# EFFECT OF IONIZING RADIATION ON SOME POLYMERIC MATERIALS

THESIS
SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS

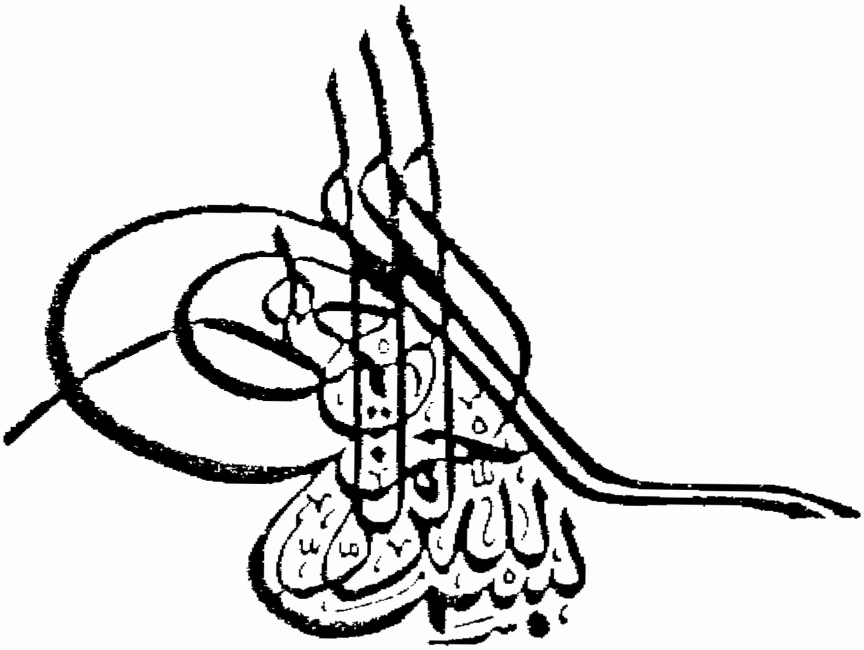
FOR (M.Sc.) DEGREE
IN
(CHEMISTRY)

TO THE
FACULTY OF SCIENCE
AIN SHAMS UNIVERSITY

BY

**SALWA IBRAHIM AHMED AMER**
Natioanal Centre for Radiation Research
and Technology - Cairo
(B.Sc.)

1989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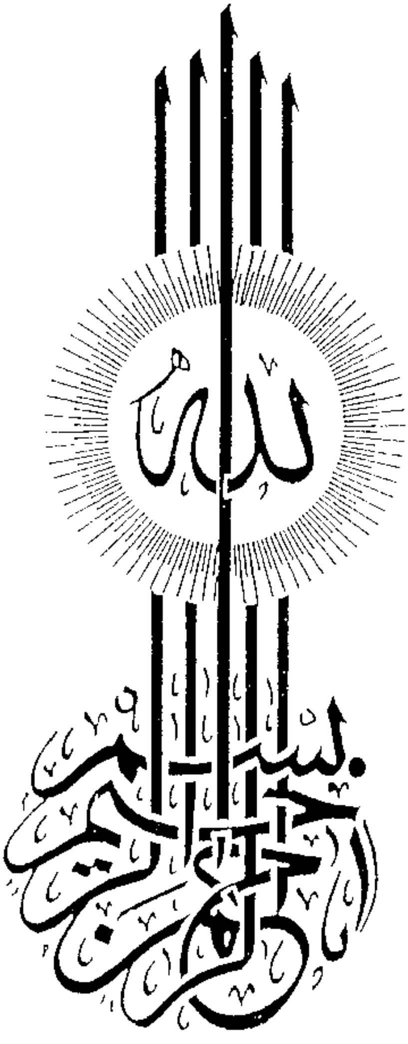
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Thesis Advisors

Approved

Prof. Dr. Abdel-Gawad M. Rabie ......................

Prof. Dr. Ahmed M. Dessouki ..A. Dessouki..

Prof. Dr. Nabila Massak Gendi
Head of Chemistry
Department

## CHAPTER IV

## RESULTS AND DISCUSSION

# ACKNOWLEDGEMENT

The author wishes to express her deepest thanks and gratitude to Prof. Dr. Abdel-Gawad M. Rabie, Chemistry Dpartment-Faculty of Science, Ain Shams University and to Prof. Dr. Ahmed M. Dessouki, National Centre for Radiation Research and Technology for supervision, helpful discussions and guidance throughout this work.

