

Graft Copolymerization of 4-Vinylpyridine and Methyl Acrylate onto Polyethylene Film by Radiochemical Method

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ABSTRACT: Graft copolymerization of 4-vinyl pyridine (4-VP) and methyl acrylate (MA) onto polyethylene (PE) was studied in aqueous medium in air by the mutual irradiation method. The percentage of grafting was determined as a function of the (i) total dose, (ii) monomer concentration, and (iii) amount of water. The effect of different alcohols such as methanol, ethanol, isopropyl alcohol, butanol, and pentanol on the percentage of grafting of 4-VP and MA was studied. The effects of different amines on the percentage of grafting of 4-VP were also studied. The graft copolymers were characterized by IR spectroscopy and thermal analysis and by identifying the isolated polymer from the grafted film. Grafted PE film was tested for permeability behavior and was found to be permeable to a 0.5% aqueous sodium chloride solution. A plausible mechanism is suggested to explain the grafting of 4-VP and MA onto PE film. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 599–610, 1998

Key words: graft copolymerization; polyethylene film; 4-vinyl pyridine; methyl acrylate; mutual irradiation; permeability

INTRODUCTION

Considerable work on the grafting of various vinyl monomers onto polyethylene (PE), using both chemical and radiation methods, has been carried out. Cation-exchange membranes from high-density polyethylene film (HDPE) were prepared by grafting styrene and diisopropenyl benzene in the presence of benzoyl peroxide.¹ Dimov and Aleksandrova² prepared chemical- and heat-resistant cation-exchange membrane from PE film grafted with styrene and divinyl benzene using benzoyl peroxide followed by sulfonation and hydrolysis. Radiation-induced grafting of styrene, in conjunction with other monomers, onto PE film was studied by Alieu and Kabanov.³ Semipermeable membranes, exhibiting reverse osmosis characteristics, have been prepared by photo-induced

grafting of acrylic acid on HDPE film.⁴ Dwarjanyn and Garnett⁵ used ionizing radiation and a photochemical method for the synthesis of bioactive polymers for medical application by grafting styrene onto PE film. Radiochemically grafted PE film with acrylic acid showed higher mechanical strength and thermal resistance.⁶ Methacrylic acid and ammonium methacrylate were grafted onto low-density polyethylene film (LDPE) using electron beams or γ -rays as initiators. The grafted film exhibited ion-exchange properties. In the present article, we report on gamma radiation-induced grafting of an electron-donor monomer, 4-vinylpyridine (4-VP), and an electron-acceptor monomer, methyl acrylate (MA), onto PE film by the mutual method. The permeability behavior of the grafted film was quantitatively studied by using a 0.5% aqueous sodium chloride solution.

EXPERIMENTAL

Materials and Methods

PE film was received from the CNRS Laboratory (Nancy, France). It was washed several times

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with methanol and dried. 4-VP (Merck, München, Germany) was freshly distilled before use. MA was washed with a 5% aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and distilled. The middle fraction was used. Distilled water was used as the reaction medium. Methanol, EtOH, iso-PrOH, BuOH, and *n*-pentanol (Ranbaxy) were used as received. Methylamine, triethylamine, pyridine, and diethylamine were used as received while aniline was distilled before use. The graft-copolymerization reaction was performed in a Gamma Chamber-900 having 2100 Ci Co⁶⁰ as a source for gamma radiation, supplied by the Bhabha Atomic Research Centre (Trombay, Bombay, India).

Graft Copolymerization

PE film (2 × 4 cm) of a known weight was placed in a flask containing a definite amount of water. A known amount of the monomer (4-VP/MA) was added to the flask. The reaction mixture was irradiated by γ -rays for different time periods at a dose rate of 0.092 Mrad/h. After a definite time period, the reaction flask was removed from the chamber and the film was washed thoroughly with water and an acetone mixture (1 : 1 v/v) for the removal of poly(4-VP) and with acetone for the removal of poly(MA). The homopolymer-free, grafted PE film was dried under a vacuum at 50°C and weighed to a constant weight. The percentage of grafting (*P_g*) was calculated as

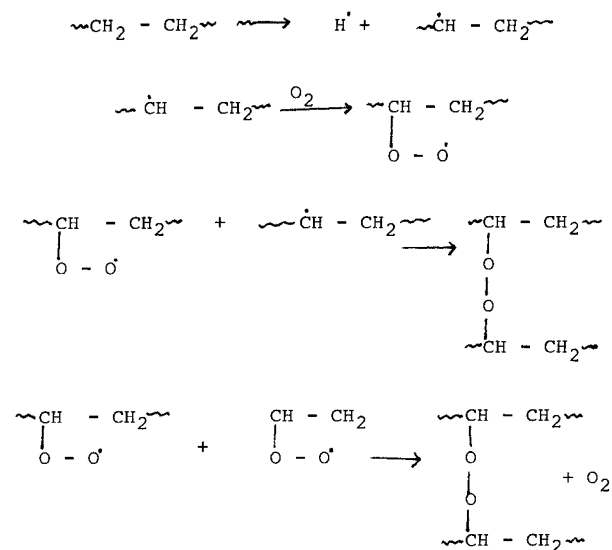
$$P_g = \frac{W_1 - W_0}{W_0} \times 100$$

where *W*₁ and *W*₀ are, respectively, the weights of grafted PE film, after complete removal of the homopolymer, and the original PE film.

