Development of Membranes by Radiation Grafting of Acrylamide into Polyethylene Films: Influence of Synthesis Conditions

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SYNOPSIS: The graft copolymerization of acrylamide monomer into polyethylene films was carried out by the preirradiation method. The influence of synthesis conditions, such as monomer concentration, preirradiation dose, reaction temperature, Mohr's salt, and pregrafting storage was investigated. The order of dependence of the rate of grafting on preirradiation dose and monomer concentration was found to be 0.87 and 1.86, respectively. An activation energy of 22.9 kJ/mol for the grafting reaction was obtained. The storage of preirradiated polyethylene film at $-4°C$ prior to the reaction showed a decrease in the degree of grafting up to 10 days, beyond which the degree of grafting remained constant. The addition of $FeSO_4$ in the grafting medium not only inhibits the homopolymerization of the monomer but also decreases the degree of grafting. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1331–1337, 2000

Key words: polyethylene; acrylamide; film; radiation; graft copolymerization

INTRODUCTION

Environmental protection has become a subject of great concern and top priority domain on a global basis. The membrane technology is one of prominent techniques to solve these environmental problems, which are mainly associated with various pollution loads such as the production of pure water as well as the recovery of dyes and chemicals.[1–2] One of the most useful domain of membranes is the recovery and separation of toxic metal ions from the waste effluent in industrial units.[3] The most attractive feature of these membranes lies in terms of their easy regeneration, which enables them to use for subsequent separation processes.[4]

The development of a membrane for specific application is a difficult task as it needs perfect control over the physical properties to achieve the best possible performance in an operation. The preparation of proton exchange membranes by radiation-induced graft copolymerization of different monomers onto several polymers has proved to be a very effective modification technique without any consideration of the shape of the material, and may be applicable on polymers in the form of films, fibers, hollow fibers, fabric, and beads.[5–12] The graft copolymers display an unique concept of combining desirable properties of two polymeric moieties. The attractive feature of radiation grafting is that the size of the grafted component can be controlled easily by proper se-

lection of the irradiation dose and its intensity.[13] This is the reason that the radiation grafting is particularly suited for the production of membranes with a wide range of physicochemical characteristics.[14–18]

Polyethylene (PE) film is an excellent matrix for the membrane development due to its chemical resistance, low density, and its relatively low cost. However, the polymer may be transformed into membranes by radiation grafting of vinyl as well as acrylic monomers. Several studies have been reported on the radiation grafting of acrylamide and acrylic acid into PE films and hollow fibers.[5,17–20] The flat sheet membranes have been found to show higher degree of swelling and extremely low resistivity—viz. 0.05–2 Ωcm^2 for the grafting higher than 300%. Our aim is to develop membranes by radiation-induced grafting of acrylamide on PE films and transform them into membranes containing amide and carboxylic groups, so that the material could act as the chelating and ion exchange membrane for the separation and recovery of toxic metal ions from an industrial effluent.

In the present study, grafting of acrylamide into polyethylene films is carried out to produce membranes with different degrees of grafting. The influence of synthesis conditions on the degree of grafting is investigated. The degree of grafting has been observed to be considerably influenced by the nature of the additive and the reaction medium and will be communicated subsequently.[21]

EXPERIMENTAL

Materials

Linear low density polyethylene films of 40 μm thickness, processed from chips (Grade F-19010, MFI 1.0), were supplied by Reliance Industries, India, for the grafting reaction. Acrylamide monomer (SISCO India) was used as received without any purification. $FeSO_4$ was used as the additive in the grafting medium. Distilled water was used for all the experiments.

Irradiation

A Co-60 γ-radiation source (900 curies) was used for the irradiation of PE films. The dose rate of radiation was 0.36 kGy/h. The irradiation was carried out in air for a desired period. The ex-

posed films were stored at $-4°C$ before grafting experiments.

