



Ain Shams University
Faculty of Science
Chemistry Department

“Gamma radiation induced preparation of microsphere Nanocomposite by Emulsion Polymerization for removal of some Radionuclides ”

*A thesis Submitted for
Doctor of Philosophy (PhD) Degree of Chemistry*

By

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2018

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا
إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ
الْعَلِيمُ الْحَكِيمُ ﴾

صدق الله العظيم

سورة البقرة الآية (٣٢)

To

My father and my mother

To

My wife

To

My brother and sisters

I hope that I fulfilled my duty to be proud of me always



Ain Shams University
Faculty of science

Approval Sheet

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Radionuclides ”**

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<i>Editors</i>	<i>Approved</i>

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Mahmoud Goneam Hamed



Introduction

Introduction

1. Radiation induced polymerization

Polymerization initiated by ionizing radiation can be carried out by both a free-radical and an ionic (cationic or anionic) mechanism. The determining factor is the nature of the end of the growing chain. Radiation induced polymerization is a reaction that involves formation of polymer, copolymer or graft copolymer by exposure to high energy radiation, which generate radicals in the system that allow the reaction to occur and complete.

Monomers may be polymerised by free radical initiation by one of five (media) methods: polymerisation in bulk, in solution, dispersed as large particles in water or occasionally in another non-solvent (suspension polymerisation), or dispersed as fine particles, less than 1.5 μm , usually less than 1 μm in diameter. The last-named process is usually known as emulsion polymerization as shown in Fig.1. Polymerization or grafting onto polymers in the emulsion media is a method for carrying out the reaction in a disperse system generally containing hydrophobic monomer and water as a dispersion medium[1]. The stability of the emulsion system containing the monomer is maintained using a surfactant[2].

In past several years, there has been a big growth in the field of surfactants. Surfactants or surface active agents are broadly defined as organic compounds that can enhance cleaning efficiency, emulsifying, wetting, dispersing, solvency, detergents, foaming/defoaming and lubricity of water-based compositions and many others [3]. Therefore,

the primary function of a surfactant is to enhance the performance properties of water based formulations composed of a range of ingredients such as solvents, thickeners and chelating agents. All surfactants have the same basic chemical structure a hydrophilic (water-loving) “head” and a hydrophobic (oil-loving) “tail” which is always a long (linear) chain of carbon atoms[4].

Therefore, the surfactant plays an important role in bringing monomers into contact with the substrate and generally acts as an emulsifier which stabilizes the emulsion medium during the reaction. In addition to forming the micelles to solubilize the water-insoluble monomers, the surfactant also decreases the surface tension at the monomer-water interface[**discussed in the next**].

1.1. Free Radical Polymerisation

Most emulsion polymerisations are free radical processes [5,6]. There are several steps in the free radical polymerisation mechanism: initiation [7], propagation and termination [8]. In the first step, the free radical are generated by initiator . The initiator decomposition rate is described by an Arrhenius-type equation containing a decomposition constant (k_d) that is the reciprocal of the initiator half-life ($t^{1/2}$). The free radicals initiate polymerisation by reaction with a proximate monomer molecule. This event is the start of a new polymer chain. Because initiator molecules constantly decompose to form radicals, new polymer chains are also constantly formed. The initiated monomeric molecules contain an active free radical end group. During propagation, the initiated monomeric species come into contact with uninitiated monomer

molecules and react to form dimers containing active end groups. The dimers react with monomer to become oligomers [9]. The oligomeric chains grow by propagation and continue to develop in molecular weight. The rate of growth of the polymer chains is synonymous with the polymerisation rate (R_p). When the free radical end group on a growing polymer chain is deactivated, the chain stops growing, and this event is known as termination. Termination is either by combination, in which two active radical end groups meet, or by disproportionation, in which the active radical is lost from a growing polymer chain by the abstraction of hydrogen from another growing chain. Chain growth may also be terminated by chain transfer [10] to another (e.g., monomeric or polymeric) species. Branching and crosslinking (gel formation) reactions may result from intermolecular chain transfer to polymer. The rate of termination is proportional to the termination rate constant, which also has an Arrhenius dependence upon temperature.

