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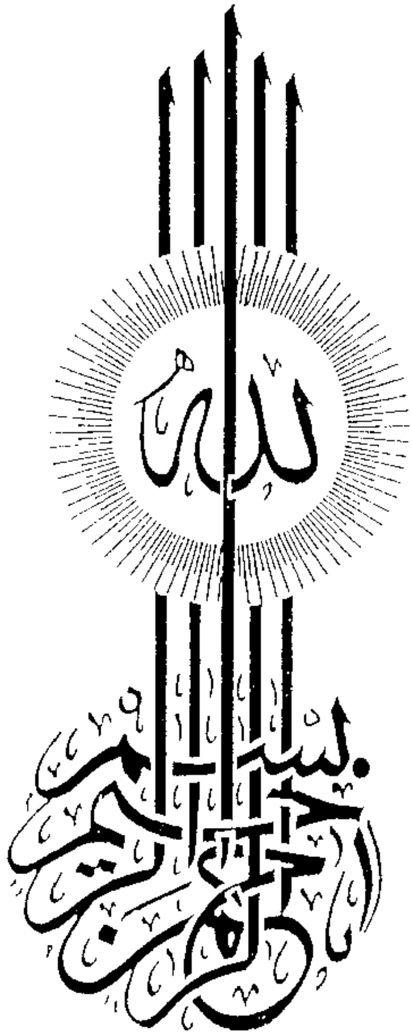
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AIM OF WORK

Interest in synthetic membranes and membrane processes is rapidly growing. For the last two decades, membranes have increasingly been introduced as an effective and economical means for the separation of molecular mixtures. Today their applications range from desalination of saline water and artificial kidneys and lungs, to separation and fractionation of gases or macromolecular mixtures.

Membranes obtained by grafting of hydrophilic monomers onto hydrophobic polymers seem to meet all the requirements due to the fact that such grafting can induce hydrophilicity as well as good electrochemical properties. Fluorine-containing polymers such as poly(tetrafluoroethylene) have drawn much attention in the past and gained wide practical use because of thier excellent thermal, chemical stability, and mechanical properties. By the grafting of vinyl and acrylic monomers onto such fluorinated polymer, graft copolymers exhibiting good properties can be obtained.

Radiation initiated grafting is a very broad field which has attracted considerable interest over the last two decades. Graft copolymers are alloys of polymers which, at least in principale, may combine the desirable properties of two polymeric components. Radiation methods are particularly suited for the production of a large variety of graft copolymers with interesting properties.

In this study, the preparation and some selective properties of graft copolymers obtained by radiation grafting of methacrylic acid onto poly(tetrafluoroethylene) and polyethylene films were investigated. The influence of grafting conditions such as solvent, type of inhibitor and its concentration, irradiation dose, irradiation atmosphere (air, nitrogen gas, and vacuum), film thickness, and monomer concentration, on the grafting yield was studied. Electrochemical and mechanical properties and swelling behaviour were also investigated. A trial has been made also on the graft polymerization of comonomer such as methacrylic acid and acrylonitrile onto poly(tetrafluoroethylene) film. The effect of comonomer composition and comonomer concentration on the grafting yield and on the properties of the obtained graft copolymers was studied.

The possibility of the practical use of such prepared graft copolymers by the radiation grafting methods were suggested in this work.

INTRODUCTION

CHAPTER I

INTRODUCTION

RADIOLYTIC GRAFTING OF MONOMERS ON POLYMERIC FILMS

A graft copolymer is composed of chains containing two or more chemically different types of monomer units, in more generally, 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 diagramatically in the following example :

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

graft copolymer

Often the grafting of monomer y on the surface of a polymer or within the polymer to a certain depth, produces significant changes in physical properties of the polymer.

The general technique has been very successful using both chemical and high energy radiation to "activate" the polymer. Radiation has been studied to the greatest extent and literally hundreds of papers have been published in this field. Three general methods have been successfully developed and these will now be described together with their attendant advantages and disadvantages. An excellent general review of all three methods which is still largely up to date, and is essential reading for those working in the field may be found in the book by Chapiro[1].

(a) The Mutual or Direct Grafting Technique :

Here the polymeric backbone is irradiated in the presence of the monomer or monomer mixture. It is clear that under these conditions the following reactions take place. Since most of the work has been concerned with radicals these will be used as examples.

A brief account of radiation - induced mutual ionic grafting will be presented later.

$$\text{Polymer A, } P_A \rightsquigarrow P_A^{\bullet} + R.$$

where $P_A^{\bullet}$ is a macroradical and $R^{\bullet}$ a radical fragment such as $H^{\bullet}$, $Cl^{\bullet}$, $CH_3^{\bullet}$ etc..

$$P_A^{\bullet} + M_B \longrightarrow P_A - P_B \text{ graft copolymer}$$

$R^{\bullet}$ can abstract a hydrogen or other atom from polymer A leading to a fresh site for grafting and a volatile fragment such as hydrogen. Alternatively $R^{\bullet}$ can directly initiate polymerization of M_B forming homopolymer B.

i.e. $\text{Monomer } M_B \rightsquigarrow M_B^{\bullet} \xrightarrow{+} M_B \rightarrow \text{homopolymer B}$

Eventually the growing graft or homopolymer chains terminate either by combination or disproportionation.