Graft Copolymerization

Graft copolymerization was carried out on irradiated PE films of 3 ×3 cm^2 size. The PE film was placed in a glass tube containing monomer solution of desired concentration. $FeSO_4$ was added to the monomer solution to overcome the formation of any homopolymer during the grafting reaction. Nitrogen was purged into the glass tube to remove air from the grafting solution. A glass tube was placed in a water bath maintained at a constant temperature. After the desired period, the glass tube was taken out and the grafted film was extracted with hot water to remove traces of any homopolymer adhering to the film surface. The grafted film was dried in air oven at 60°C and weighed. The degree of grafting in PE film was calculated from the following equation:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_0}{W_0} \times 100$$

where W_o and W_g are the weights of ungrafted and grafted films, respectively.

RESULTS AND DISCUSSION

The radiation-induced graft copolymerization of acrylamide into PE films is carried out to investigate the influence of reaction conditions on the degree of grafting so that membranes with tailored characteristics may be developed. Consequently, the influence of monomer concentration, preirradiation dose, reaction temperature, storage period, and additives on the grafted polyacrylamide content was studied. The grafting was carried out using unpurified acrylamide monomer so as to reduce the monomer purification step, which would make this membrane development process industrially viable on an economic front.

Influence of Ferrous Sulfate

It is observed that the grafting does not take place if no additive is added to the monomer solution. Instead, vigorous homopolymerization proceeds right from the beginning of the reaction. This leaves hardly any monomer for the grafting reaction to take place. In this system, the grafting is initiated by the decomposition of hydroperoxides
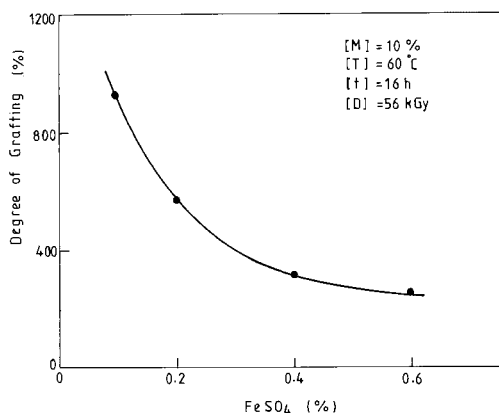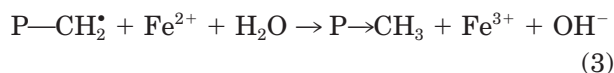
Figure 1 Variation of the degree of grafting with the ferrous sulfate concentration.

in the irradiated film. It is the hydroxyl radical that initiates the homopolymerization. It is observed that the addition of $FeSO_4$ to the grafting medium is very effective in preventing homopolymerization. In the presence of ferrous sulfate, the decomposition of peroxide as per eq. (1) is replaced by eq. (2), where ferrous sulfate is directly involved in the redox process with the hydroperoxides, and hydroxyl radical no more exists.

$$POOH \rightarrow PO^{\bullet} + OH^{\bullet} \qquad (1)$$

$$Fe^{2+} + POOH \rightarrow POO^{-} + Fe^{3+} + OH^{-} \qquad (2)$$

$$P\text{—}CH_2^{\bullet} + Fe^{2+} + H_2O \rightarrow P\rightarrow CH_3 + Fe^{3+} + OH^{-} \qquad (3)$$

The influence of $FeSO_4$ on the degree of grafting is presented in Figure 1. The degree of grafting decreases very fast, initially up to 0.2%, beyond which the decrease is slow. It seems that the Fe^{2+} ions not only inhibit the homopolymerization but also are involved in the partial deactivation of growing chains, i.e., termination . Even if any homopolymer chain is initiated, this will also terminate as per eq. (3). Although there is complete inhibition of homopolymerization, the degree of grafting decreases only to a limited extent. This may be due to the fact that Fe^{2+} ion concentration within the swollen film is very low as compared to the outside medium.[22] In our earlier studies on the grafting of acrylic acid on PE films, similar diminishing effect of Fe^{2+} on the degree of grafting was observed.[5] Based on these studies, for all subsequent work we selected a concentration of Mohr's salt of 0.1%, which inhibits ho-

mopolymerization completely and allows reasonable grafting to take place.

