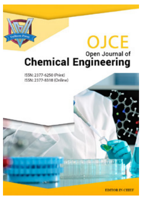
Open Journal of Chemical Engineering (OJCE)

DOI: http://doi.org/10.7508/ojce.01.2021.08.11



ISSN: 2377-6250 (Print)
ISSN: 2377-8318 (Online)
CODEN : OJCEB4

ARTICLE

PROGRESS IN RADIATION POLYMERIZATION AND MODIFICATION OF POLYMERS

Silvana Grimaldi*

School of Chemistry, University of Bristol, Bristol, BS8 1QU, United Kingdom
**Corresponding Author E-mail: Grimaldi @gmail.com*

ARTICLE DETAILS

Article History:

Received 22 September 2021
Accepted 2 December 2021
Available online 12 December 2021

ABSTRACT

The radiation polymerization process is easy to control, and the radiation modified products are relatively pure. Radiation polymerization and radiation modification have become an important aspect of polymer synthesis. The mechanism, synthesis and application of radiation polymerization and radiation modification were reviewed. The research progress of radiation polymerization and radiation modification in recent years was introduced. Finally, the problems and prospects of radiation polymerization and radiation modification were discussed.

KEYWORDS

Radiation polymerization; radiation modification; radiation grafting; cross-linking

1. RADIATION POLYMERIZATION

Polymer materials have excellent comprehensive properties and have been widely used in modern industrial production and daily life. The synthesis of polymer materials is mainly chemical synthesis. Radiation polymerization has become a new method for polymer material synthesis since Hopwood and Phillips [1] irradiated polymers made of liquid methyl methacrylate, styrene, and vinyl acetate with gamma rays and neutrons. After decades of research, great progress has been made in the initiation mechanism, synthesis method, and application of radiation polymerization of polymers. The polymer obtained by radiation polymerization has high purity. There is no residue from chemical initiators and it is easier to control. The high ray energy can make the monomers that are difficult to polymerize, and it occupies an increasingly important position in the synthesis of polymers [2].

There are many methods for polymer surface modification, such as ozone treatment, surface coating, flame treatment, acid etching treatment, and high-energy radiation [3]. The radiation modification of polymers has attracted great research interest since Charlesby and Dloe respectively introduced polymers into radiation fields in the early 1950s. Radiation can cause changes in the microstructure and macroscopic properties of the material surface [4]. Therefore, radiation modification has been used in the research work of modifying polymer materials in recent years. For example, radiation modification is widely used in the production of medical polymer materials, the preparation of ion exchange membranes, and the surface modification of fibers. It is used in the cross-linking of wires and cables, the vulcanization of rubber, the preparation of foamed materials, the processing of heat shrinkable materials, and the curing of coatings. It is also used in the recycling of polymer materials, waste treatment, and molecular weight regulation. In this paper, the principles, synthesis methods, and applications of radiation polymerization and radiation modification are reviewed. The latest research progress on radiation polymerization and radiation modification is mainly introduced, and the existing problems and future research directions of radiation polymerization and radiation modification are discussed.

1.1 Radiation polymerization and its mechanism

Radiation polymerization is also known as radiation-induced polymerization. A polymerization reaction occurs when a monomer is irradiated with high-energy ionizing rays (α rays, β rays, γ rays, x-rays, and electron beams) to generate ions or free radicals to form active centers.

Radiation polymerization is that under the action of high-energy ionizing radiation, the polymerization system can simultaneously generate free radicals, anions, and cations. The radiation polymerization mechanism includes the free radical mechanism, the cationic mechanism, and the anionic mechanism. Due to the cage effect in the cloud, free radicals, anions, and cations can recombine rapidly, and only a small part can escape from the cloud to form a steady-state condition. Usually, free radicals have a much greater chance of escaping out of the cloud than anions and cations. Therefore, most of the polymerization systems without special drying and with relatively low dosage rates are based on free radical polymerization.

1.2 Characteristics of radiation polymerization

(1) Radiation polymerization does not require the addition of initiators and catalysts, and the resulting polymer is purer, which is particularly important for the synthesis of biomedical polymer materials.

