alcoholic solution by using both 5 MeV electron beam and ^{60}Co gamma rays. The effects of absorbed dose, dose rate on the size and characteristics of gold nanoparticles were studied. The catalytic activity of gold nanoparticles supported on PAA-g-PET TeMs was tested for the reduction reaction of 4-nitrophenol [74].

A recent review on track-etched nanopore membranes provides an overview on the fabrication and functionalization methods, describing the fundamentals in transport phenomena near the interface, in nanofluidics with or without surface charges and summarizes the applications of TeMs in stimuli-responsive membranes, ion-gating/sensing and energy conversion [75].

6.2. Fuel Cell Membranes

Polymer electrolyte membranes are one of the key components in electrochemical power sources. Fluorinated polymers with their unique properties have been the material of choice to be used as membrane materials. Despite their superior properties, however, they are nonconducting, which is remedied by radiation-induced grafting of polyelectrolytes. A recent review addresses the advances in radiation-induced grafting techniques for the preparation of polymer electrolyte membranes for fuel cell, battery and supercapacitor applications [76].

Proton-conducting poly(ethylene-alt-tetrafluoroethylene) (ETFE) based membranes were prepared by gamma irradiation grafting of styrene with further sulfonation to make the polystyrene grafts conductive [77].

Track-etched polymer thin films were also used in developing proton exchange membranes with high conductivity by radiation-induced grafting. The cylindrical pores in TeMs provide short pathways for the proton transfer. Radiation-induced grafting of polyelectrolytes from the inner surfaces of nanopores increases the durability of the pore-filled membranes by eliminating the risk of leaching of physically trapped polyelectrolytes during application. PVDF based proton exchange membranes were prepared by ion-track grafting via a similar approach. Gamma-irradiated track-etched PVDF films were grafted with pure styrene and subsequently sulfonated to form conductive domains within PVDF [78]. Novel proton exchange membranes were prepared via radiation-induced grafting of styrene from ETFE film in the presence of a RAFT agent. Both the molecular weight and polydispersity of graft chains were controlled via RAFT mechanism. Controlling of graft copolymerization enhanced the structural uniformity and performance in terms of proton conductivity compared to similar ETFE membranes prepared by conventional method [79]. It is anticipated that the use of RAFT polymerization in radiation-induced grafting techniques will open the door for designing new tunable membranes in a controlled way by a one-step method under mild conditions.

6.3. Cell Sheet Harvesting

Polymeric nanostructures find a wide range of applications in biomedicine. Drug delivery, gene carriers, bioimaging and tissue engineering and regenerative medicine are the applications with the most pronounced effects [80]. The important role of “nanogels” was already discussed in terms of their use as drug delivery platforms and gene carriers in previous sections. Recent developments on the synthesis of Quantum Dots clearly showed their potential in better bioimaging. In this section, how radiation-induced grafting

in nanoscale contributes to the development of thermoresponsive cell culture surfaces is discussed.

At 37 °C, poly(*N*-isopropyl acrylamide) (PNiPAAm) grafted cell culture surface typically made of polystyrene is hydrophobic and allows cells to adhere and proliferate on modified surface. The lower critical solution temperature of PNiPAAm is around 32 °C which makes it thermoresponsive and it becomes hydrophilic below this temperature. Therefore, at temperatures below 32 °C, cells grown on the surface detach themselves from hydrophilic surface spontaneously. Based on this approach, cell sheet engineering technology was developed by Okano and his team and has become an established method of harvesting cell sheets noninvasively [81,82].