Influence of Preirradiation Dose

The influence of preirradiation dose on the variation of degree of grafting with time is presented in Figure 2. The results show that the degree of grafting increases with time up to 2–4 h and then tends to level off. The higher the dose of preirradiation, the higher is the degree of grafting. Such a behavior may be understood from the generation of higher number of radicals at higher dose, which are available for the grafting reaction with the monomer. Ishigaki et al.[22] have compared the grafting reaction between LDPE and HDPE and found that the rate of grafting tends to be linearly proportional with the radical concentration. High levels of grafting in LDPE was attributed to the high concentration of radicals and higher diffusion rate of monomer in these films.

The variation of the final degree of grafting with the preirradiation dose is presented in Figure 3. The intercept on the grafting axis suggests additional grafting during the initial stages of the reaction via the *mechano-chemical* route as we have observed in our previous system involving grafting of acrylic acid onto polyethylene films.[5] This may be understood from the fact that the initial grafting starts on the film surface only and moves further within the film. This leaves behind a structure where the matrix contains both the
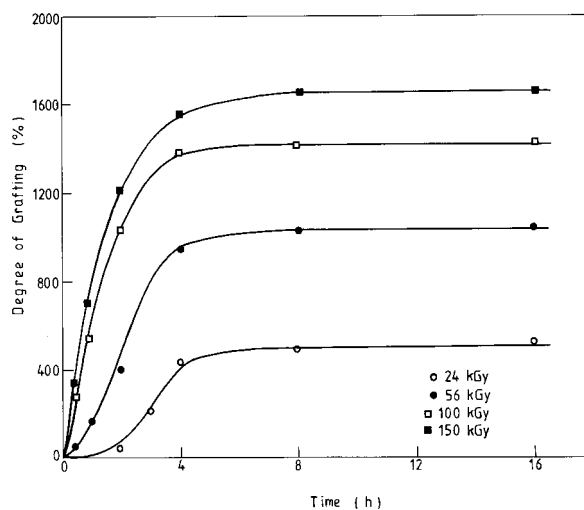

Figure 2 Variation of the degree of grafting with the time for different preirradiation doses. monomer concentration, 10%; temperature, 60°C; $FeSO_4$, 0.1%.
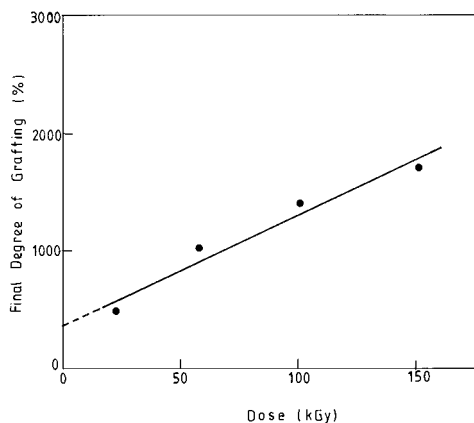
Figure 3   Variation of the final degree of grafting with the preirradiation dose. Grafting conditions same as in Figure 2.

polar grafted zones and nonpolar domains. This leads to the swelling of the grafted zones in aqueous medium but leaves behind the nonpolar zones unaffected. As a result, strong strains develop within the polymer matrix and chains are fractured to produce new polymeric radicals and enhance the grafting.

The log–log plot of the rate of grafting vs dose is presented in Figure 4. The dependence of the rate of grafting on preirradiation dose as obtained from the slope of the plot was found to be 0.87. This value is higher than 0.5, as observed in the classical free radical polymerization. Higher dependence of rate of grafting on the preirradiation dose, i.e., 1.30, has also been reported for the grafting of acrylamide on polypropylene (PP) films by Hegazy.[23] It is important to note that there are some changes in the physical structure
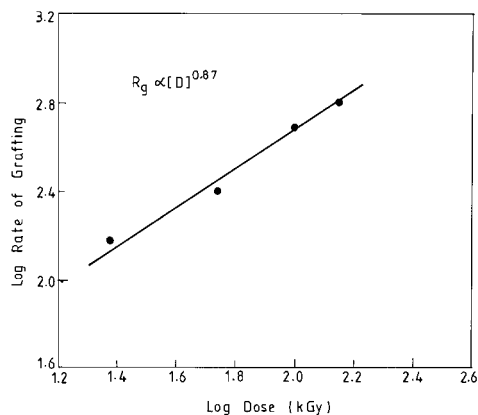