The Author would like to express her deepest thanks to Prof. Dr. H. Roushdy, Chairman of the Atomic Energy Authority, for encouragement and help in various ways. Many thanks are also due to my colleagues at the National Centre for Radiation Research and Technology.

## AIM OF WORK

It would be difficult at present to find a branch of industry which could dispense with the use of ion exchangers. They are used in chemical, metallurgical and food industries, in the manufacture of antibiotics, purification of water, etc. During the past four decades ion-exchange technology has assumed particular importance in connection with the processing of solutions containing radioactive elements. Such use of ion exchange resins has its own typical features, since ionizing radiations produce changes in the physical and physicochemical properties of the ion exchangers. Irradiation of the resins is accompanied by changes in their exchange capacity, swelling tendency, selectivity of sorption, exchange kinetics, etc. At high integral doses (above $10^8$ rad) the decrease in the original capacity, caused mainly by the cleavage or destruction of ionogenic groups, as well as the contamination of the processed solutions by the products of radiation-chemical decomposition of the sorbents, may be so considerable that the resins can no longer be employed in the processing of radioactive solutions.

In the present study, the radiation-chemical stability of a strongly acidic cation exchanger of the polymerization type based on styrene-divinylbenzene copolymers and a weakly acidic cation exchanger of the polymerization type based on acrylic acid-divinylbenzene copolymers was investigated. The radiation stability of the resins was assessed from the change in exchange capacity, loss in weight, change in swelling behaviour and the

formation of new exchange groups. The resins were irradiated in air and in vacuum, in the air-dry state and in solution and in the $H^+$- and $Na^+$- forms. Nuclear magnetic resonance and electron spin resonance studies were carried out. The limits and possibility for the use of these two cation exchange resins in an intense radiation field are discussed.

# CHAPTER I

# INTRODUCTION

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It is almost impossible to discuss the radiation-chemical processes which take place in individual ion exchange resins in solution without a preliminary survey, however brief, of the general problems of the radiation chemistry, which have a direct relevance to the radiolysis of these systems. Since the great majority of all ion-exchange resins used at present are high molecular organic compounds, their irradiation is accompanied by various radiation-chemical reactions typical of high polymers in general. Cross-linking, degradation, gas evolution, change in the degree of unsaturation, oxidation, change in physical and physico-chemical parameters ..etc; all take place on the irradiation of ion exchange resins. It should be remembered, however, that ion exchangers in operation are exposed to ionizing radiations while in water or in aqueous electrolyte solutions. Reactions with the radiolysis products of the solutions and other secondary reactions may substantially affect the course of radiation-chemical reactions in the system resin-soulution; in addition the presence of functional groups in ion exchangers renders the mechanism of these reactions more complex. The general relationships governing the radiation chemistry of high polymers and the radiation chemistry of water and aqueous solutions will be briefly discussed.

## RADIATION CHEMISTRY OF HIGH POLYMERS:

The action of ionizing radiation on high polymers alters almost all their original properties. Even though radiation-chemical processes in high polymers take place in relatively low yields, the effect of the radiation on physical, mechanical and physicochemical properties of the organic polymer may be considerable. The course and yield of most radiation-chemical reactions, especially in certain individual polymers, is independent of the absorbed dose rate and is determined almost exclusively by the total integral dose absorbed. When high polymers are irradiated in the presence of oxygen or in solution, radiation-chemical yields of various processes (including oxidation, cross-linking and degradation) may depend both on the absorbed dose rate and on the relative proportions of the components of the irradiated system. Many high polymeric materials are utilized in radiation fields of high intensities, so that their radiation stability is an important factor. Radiation stability is expressed as the maximum value of the absorbed dose at which the irreversible radiation-chemical changes taking place in high polymers are still without a marked effect on their proprties. In most organic high polymers, a dose of $10^9$ rad or higher results in a sufficient damage to the polymer to render it unserviceble.

The action of ionizing radiation on high polymers may bring about the following main types of reactions:(1-6)

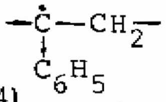
1) formation of chemical bonds between the polymer chains

(cross-linking, formation of tridimentional structures, vulcanization); 2) scission of chemical bonds in polymer molecules accompanied by a decrease in the molecular weight (degradation); 3) gas evolution; 4) oxidation (in the presence of oxygen, water, aqueous solutions and other oxygenated compounds; 5) change in the concentration and nature of double bonds. It is well known that radiation-chemical reactions involving high polymers mostly proceed with the participation of free radicals formed as a result of irradiation. It is therefore expedient to begin the discussion of radiation-chemical reactions taking place in high polymers with free radical formation and subsequent radical reactions.