The thickness of the grafted PNiPAAm layer, which should be controlled within the 100 nm range, is one of the key parameters affecting hydration/dehydration phenomena, hence, cell sheet recovery [83]. This is where nanostructuring of polymers comes into play. A rapid cell sheet recovery is essential for clinical applications. Slow hydration of the PNiPAAm layer is the bottleneck of this process. In order to accelerate cell sheet recovery, several solutions were attempted such as using porous PS substrate and the incorporation of PEG into the PNiPAAm matrix. A better solution was found by first grafting a hydrophilic monomer, acrylamide, as the basal plane on PS then continued with grafting of *N*-isopropylacrylamide as the top layer to accelerate hydration PNiPAAm in the graft layer [84]. Thus, a double polymeric layer was formed like an interpenetrating network structure. The solution we proposed to this problem, however, is more systematic. First, a very thin layer of PAAm was grafted from the e-beam-irradiated PS surface via RAFT mechanism. Reactive RAFT moieties at PAAm chain ends were used to extend these chains by PNiPAAm chains growing to desired lengths, as shown schematically in Figure 3. Ellipsometric measurements revealed that after constructing a PAAm layer of ~58 nm, the thickness of top PNiPAAm layer could be controlled in 23–90 nm range as a function of duration of grafting [85]. Water contact angle measurements made below and above the lower critical solution temperature of PNiPAAm, namely 32 °C, revealed a perfect control of hydrophobic/hydrophilic balance in the graft layer, which enhanced the rate of hydration of PNiPAAm.

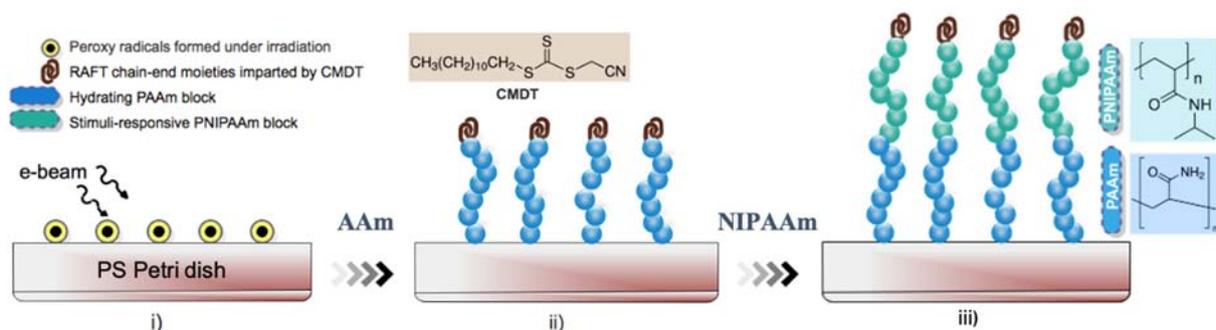


Figure 3. Modification of PS cell culture surface by consecutive grafting of PAAm and PNiPAAm via RAFT mechanism. Reprinted with permission from Ref. [85]. Copyright 2021 Elsevier. (i) E-beam irradiation of PS dish surface; (ii) Acrylamide grafting from the surface via RAFT agent CMTD; (iii) Chain extension by copolymerization with PNiPAAm.

It has been elaborated that PNiPAAm-based thermoresponsive surfaces provide new types of biomedical applications. These nanomanufactured surfaces have been developed for separating and purifying pharmaceutical proteins and therapeutic cells. Successful biomedical applications of PNiPAAm-modified surfaces were discussed in a recent review [86]. Thermoresponsive chromatography has been considered as a new separation and analysis tool.

7. Conclusions

Nanomaterials are being used to improve many sectors of industry such as information technology, healthcare, energy, transportation, environmental science and technology and materials science and engineering. Many commercial products that are currently on the market and in daily use rely on the development and availability of nanomaterials. Although the famous lecture given at Caltech in 1959 by Feynman and the description of nanotechnology for the first time by Taniguchi in 1974 showed us the way to so-called molecular manufacturing, it was only in early 2000 that consumer products making use of nanotechnology began appearing in the market place. Most nanomaterials are being developed for laboratory-scale applications and a high level of engineering efforts are needed to bring them into the market. Radiation engineering is one of the green technologies that has the potential to revolutionize the preparation and modification of nanomaterials, as described in this review. It has been amply shown that the use of ionizing radiation can reduce energy requirements and provide a more environmentally friendly approach in comparison to conventional methods. The prospect of using ionizing radiation for the preparation of nanomaterials will not be limited to the current applications but will diversify to replace other conventional techniques as new nanomaterials will be developed.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Request: Any data will be provided by the author upon request.

Conflicts of Interest: The author declares no conflict of interest.

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