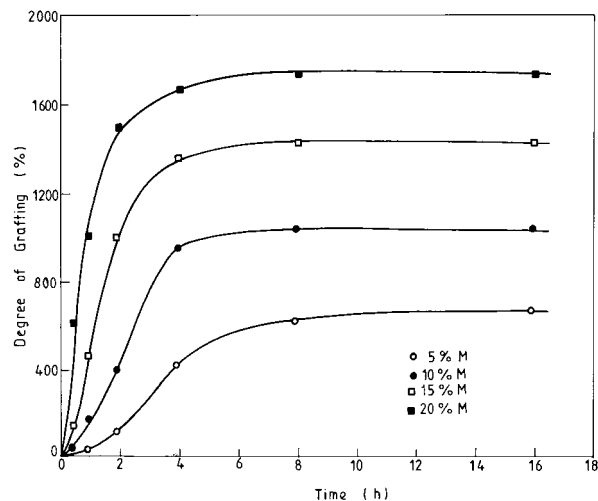**Figure 4**   Log–log plot of the rate of grafting vs preirradiation dose.

Figure 5   Variation of the degree of grafting with the time for different monomer concentrations. Preirradiation dose, 56 kGy; temperature, 60°C; $FeSO_4$, 0.1%.

of the polyethylene film with the increase in the irradiation dose.[24] These changes are expected to have their own impact on the grafting reaction, which we are not taking into account at this stage.

Influence of Monomer Concentration

The variation of degree of grafting with monomer concentration is presented in Figure 5. The results show an initial increase in the degree of grafting with time up to 4 h and tend to reach saturation beyond 8 h of the reaction. The final degree of grafting increases with the time for all monomer concentrations in the range of 5–20%. The increase in the degree of grafting at higher monomer concentration may be understood from the fact that the monomer availability to the grafting sites is enhanced at the higher monomer concentration.

The variation of the rate of grafting with the monomer concentration is shown in Figure 6. The dependence of the rate of grafting on monomer concentration as obtained from the slope of the plot was found to be 1.86. This value is much higher than the first-order dependence of a classical free radical polymerization. The higher value of dependence on monomer concentration have been observed in other systems as well.[10,23] Based on the above results, following kinetic rate expression for the dependence of the rate of grafting on the preirradiation dose and monomer con-
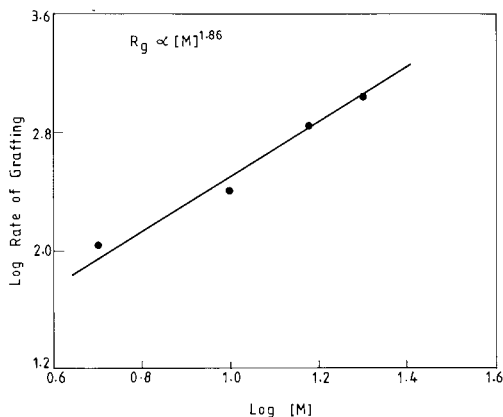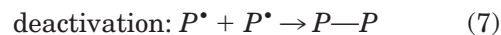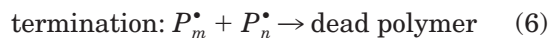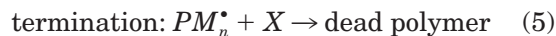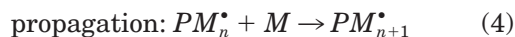
Figure 6 Log–log plot of the initial rate of grafting vs monomer concentration. Grafting conditions same as in Figure 5.