## 1. Free Radicals:

When acted upon by ionizing radiation, high polymers just like any other compounds, form excited and ionized molecules which may produce free radicals as a result of various transformations. The free radicals then participate in numerous chemical reactions which are responsible for changes in the properties of the high polymer. The yield of free radicals, like the yield of any other product of radiolysis, may be described in terms of the G-value (radiation-chemical yield), which is the number of free radicals formed as a result of the absorption of 100 ev of the ionizing radiation. As a rule, the yield of the free radicals formed by the irradiation of high polymers is determined by the method of electron spin resonance (ESR)(7). The identification of various radicals from the ESR spectra of the irradiated polymers is mostly very difficult. For this reason, the ESR method often only determines the total number of paramagnetic particles in the polymer samples and their life times as a function of the experimental conditions. The radical yield is not constant, but may vary for the same polymer with temprature, degree of crystallinity, etc. The free radicals formed in irradiated high polymers may exist at room tempreature for several days or even monthes. When the irradiated high polymer is heated, the rate of disappearance of free radicals increases. The maximum rate of disappearance of free radicals in irradiated polymers is usually noted in certain definite temperature ranges, corresponding to a considrable increase in the mobility of single segments or whole macromolecular chains. In certain polymers (e.g., in tetrafluoroethylene) free radicals are stable even at 150-200°(5). The rate of disapearance of free radicals in amorphous polymers is higher than in crystalline polymers. The radical yield measured by the ESR method also depends on the degree of crystallinity of the sample. On one hand, the radical yield in crystalline polymers should be less than in the amorphous ones, since in crystalline structure there is the important cage effect as a result of which many of the formed radicals disappear because of recombination in situ. On the other hand, in a crystal lattice network the rate of disappearance of free radicals is usually much slower than in the amorphous polymer.

The rate of disappearace of free radicals is also affected to a certain extent by the radiation; it is much higher during than after the irradiation(8). When an ionizing radiation is made to act on high polymers, their free radical concentration increases up to a certain value, after which it does not increase any more on further irradiation. The limiting concentration of free radicals depends on many factors and is usually $10^{18}$-$10^{20}$ radicals/gram for high polymers(9). The concentration of free radicals usually ceases to increase at integral doses of $10^{8}$-$10^{9}$ rad.

In most hydrogenated high molecular compounds the formation of a primary radical involves a hydrogen atom which is split off the polymer chain. The formation of radicals of type  $-\dot{C}(C_6H_5)-CH_2-$ in the irradiation of polystyrene may serve as example(4). Further reactions involving such polymeric radicals and H atoms result in numerous radiation-chemical transformations taking place in the polymers, in the apearance of new free radical, and in the evolution of hydrogen or other gaseous products of radiolysis. The irradiation of polymers containing a quaternary carbon atom usually results in the formation of free radicals not only through the cleavage of hydrogen atom, but also as a result of the scission of the main chain.

## 2. Cross-linking Versus Degradation:

Of the numerous processes which take place during the irradiation of high polymers, cross-linking and dgradation occur most often in practice. The radiolysis of any high polymer involves simultaneous cross-linking and degradation. One of these two processes is usually predominant and high polymers can be grouped in two classes: those which are cross-linked and those which are degraded under irradiation (4,5,10,11) (Table 1). The cross-linking polymers gradually become insoluble when exposed to irradiation, and their molecular weight increases until a completely cross-linked tridimentional structure is formed. In most cases the elasticity modulus and the tensile strength increase, the elongation-at-break decreases, the chemical and thermal resistance increase and the polymer no longer becomes a visco-fluid on being heated. Polymers which undergo degradation show a decrease in their molecular weight and viscosity on being irradiated. Most of their physical and mechanical parametars deteriorate, their chemical stability decreases and, if the integral dose is sufficiently high, the polymer may be converted into a viscous liquid.

Divergent opinions on the mechanism of radiation-chemical cross-linking and degradation have been put forward. It is most often assumed that these are free radical reactions (12). The cross-linking of many polymers may be interpreted as recombination of polymeric free radicals formed as a result of two separate acts of ionization or excitation and valency migration along the chain. According to another view, the formation of a cross-link is the result of single act of excitation or ionization; the molecule which has been activated by the radiation reacts