SYNTHESIS AND CHARACTERIZATION OF SOME GRAFTED POLYMERS WITH ACRYLIC AND VINYL MONOMERS

THESIS

Submitted in Partial fulfilment of the requirements for (M.Sc.) Degree in Chemistry

By

Gamal Abd El Aziz Melegi

(B.Sc.)

Demonstrator – Faculty of Science

Supervised by

Prof. Dr. Abd El-Gawad M. Rabie

Prof. Dr. Ashraf A. M. Hamed

Dr. El-Sayed A. Hegazy

Ain Shams University

Faculty of Science

Cairo - E.A.R.

1990

الله

بسم الله الرحمن الرحيم

سُبحانكَ لَا عِلمَ لَنَا إِلَّا مَا عَلَّمتَنَا
إِنَّكَ أَنتَ العَلِيمُ الحَكِيمُ

صدق الله العظيم

بسم الله الرحمن الرحيم

SYNTHESIS AND CHARACTERIZATION OF SOME GRAFTED POLYMERS WITH ACRYLIC AND VINYL MONOMERS"

Thesis Advisors

Prof. Dr. A.M. Rabie
Prof. Dr. A. A.M. Hamed
Dr. E.A. Hegazy.

Approved

..............AMR..
.......A. Hamed..
......E. A. Hegazy.

N. El Gaindy.

Head of Chemistry Department Faculty of Science, Ain Shams University

1990

ACKNOWLEDGEMENT

The author wishes gratefully to express his sincere thanks to Prof. Dr. Abdel Gawed M. Rabie and to Prof. Dr. Ashraf Hamed, Chemistry Department, Faculty of Science, Ain Shams University, and to Associate Prof. Dr. El-Sayed A. Hegazy, Radiation Research of Polymer Chemistry Department, National Centre for Radiation Research and Technology (NCRRT), Cairo, for suggesting the point of research , Supervision, continuous guidance and helpful discussions throughout this work.

The author wishes to express his thanks to Dr. Naeem El-Sawy, Radiation Research of Polymer Chemistry Department, National Centre for Radiation Research and Technology (NCRRT), Cairo for the help and support during the experimental work and discussion of results.

Many thanks are to the staff of Chemistry Department, Faculty of Science, Ain Shams University and to members of the Radiation Chemistry Department for their help and support.

C O N T E N T S

CHAPTER IV

RESULTS AND DISCUSSION

Aim of The Work

Radiation induced grafting is one of the more effective and convenient approaches for preparing ion exchange membrane, especially for fluoro-containing ones. Fluorine-containing polymers have drawn much attention in the past and gained wide practical use because of their excellent electric, thermal, mechanical, and chemical properties as compared with the properties of unfluorinated polymer such as polyethylene.

Synthetic membranes have achieved a wide range of application in biomaterial, pharmaceutical purposes, food, and chemical industries. Such synthetic membranes are used for a great variety of separation processes such as dialysis, electrodialysis and hyperfilteration.

In this connection, the simultaneous radiation grafting of hydrophobic monomer such as vinyl acetate, VAc, onto both hydrophobic polymers such as low density polyethylene, LDPE, and poly(tetrafluoroethylene-perfluorovinyl Ether) copolymer, TFA, films will be investigated and the possibility of producing a hydrophobic graft copolymer will be examined. The influence of grafting condition on the grafting process will be studied. The effect of hydrophilic monomer such as acrylic acid (AAc) onto the films grafted by hydrophobic monomer (VAc) or the effect of VAc onto the hydrophilic grafted films will be investigated.

Some properties of those materials such as swelling behaviour, electrical conductivity and mechanical properties will be also investigated. Moreover, the modification of the membranes carried out by grafting with vinyl acetate followed by hydrolysis will lead the physical, mechanical and electrical properties of the corresponding membranes.

CHAPTER I

GENERAL INTRODUCTION

INTRODUCTION

Research activity is still on the increase in the field of radiation graft polymerization present, spurred by the now proved fact that desirable modifications of many polymers can be induced by radiation.

Small chemical changes produced by moderate radiation doses can cause effects onthe physical properties of polymers. A polymeric substance becomes essentially one large molecule when an average of about one cross-link unit per molecule has been produced by irradiation. A graft copolymer is composed of chains containing two or more chemically different types of monomer units. It is made up of a backbone chain consisting entirely of monomer x, attached to one or more side chains composed of monomer y, as shown diagrammatically in the following example :

```
                    y-y-y-y-y-y-
                    |
-x-x-x-x-x-x-x-x-x-x-x-x-x-x-x-
           |
           y-y-y-y-y-y-
```

graft copolymer

One of the reasons such graft copolymers are of interest of the polymer chemist is that a film of a chain of x's can be surface grafted with branches of y's to increase surface water repellency, dyeability, solvent resistance, light resistance, mildew resistance, etc. Often the grafting of monomer on the surface of a polymer, or within the polymer to a certain depth, produces significant changes in physical properties of the polymer.

The synthesis of graft copolymer is based on the production of one or more active sites on the backbone of the original polymer. Monomer y units then add successively at each active site, producing long chains of y extending out from the backbone as shown in the above drawing.(1)

Three general methods have been successfully developed and these will now be described together with their attendant advantages and disadvantages.