centration for the present grafting reaction may be represented:

$$Rg \propto [M]^{1.86}[D]^{0.87}$$

The higher dependence of the rate of grafting on monomer concentration suggests that the propagation step where monomer addition to growing chain occurs is considerably diminished. The PE film does not swell in water as the reaction medium. Therefore, the grafting proceeds by the diffusion controlled mechanism. The initial grafting takes place at the film surface only. These grafted surface layers swell in the grafting medium and further grafting proceeds deep into the middle of the film by progressive diffusion of monomer through the swollen grafted layers. It may be mentioned that a polymer swollen in solvent represents the medium of high viscosity that determines the diffusion of monomer into the bulk of the matrix. Therefore, the grafting process becomes greatly dependent on the diffusivity and the availability of monomer in the vicinity of the growing chain within the film. Under such circumstances, where viscosity of the water-swollen grafted layer is very high, the addition of monomer to the growing chain, may be considerably lowered [eq. (4)]. The mobility of growing chains in such a medium will be lower enough to hinder the termination by mutual recombination [eq. (6)]. At the same time, the termination of growing chains may be confined more to some impurities present in the grafting system [eq. (5)] leading to the higher dependence of the rate of grafting on the monomer.[25]

propagation: $PM_n^{\bullet} + M \rightarrow PM_{n+1}^{\bullet}$ (4)

termination: $PM_n^{\bullet} + X \rightarrow$ dead polymer (5)

termination: $P_m^{\bullet} + P_n^{\bullet} \rightarrow$ dead polymer (6)

deactivation: $P^{\bullet} + P^{\bullet} \rightarrow P{-}P$ (7)

The higher dependence of rate on preirradiation dose in rate expression indicates that the primary radicals have higher efficiency in initiating the grafting reaction. One may certainly expect the deactivation of primary radical by mutual recombination [eq. (7)] to take place as mentioned by Ishigaki et al. in his studies on the grafting of acrylic acid into PE films.[22] We, however, expect that primary radical termination has a negligible impact in our system and a major contribution of mechano-chemical grafting in raising dose dependence may arise by generating new radicals within the film that take part in the grafting reaction.[10]

Influence of Reaction Temperature

The variation of the degree of grafting with the reaction temperature in the range of 50–80°C is presented in Figure 7. From the slope of the plots, it may be stated that the initial rate of grafting increases with the increase in the reaction temperature. However, the final degree of grafting (at 16 h) shows a decreasing trend with the increase in the temperature. For all temperatures, the degree of grafting tends to reach saturation after 8 h of the reaction time. Similar observations have
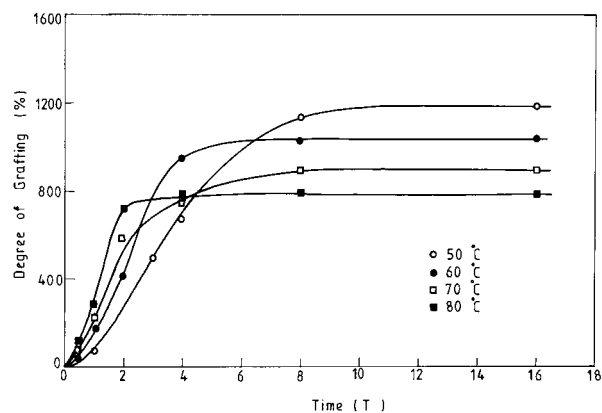

Figure 7 Variation of the degree of grafting with the time for different temperatures. Preirradiation dose, 56 kGy; monomer concentration, 10%; FeSO$_4$, 0.1%.
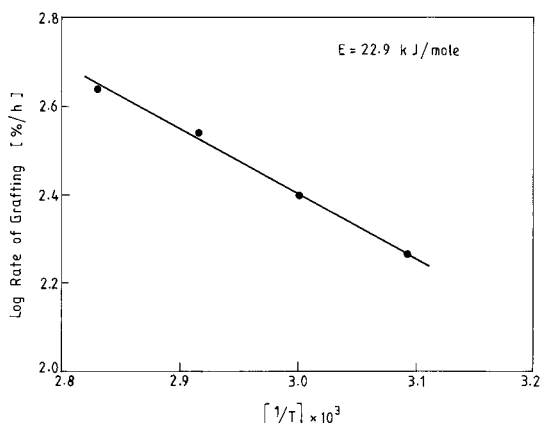
Figure 8   Arrhenius plot of rate of grafting vs [1/T]. Grafting conditions same as in Figure 7.

been made in our earlier studies on the grafting of acrylic acid and styrene into polyethylene and poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films, respectively.[5,10]

As discussed earlier, the grafting is governed predominantly by the reactivity of radicals and monomer availability at the grafting sites within the film matrix. The higher temperature is expected to enhance reactivity of radicals toward monomer resulting into faster chain initiation. At higher temperature, the monomer diffusion within the bulk of the film is enhanced. As a result, the local stationary concentration of monomer around the growing chain is increased, thereby leading to the higher rate of propagation.