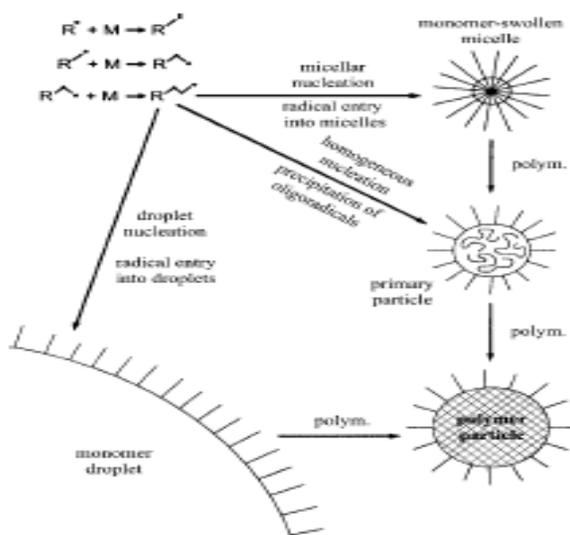


Figure (1) :- Homogenous, Micellar and droplet nucleation mechanism.

1.2. Methods of radiation-induced polymerization

Radiation-induced polymerization can be carried out in bulk, in solution, in emulsion (suspension), in the gas and solid states, and in the glassy state in other words, just as in other methods of initiation (conventional, thermal, photochemical initiation, etc.).

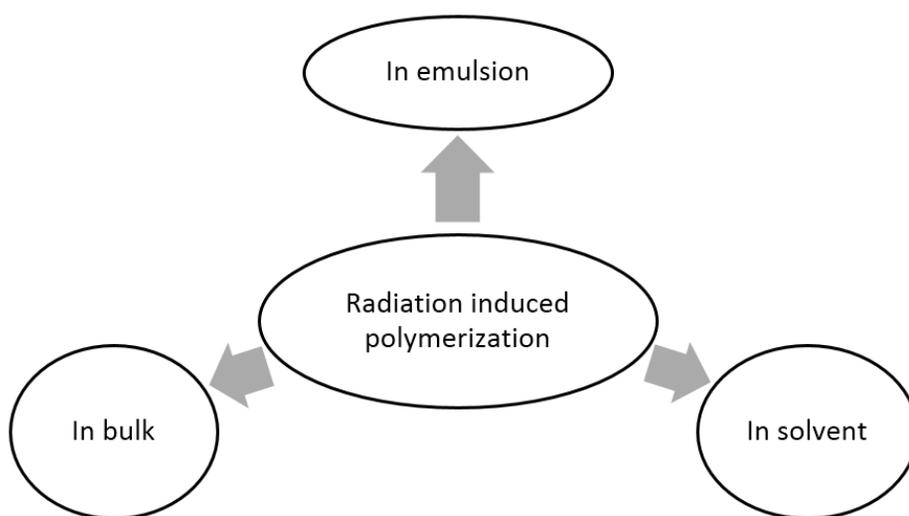
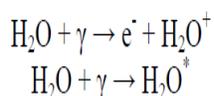


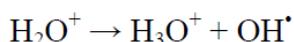
Figure 2. Representation of radiation induced polymerization in various media.

Radiation-initiation is a complex procedure which the consequence of ionization and excitation depends on the physical state and composition of material and type of radiation source [11]. In monomer ionization due to Compton's effect, the electron formed can induce many secondary ionization acts. Losing its energy after these secondary acts and thus causing the formation of numerous ions and electrons of high energy, this primary electron e is transformed into a

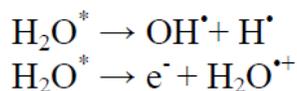
`thermal' electron e' , i.e. it attains thermal equilibrium with the medium. The thermal electron can be trapped by ions formed from monomers M^+ with their conversion into activated molecules. Upon irradiation, some primary products formed due to the breaking of indiscriminate chemical bond. These primary products may either react with other materials or recombine to produce even more secondary products [12]. In initiation of RIEP, water is a very important component. Pure water molecules undergo radiolysis to yield solvated electrons ($e^-_{(aq)}$), protons and hydroxyl radicals [13]. The undergoing reactions in the radiolysis of water are shown below [14]:



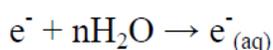
H_2O^+ rapidly react with water to produce hydroniums and hydroxyl radicals.