(2) Due to the strong penetrating ability of the rays and the uniform distribution in the irradiated system, the solid-phase polymerization of radiation can be carried out.

(3) Chemical polymerization often requires higher temperatures, while

Cite The Article: Silvana Grimaldi (2021). Progress in Radiation Polymerization and Modification of Polymers. *Open Journal of Chemical Engineering, 4(1) : 08-11.*

radiation polymerization can be carried out at room temperature or low temperature.

(4) Radiation polymerization is easy to control, such as reaction speed and molecular weight, etc., which can be quantitatively controlled by adjusting the dose and dose rate at the beginning and end of the reaction.

1.3 Applications of radiation polymerization

The study of radiation polymerization started relatively early.

Stimuli-sensitive polymers and hydrogels have been developed in recent decades.

Among them, there are sensitive materials such as temperature, pH value, solvent, and voltage. Polymers such as temperature-sensitive polymers and hydrogels are in the physiological temperature range (0-30°C). This series of polymers has extremely wide application prospects in biological and medical materials. Shao et al. [5] used 60Co-γ ray to initiate radiation polymerization and synthesized several polymer water-absorbing agents such as sodium polyacrylate, polyacrylic acid-acrylonitrile, polyacrylic acid-vinyl acetate, polyvinyl alcohol grafted acrylic acid. Research on the synthesis of superabsorbent resin by microwave method is very active. Xu et al. [6] synthesized starch/AMPS/ sodium acrylate superabsorbent resin with ammonium persulfate as initiator and microwave irradiation. Zhao et al. [7] used the redox system of potassium persulfate and sodium thiosulfate as initiators to synthesize cellulose-based superabsorbent resin by microwave irradiation. Xu et al. [8] prepared organic/inorganic composites by applying ultrasonic waves to organic/inorganic hybrid systems. Through instrument observation, these composite particles have a uniform dispersion state. Dai et al. [9] synthesized methyl methacrylate-styrene copolymer (Ms) resin by irradiation polymerization. It has good optical properties and good toughness.

2 RADIATION MODIFICATION

The radiation modification of polymers mainly includes radiation grafting, radiation crosslinking, and radiation degradation. The principle and method of radiation grafting of polymers and the research progress of the influencing factors of radiation grafting are mainly discussed below.

2.1 Radiation grafting

2.1.1 Principle and method of radiation grafting

Radiation grafting of polymers refers to the generation of one or several active sites on the backbone of the polymer under the action of high-energy rays. Monomers are then successfully attached to each active site, resulting in long terminated chains that grow from the backbone. The process in which the backbone polymer and the monomer are polymerized on the side chain to form a graft copolymer. The radiation sources used in radiation grafting are divided into natural radioactive sources and artificial radioactive sources (gamma rays, etc.), and various types of accelerators (such as X-ray tubes, electron accelerators, and other high-energy devices) [10].

According to different process conditions, the radiation grafting process can be divided into two types: free radical mechanism and ionic mechanism. Most of the radiation grafting is carried out according to the free radical mechanism. According to the characteristics of the irradiation process and the grafting process, it can be divided into three grafting methods: co-radiation grafting (direct radiation grafting or simultaneous radiation grafting); pre-radiation grafting; peroxide grafting.

In the co-radiation grafting method, the radiation is carried out under the condition that the backbone polymer and the grafted monomer are kept in direct contact. Monomers can be vapors, liquids, or solutions. After irradiation, active particles are generated in both the polymer and the monomer, resulting in a graft copolymerization reaction. Both the backbone polymer and the grafted monomer are produced as graft copolymers, and the grafted monomers are also produced as homopolymers. Advantages of co-radiation grafting High free radical utilization (100%) of polymers. Once free radicals are generated, they are immediately used to initiate the graft polymerization reaction. Irradiation and grafting are done in one step at the same stage. The technical operation is relatively simple. Most of the monomers can be used as radioprotectants for polymers, reducing the degree of polymer radiation cracking. The biggest disadvantage is that when the mixed system of polymer and monomer is irradiated at the same time, the homo-polymerization of monomer will inevitably occur. The co-radiation grafting method can be realized in the following ways: homogeneous solution method, swelling method, liquid phase immersion method, and gas phase grafting method [11].