The faster leveling off in grafting at higher temperature seems to be fallout of the enhanced deactivation of primary radicals, even before any grafting is initiated, as per eq. (7). As the water swollen film is a highly viscous matrix, the termination of two growing chains by mutual recombination should be hindered. But with the increase in the temperature, this bimolecular termination as per eq. (6) would be facilitated and would lead to lower graft levels.

The Arrhenius plot of the initial rate of grafting vs inverse temperature is presented in Figure 8. The activation energy of the grafting reaction as calculated from the slope of the plot was found to be 22.9 kJ/mol. This value is well in agreement with the activation energy value (13.6 kJ/mol) in studies of Hagazy[23] for the grafting of acrylamide on PP film for this temperature range. Mori et al.,[26] on the other hand, found activation energy of 50 kcal/mol for the polyethylene-g-acrylonitrile system. It appears that in our system, the pres-

ence of Mohr's salt facilitates the decomposition of peroxides, which may lead to lower value of activation energy.

Influence of Pregrafting Storage

The storage of irradiated films prior to the grafting at −4°C was found to decrease the degree of grafting. The decrease is very fast initially up to one week and then tends to stabilize (Fig. 9). Similar observations have been observed for the PE-g-acrylic acid and PP-g-acrylonitrile systems.[10,11] Sundardi et al.[27] have also reported that the storage of irradiated PP fiber at room temperature leads to the continuous decrease in the rate of grafting up to one week. Ishigaki et al.[22] have carried out extensive studies on the influence of storage conditions on degree of grafting of acrylic acid on PE films. The degree of grafting was found to decrease irrespective of the storage temperature between −24 to +22°C. Our observations for storage at −4°C are in agreement with these observations.

CONCLUSION

The radiation grafting of acrylamide into PE films leads to the development of membranes with different degrees of grafting. The degree of grafting is considerably influenced by the preirradiation dose and follows 0.87 order of dependence. The monomer dependence was found to follow an order of 1.86. The grafting reaction is a diffusion-controlled process and is governed by the reactivity and the diffusion of monomer, and its avail-
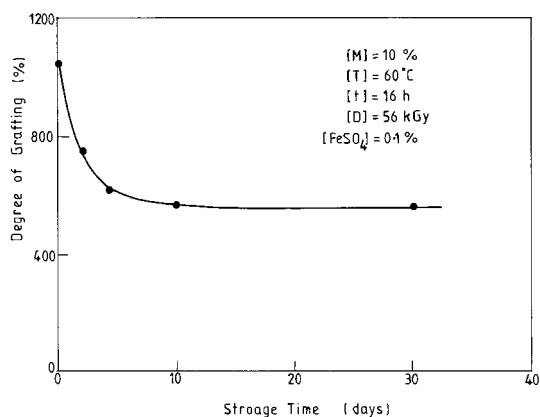

Figure 9   Variation of degree of grafting with the storage of the preirradiated films.

ability in the vicinity of the growing chains within the film. The presence of ferrous sulfate is effective in inhibiting homopolymerization. In the absence of ferrous sulfate, the intense homopolymerization sets in before any grafting could take place. The initial rate of grafting increases with the increase in the reaction temperature. However, the final degree of grafting shows an opposite trend. A relatively low value of activation energy, 22.9 kJ/mol, is in line with the assumption that the ferrous sulfate facilitates the decomposition of peroxides by the redox process. The storage of the irradiated PE films at $-4°C$ prior to the reaction decreases the degree of grafting. These membranes show promising matrix for the metal ion separation and is the subject of our current study.

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