1. The mutual or direct radiation grafting of a vinyl monomer onto polymer.

The direct method of irradiating the polymer in the presence of monomer is perhaps the most efficient method of grafting because the free radicals are utilized to initiate chains of y as fast as they are produced. These will be used as examples :

$$\text{Polymer } A\sim\sim\sim A,\ P_A\sim\sim\sim \longrightarrow \dot{P}_A + \dot{R}$$

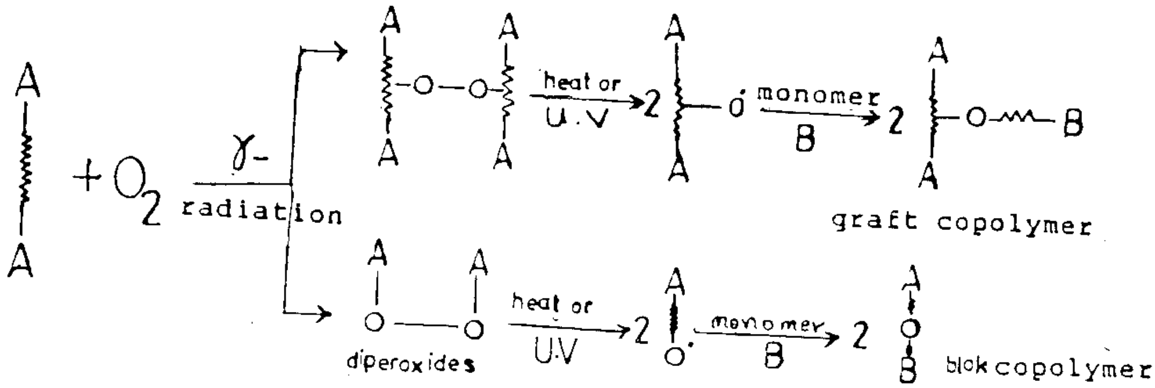
Where $\dot{P}_A$ is a macroradical and $\dot{R}$ is a radical fragment such as $\dot{H}$, $\dot{Cl}$, $\dot{CH}_3$, $\dot{F}$ ....etc.

$$\dot{P}_A + M_B \rightarrow P_A + P_B \text{ graft copolymer}$$

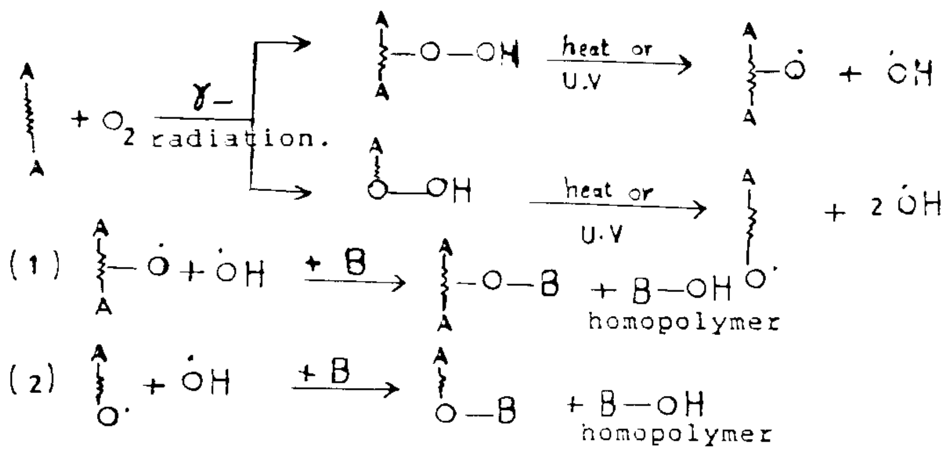
where M_B is monomer B. $\dot{R}$ can extract a hydrogen or other atom from polymer A leading to a fresh site for grafting and a volatile fragment such as hydrogen.(2) Alternatively, $\dot{R}$ can directly initiate polymerization of M forming homopolymer B. Monomer $M_B \rightsquigarrow M_B^{\cdot} \xrightarrow{+\dot{R}}$ homopolymer B. A disadvantage is the fact that some homopolymerization of y takes places, initiated possibly by free radicals formed in the irradiation of monomer y. Homopolymerization is promoted in cases where monomer y is present in excess, which is generally true when this technique is employed.[1] A free radical inhibitor could be added to the monomer, Cu^{++} or Fe^{++} salts, are examples which have been used successfuly for the mutual grafting of vinyl monomer onto TFA Poly-(tetrafluoroperfluoro vinyl ether) and PE (Polyethylene) films[3] Homopolymer may also be initiated by the small radical fragments $\dot{R}$ produced by the radiolysis of polymer A. This can be minimized by keeping the concentration of the monomer in polymer A to a minimum[2-4]. An advantage of the mutual method is that most monomers act as radiation protectors reducing any degradation of polymer A by the radiation itself[2]. Dose rate can also be an important variable, if too high, the radicals tend to terminate before leading to adequate grafting.[5]

2. Grafting on radiation-peroxidized polymers.

In this technique, the polymer may be irradiated in oxygen to produce a variety of free radicals through the oxidation process. Such free radicals can be preserved within the polymer by storage under appropriate conditions and then employed later to initiate the grafting of monomeric side chains. This method can be illustrated schematically in the following way :



Here again graft or block copolymers are expected. In this case no homopolymerization of the monomer B occurs other than by chain transfer to the monomer or by thermal polymerization. If the peroxidation of $(A)_n$ leads to hydroperoxides, the following reactions are expected to take place :



It appears that the thermal dissociation of the hydroperoxidation gives rise to equivalent amounts of graft copolymer and homopolymer molecules. In the second stage a homopolymer will result from initiation of polymerization by $\dot{O}H$ radicals. In general with most polymers, hydroperoxides are by far the most