The pre-radiation grafting method is to irradiate the polymer matrix in the case of deoxygenation (vacuum, N2, and other inert gases). A relatively stable trapped free radical is produced. The graft copolymerization reaction with de-aired monomers is then carried out under heating outside the radiation field. Irradiation and grafting reactions are two separate processes in pre-radiation grafting. It is extremely convenient for research and production. The pre-radiation grafting process is not dose rate limited because the monomers are not irradiated. Pre-irradiation techniques produce substantially few homopolymers. The disadvantage is the low availability of polymer-free radicals.

The peroxide grafting method is to first irradiate the polymer in the active oxygen in the air. Peroxides or hydroperoxides are formed in the irradiated material. These peroxides are relatively stable out of the radiation field and can remain for a considerable period. The polymer is peroxidized and then contacted with the monomer. Under the condition of air or vacuum, the graft copolymerization reaction is carried out at elevated temperatures. Peroxide grafting can generate stable peroxides, which is beneficial to the preservation of polymer-free radicals. The utilization rate of polymer-free radicals in the grafting process is relatively high. Irradiation and grafting are two stages, and the process is not limited by time and place. The disadvantage of this method is that oxidative degradation of the polymer moiety during radiation treatment affects the properties of the graft copolymer.

2.1.2 Influencing factors of radiation grafting and its research progress

There are many factors affecting radiation grafting. The reaction kinetics, the nature of the polymer and the monomer, the concentration of the monomer, the type of solvent, and the radiation dose will all have an important influence on the graft ratio and the structure and morphology of the graft.

(1) Reaction kinetics

Studies on gas-phase and liquid-phase radiation grafting of a variety of monomers show that the reaction conditions and different periods during the reaction process determine whether the radiation grafting reaction is kinetically or diffusion-controlled.

Yu et al. [12] studied the reaction kinetics of high-density polyethylene (HDPE) pre-irradiated grafting sodium styrene sulfonate (SSS) and acrylic acid (AA) systems. It can be seen that the grafting rate not only depends on the fall free. The reaction efficiency of the group and the monomer is related to the diffusion rate of the monomer to the matrix. Jiang et al. [13] found that in the initial stage of the reaction of grafting acrylic acid by co-irradiation of polyethylene film (PE), the grafting reaction is controlled by kinetics, and the reaction rate depends on the number of active sites on the substrate. However, as the grafting reaction continues, the grafting reaction at this time becomes diffusion controlled.

(2) Influence of the bulk properties of the grafted polymer and grafted monomer

The chemical structures of polymers and grafting monomers are different, and the ability of radiation grafting is very different. Using ethanolamine vinyl ether as the grafting monomer, under the same irradiation conditions, the grafting rate of polypropylene (PP) substrate is higher than that of PE. Because the reactivity of PP under ionizing radiation is higher than that of PE. high [14].

(3) Influence of monomer concentration

The increase of the monomer concentration is beneficial to the increase of the grafting rate. But as the monomer concentration increases to a certain extent, the self-polymerization will be intensified. Bai [15] prepared acrylic acid solutions with different concentrations and carried out the grafting reaction with polyethylene terephthalate (PET) respectively. It was found that the grafting rate increased with the increase of monomer concentration. The increase in monomer concentration increases the number of acrylic acid molecules diffusing into the PET macromolecules, promoting the grafting reaction. However, when the concentration exceeds 6%, the self-polymerization of acrylic acid directly induced by UV light at higher temperatures also intensifies because the viscosity of the system will increase significantly. The resulting homopolymer thus reduces the grafting rate.

Influence of solvent

Odian et al. found that adding a solvent that is extremely sensitive to radiation and can swell the polymer in the grafting liquid system can increase the grafting rate. When exposed to radiation, unstable hydrogen atoms are generated, creating active sites in the polymer that can be used to initiate grafting reactions. Peng et al. [16] used methanol as a solvent to prepare PLLA-g-PVP graft copolymer by irradiation. This indicates the promoting effect of the methanol grafting reaction. Nasef [17] studied the grafting of fluoropolymer to styrene and found that compared with using benzene or methanol as solvent, using dichloromethane as solvent could obtain a higher grafting rate.