To optimize the formation of graft copolymer with the minimum of contaminating homopolymer there are certain conditions which need to be met. Most importantly the yield of radicals from the radiolysis of the polymer must be, as much as possible, in excess more than that from the monomer. Thus the grafting of styrene to poly(methyl acrylate) would be highly favoured, G (rad.) value for styrene is $\sim$ 0.7, compared with about 5 for poly(methyl acrylate). The other way round (or similar G (rad.) values) would be unfavorable and mainly homopoly(methyl acrylate) would result.[2] There are methods of overcoming this problem, a free radical inhibitor could be added to the monomer, Cu^{++} or Fe^{++} salts are examples which have been used successfully, for the mutual grafting of acrylic acid to polyethylene[3]. A second effective method is to have the monomer present in the vapor phase. Since the radiation is absorbed on a density basis this largely eliminates the problem. This method has been used practically for the grafting of acrylic acid to poly(ethylene terephthalate) for example. Homopolymer may also be initiated by the small radical fragments R$^\bullet$ produced by the radiolysis of polymer A. This can be minimized by keeping the concentration of the monomer in polymer A to a minimum. The use of monomer swollen polymer A with monomer B is practicable and is a good method to bring this about. An advantage of the mutual method is that most monomers act as radiation protectors reducing any degradation of polymer A by the radiation itself. Dose rate can also be an important variable, if too high the radicals tend to terminate before leading to adequate grafting. Chapiro has discussed this with particular reference to the grafting to Teflon where the effect is particularly severe[4].

(b) The Preirradiation Grafting Technique :

In this method the polymeric substrate is irradiated in the absence of air, subsequently the deaerated monomer (S) is introduced into the vessel containing the irradiated polymer. The free radicals trapped in the polymer react with the monomer forming the graft copolymer. Since there is plenty of apportunity for the R' (small radical components) to abstract hydrogens etc. very little homopolymer is produced in this method. It is a technique which is also not limited to any particular monomer-polymer combinations since the monomer itself is never exposed to radiation. A disadvantage of this method is that there is no protection of the substrate polymer by the monomer and some degradation can occur.[2] In this case the product would be a mixture of block and graft copolymers. The method is limited to glassy and semicrystalline polymers. With amorphous polymers in the rubbery state, the radicals produced by the radiation do not survive long enough to subsequently initiate grafting. Unlike the mutual method there is no limit to the dose rate which can be used, consequently the method is very suitable for electron beam irradiation providing that the penetration of the sample thickness is adequate. It has been found, even with the mutual method, that grafting can be effected by electron beams. This is achieved, in spite of the unfavorable kinetics, by the build up of trapped radicals followed by postpolymerization. In a sense therefore this could be regarded as similar in mechanism to the preirradiation method itself.

(c) The Peroxide Method :

This method can be illustrated schematically in the following way [2] :

(i) Polymer A + O_2 (air) $\rightsquigarrow$ polymer A.OOH + some polymer A-O-O-A polymer.

(iia) Polymer AOOH $\xrightarrow{\text{heat or UV}}$ Polymer AO.+.OH

or

(iib) Polymer AOOA polymer $\xrightarrow{\text{heat or UV}}$ 2 polymer AO.

If stage (ii) is carried out in the presence of monomer B, in the absence of oxygen, it is clear that grafting will occur. In the case of (iia) homopolymer will result from initiation of polymerization by the .OH radicals. In general, with most polymers, hydroperoxides are by far the most prevalent and so the homopolymer can become a problem. In the correct circumstances this can be alleviated by the use of redox systems.

e.g. polymer AOOH + Fe^{++} $\longrightarrow$ polymer AO.+OH^{-}+Fe^{+++}.

In this way the production of homopolymer can be largely avoided.

The above discussion has, even in the case of mutual grafting, implied a heterogeneous reaction. In the trapped radical method this is essential but in the mutual and peroxide methods the reactions can be carried out in solution. The gel effect, however, plays an important role in promoting the growth of long grafted side chains, and hence the yield, that heterogeneous methods are almost universally used.

Theoritical Considerations In Grafting :

Experimental observations on radiolytic grafting have attracted the interest of a large number of investigators. Some phenomena particularly worth noting include the generation and preservation of free radicals in the polymer substrate, the effect of oxygen on radical generation, the dependence of grafting rate on dose rate, the importance of chain transfer, the promotion of grafting when termination is hindered, and the limitation of grafting sometimes