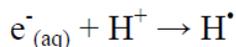
The exact nature of the water in the excited state (H_2O^*) remains uncertain but it seems likely that radicals will be produced on decomposition of excited state.



In the absence of reactive species electrons are rapidly solvated:



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



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

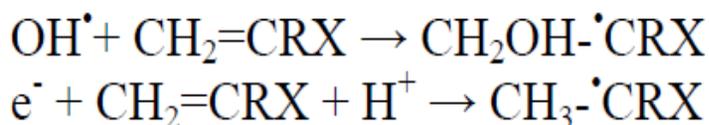


Table 1. Previous studies on preparation of polymers and copolymers by radiation induced emulsion polymerization.

Starting monomer	Source	Surfactant	Ref
Vinylacetate	Gamma rays	Sodium lauryl sulphate	[26]
Styrene	Gamma rays	Poly(vinyl pyrilidone)	[27]
Styrene-divinyl benzene	Gamma rays	Non ionic surfactant	[28]
Butylacrylate / A.Nitrile	Gamma rays	Sodium alkylsulfonate	[29]

1.3. Main features of radiation-induced emulsion polymerization

1.3.1. Emulsion polymerization

Emulsion polymerization is a general term, which known to be a method of carrying out polymerization in a disperse system in which water is usually the dispersion medium. In order to ensure the stability of an emulsion containing monomer and emulsifier. They are compounds of

diphilic type, surfactants which decrease the surface tension at the hydrocarbon-water interface. This decrease facilitates the emulsification of the monomer in water and favours the stabilization of the emulsion. Polymerization starts in the micelles of the emulsifier, because a considerable part of the monomer is dissolved in its hydrocarbon moiety. There are conversion of the monomer, emulsifier micelles percent completely destroyed, and the emulsifier passes into the adsorption layer on the surface of polymer particles. Apart from emulsion polymerization, in practice suspension polymerization is also used. This process occurs directly in the monomer drop with the formation of a solid polymer in the form of grains. Therefore this polymerization is also called bead or gran polymerization.

Apart from the advantages of radiation emulsion polymerization indicated above and those characteristic of radiation-induced polymerization in general, the following advantages should also be mentioned.

(1) When post-polymerization occurs, a very monodisperse polymer is obtained, and conversion may attain 100%.

(2) Since ionizing radiations stabilize the emulsion system because a charge is generated in the dispersed particles, emulsifier consumption is two to three orders of magnitude lower (down to 0.04%) than in conventional initiation, and the emulsifier is recycled.

(3) There is no need to purify waste-water because after the isolation of the polymer this water can be recycled. This is very important from economical and ecological standpoints because the

problem of sewage treatment in industry in emulsion polymerization is very complex.

(4) Polymers of extremely high molecular weight are obtained (for instance, up to 2×10^7 for polystyrene). Hence, they exhibit high Bending strength , Tensile strength and thermal stability but are difficult to process.

The interest in using emulsion polymerization is increasing due to their widespread applications in the production of functional polymers. The functional polymers are materials that have advanced properties suitable for energy and environmentally related areas such as stimuli-response, chelating adsorbents, polymer electrolytes and adhesives applications [15,16].

Emulsion polymerization covers several processes including conventional, inverse, mini, micro, and nano emulsion polymerizations[17,18]. Normally, the conventional emulsion polymerization involves emulsification of the relatively hydrophobic monomer in water by proper emulsifier, followed by the initiation reaction either with chemical or radiation methods. Both water and oil soluble initiators (e.g. sodium persulfate, azo initiators and 2-2'-azobisisobutyronitrile (AIBN)) have been used to initiate the polymerization reactions [19]. The polymerization is initiated by activation of initiators (e.g. by increasing the temperature) and formation of radicals. Therefore, the required conditions for producing the radicals control the polymerization temperature and subsequently influence the polymer properties. In this method, the reaction can be initiated by either ultrasonic irradiation [20,21] or high energy radiation in form of