Influence of radiation dose

Generally, the grafting rate of radiation grafting is proportional to the absorbed dose. However, the increase in grafting rate tends to be slow when the dosage exceeds a certain range. Research by Deng et al. [18] showed that the grafting rate and water absorption rate increased with the increase in radiation dose. When the radiation dose is too low, the irradiated product cannot absorb water. When the radiation reaches a certain dose, the water absorption rate increases. When the irradiation time is further prolonged and the radiation dose is further increased, self-crosslinking occurs between the carboxyl groups, the photopolymerization reaction is strengthened, and the grafting rate is reduced. When the irradiation dose of some grafting reactions is within a certain range, the grafting rate increases with the increase of the irradiation dose. When the radiation dose is greater than a certain value, the upward trend of the curve gradually flattens. The rate of increase of the grafting rate slowed down, and the grafting rate remained constant in the final stage of the grafting reaction. This is due to the increase in the probability of bonding between the matrix-free radicals with the extension of the reaction time [19].

The additives in the polymer, fillers, radiation atmosphere (such as air, vacuum, inert gas), reaction temperature, and time all affect the grafting. In addition, the acid can increase the H atom concentration in the co-irradiation grafting reaction, the solubility of the grafting monomer in the solution, and the viscosity of the system, which can significantly increase the grafting rate.

2.2 Radiation crosslinking

Crosslinking refers to the phenomenon in which polymer molecules are bridged together by bonds. The result of radiation crosslinking is that the molecular weight of the polymer increases with the amount of absorber until each chain has an average of one bond to the other. molecular chains to form a three-dimensional network structure.

Radiation crosslinking is widely used and can improve the heat resistance of its products. Mitomo [20] and Nagasawa [21] et al. improved the heat resistance of polylactic acid (PLA) by strengthening radiation cross-linking. The heat resistance of PLA increased to 70°C after cross-linking. This is mainly due to the lower crosslink density. Styrene-Butadiene-Styrene block copolymer (SBS) undergoes cross-linking reaction under certain irradiation conditions Compatibility improvement of SBS with nylon 6 (PA6) is enforced by the generation of a three-dimensional network structure [22–24]. Tang et al. [25] prepared cross-linked PTFE samples by irradiating polytetrafluoroethylene (PTFE) at high temperatures with electron beams. The research results show that the transparency of the cross-linked PTFE is significantly increased, the melting point is decreased, and the wear resistance is significantly improved compared with the unirradiated PTFE. Radiation cross-linking can also be applied to the preparation of heat-shrinkable films, tubes, and tapes to impart memory effects to polymers. The polyethylene film of radiation cross-linked polyethylene after thermal expansion and rapid cooling will not expand when reheated but will shrink so that it returns to its shape before thermal expansion. This bizarre property is the so-called memory effect. It can use this film for commodity packaging. When blown with hot air, the film shrinks and wraps the product tightly, which becomes a very practical and beautiful product packaging method.

2.3 Radiation degradation

Radiation degradation refers to the process in which the main chain of a polymer is broken under the action of high-energy radiation. The result of radiation degradation is that the molecular weight of the polymer decreases with an increasing amount of absorption. Some polymer molecules even degrade into monomeric molecules.

Radiation degradation is a reaction that does not require additives. The reaction is easy to control and saves energy. The polymer can be degraded by irradiation to obtain a product with better homogeneity, and biocompatibility is not affected. Radiation degradation of polymers has been applied to the recycling of polymer materials, waste treatment, and molecular weight regulation. For example, polytetrafluoroethylene has excellent mechanical, electrical, and chemical properties and is known as the king of plastics. Its application range is very wide. After the waste PTFE is irradiated and heated, it changes from a macromolecular polymer with a high molecular weight to a polymer with a low molecular weight and becomes a very fine powder. This powder is called Teflon wax. It has the characteristics of antistatic and low friction coefficient and can be used to manufacture lubricants with excellent performance. Yu et al. [26] used γ-rays to degrade the sarin simulant O, O′-dimethylmethylphosphonate (DMMP) by radiation. Phthalates have become a global pollutant. Lau et al. [27] utilized UV light to degrade dibutyl phthalate (DBP). Doggrell uses the radiation method to degrade chitosan, and a lower concentration of radiation chitosan can play an obvious bacteriostatic effect.

3. OUTLOOK

The radiation modification of polymers is simple to operate, easy to control, energy-saving and pollution-free. It has been widely used in various fields of the national economy. Polymers have obvious effects under the action of radiation. But radiation-modified polymers still need further refinement:

The radiation resistance of some polymer materials is poor. Under the action of rays, fluorine-containing polymer films (ETFE, PVDF, PVF) are prone to chain-cutting reactions and degradation and aging. Part of fluorinated polymer films is easy to cause polymer chains. cross-linking reaction.

During the grafting reaction, the grafting ratio and grafting efficiency increase with the increase of the monomer concentration. However, the increase in the monomer concentration will cause a serious photopolymerization phenomenon, inhibit the diffusion of the monomer to the matrix, and lead to the total grafting ratio Decrease. The graft initiation rate increases with the increase of the reaction temperature. However, if the temperature is too high, the monomer photopolymerization phenomenon is serious, which leads to a decrease in the monomer concentration, and the graft rate does not increase anymore. The polymerization inhibitor effectively overcomes the photopolymerization reaction between the monomers, but at the same time causes free radical deactivation, inhibits the copolymerization reaction, and thus reduces the grafting rate.

In the treatment of irradiated products, the separation of polymer and monomer usually relies on extraction methods. However, this method requires a large amount of solvent, which is not conducive to industrial production. The surface properties and biodegradability of radiation-modified polymers need to be further studied.

At present, the radiation modification of polymers is not perfect. There is still a lot of work to be done to realize the industrial application. However, it is believed that soon, the clean and simple synthesis methods of radiation polymerization and radiation modification will gradually become industrialized, which will truly change the high pollution and high energy consumption caused by traditional dyeing and finishing processes.

REFERENCES

[1] Cleland, M.R., Parks, L.A., Cheng, S. 2003. Applications for radiation processing of material. Nuclear Instruments and Methods in Physics Research, 2003, 208: 66-71.

[2] Kirsh, Y.E., Yanul, N.A., Kalninsh, KK. 1999. Structural transformations and water associate interactions in poly-N-vinylcaprolactam-water system. European Polymer Journal, 35:305-316.

[3] Macmanus, L.F., et al. 1999. Study of ultraviolet light and ozone surface modification of polypropylene. Journal of Polymer Science Part A: Polymer Chemistry, 37(14): 2489-2501.

[4] Sutherland, I., et al. 1991. Modification of polypropylene surfaces by flame treatment. Surface Interface Analysis, 17(7): 507-510.

[5] Shao, S., Deng, G.Q, Peng, X.M, et al. 2006. Preparation of spherical water-absorbent resin by radiation suspension polymerization. Elastomer, 16(6): 14-16.

[6] Xu, K., Zhang, W. D., Yue, Y. M., et a1. 2005. Swelling behaviors of a three-component copolymer (starch graft sodium acrylate and 2-acrylamido- 2- methylpropanosulfonic acid) synthesized by microwave polymerization. Journal of Applied Ploymer Science, 2005, 98: 1050-1054.

[7] Zhao, B.X., Wang, P., Zheng, T. 2005. Synthesis process and properties of cellulose-based superabsorbent resin by microwave irradiation. Polymer Materials Science and Engineering, 21(4): 133-136.

[8] Xu, G.C., Wang, Z., Xiong, J. Y., et al. 2006. In situ ultrasonic synthesis and characterization of nanogallium/polymethylmethacrylate composites. Modern Chemical Industry, 26(2): 37-40.

[9] Dai, X.H., Peng, J., Zhai, M.L. 2005. Radiation Synthesis and Characterization of High Transparent Impact Polystyrene Resin. Acta Polymerica Sinica, (3): 403-407.

[10] Luo, Y.L. 1998. High polymer radiation grafting technology and its application [J]. Synthetic Rubber Industry, 1998, 21(3): 142-145.

[11] Han, C.Y. 2004. Study on Radiation Modification of Polymers. Liaoning Chemical Industry, 33(3): 159-163.

[12] Yu, C.H., Zu, J. H., et al. 2005. Study on the reaction kinetics of HDPE pre-irradiation grafted SSS and AA system. Journal of Radiation Research and Radiation Technology, 23(3): 169-173.

[13] Jiang, Q.K., Sun, H.B. 1995. Radiat Res Radiat Process, 13(3): 161-166

[14] Aal, A.S.A., Khutoryanskiy, V.V., et al. 2002. Radiation grafting of vinylether of monoethanolamine on polypropylene films for application in wastewater treatment. Mater Chem, 12(9): 2692-2695.

[15] Bai, H.Y., Ai, L., Sun. Y.J., et al. 2010. Surface grafting modified PET film by ultraviolet radiation method. Spectroscopy Laboratory. 27(1): 32-36.

[16] Peng, C.R., Wang, J.X., Chen, Z.P. 2009. Study on the radiation grafting of N-vinylpyrrolidone with poly-L-lactic acid. Journal of Radiation Research and Radiation Technology, 27(2): 75-78.

[17] Nasef, M.M. 2001. Effect of solvents on radiation-induced grafting of styrene onto fluorinated polymer films. Polymer International, 50(3): 338-346.

[18] Deng, X., Pan, S.Y., Lin R.T. 2005. Study on the reaction conditions of acrylic acid graft copolymerization of konjac glucomannan by irradiation method. Food Science, 26(8): 225-229.

[19] Seong, H.C., Young, C.N., et a1. 1999. Adsorption of Pb2+ and Pd2+ on polyethylene membrane with amino group modified by radiation-induced graft copolymerization. Journal of Applied Polymer Science, 71(4): 643-650.

[20] Mitomo, H., Kaneda, A., Quynh, T.M., et a1. 2005. Improvement of heat stability of poly (L-lactic acid) by radiation-induced cross-linking. Polymer, 2005, 46(13): 4695-4703.

[21] Nagasawa, N., Kaneda, A., Kanazawa, S., et al. 2005. Application of poly (lactic acid) modified by radiation cross-linking. Instrum. Methods Phys. Res., Sect. B, 236 (1- 4): 611-616.

[22] Zhang, Y., LI, Y. T., Zhao, S. F., et a1. 2008. Compatibility effect of radiation- grafting- functionalized styrene- butadiene- styrene on polyamide 6/styrene- butadiene- styrene blends. Journal of Applied Polymer Science, 108(2):1029-1036.

[23] Chen, J.Z., Liu, W.T., Tan. X. L., et a1. 2007. Effect of radiation on the properties of the PP/PUR-T blends. Engineering Plastics Application, 35(12): 43-45.

[24] Elmaghor, F., Zhang, L., LI, H.Q., et al. 2002. Effects of high energy radiation and compatibilizer on toughness and morphology of recycled hybrid polyolefin. China Synthetic Rubber Industry, 25(3): 175- 179.

[25] Tang, Z.F. 2008. Wang Mouhua, et al. Radiation crosslinking of PTFE and its application. Organofluorine Industry, (3): 3-6.

[26] Yu, W. F., Zhang, Y., Hu, S. 2010. Radiation degradation of sarin mimetic O, O′-dimethylmethylphosphonate by gamma rays. Nuclear Chemistry and Radiochemistry, 2010, 32 (1): 52-56.

[27] Lau, T.K., Chu, W., Graham, N. 2005. The degradation of endocrine disruptor din butyl phthalate by UV irradiation: A photolysis and product study. Chemosphere, 60(8): 1045-1053.

◆

Cite The Article: Silvana Grimaldi (2021). Progress in Radiation Polymerization and Modification of Polymers. *Open Journal of Chemical Engineering, 4(1) : 08-11.*