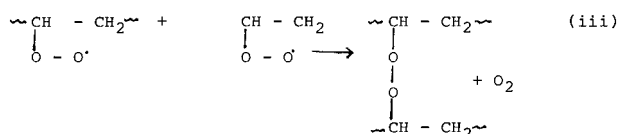
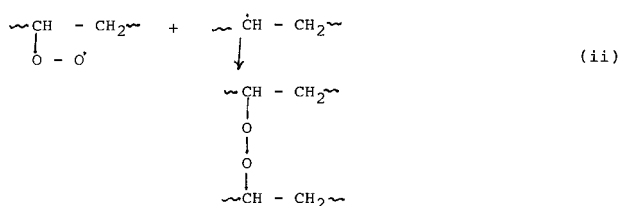
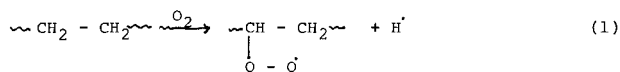
RESULTS AND DISCUSSION

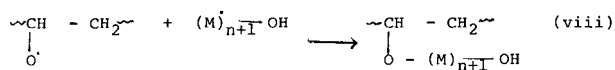
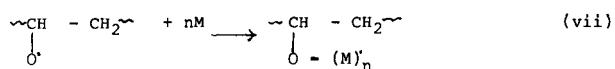
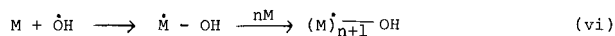
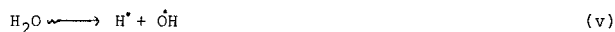
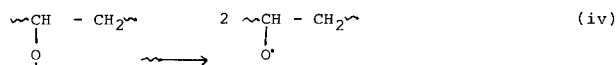
In the case of ionizing radiation, the primary event of radiation is the ionization or excitation of the molecules. In fact, ESR spectra due to trapped electrons⁸ and cation radicals⁹ in PE have been reported and several mechanisms for alkyl radical formation have been suggested. It is most likely that, when irradiation is carried out in air, some of the polymeric radicals, which would otherwise

lead to crosslinking, react with oxygen to form peroxidic structures via the following reaction steps:



The fact that peroxidic structures primarily arise at low dose rates is undoubtedly related to the low diffusion of oxygen in the polymer backbone. Bach¹⁰ found that X-ray-induced autooxidation of hydrocarbons results in the formation of peroxides and carbonyl compounds. The peroxides are predominantly dialkyl peroxides rather than hydroperoxides. Such a mechanism for the peroxidation of PE film was confirmed by further experiments which showed that such air-irradiated polymers are capable of initiating graft copolymerization.¹¹ These peroxide groups provide active sites for the grafting of vinyl monomers onto the polymeric backbone. On the basis of this, the following tentative mechanism is proposed for the grafting of 4-VP and MA onto PE film by the mutual method:





The effect of different parameters such as total dose, monomer concentration, and amount of water upon the P_g was studied. The effect of alcohols of different chain lengths and several amines, on the P_g of 4-VP and MA, was also studied.

Effect of Total Dose

The percentage of grafting of 4-VP and MA onto PE was determined as a function of total dose and the results are presented in Figure 1. It is observed from the figure that the P_g of both monomers shows an inconsistent increase and decrease in the grafting with increasing total dose. The P_g of 4-VP increases with increase in the total dose, reaches a maximum (76.76%) at a total dose of 2.02 Mrad, and then decreases up to 2.20 Mrad. Beyond 2.20 Mrad, further increase in the total dose leads to a slight increase in P_g up to 2.57 Mrad and then decreases, giving a minimum in grafting (30.4%) at a total dose of 2.64 Mrad, beyond which P_g increases again.

With MA, the P_g (52%) was obtained at a lower total dose of 0.52 Mrad. Further increase in the total dose decreases the percentage of grafting, giving a minimum percent grafting (28%) at a total dose of 1.40 Mrad. The maximum P_g (90%) of MA was obtained at a higher total dose of 1.76 Mrad. Such a peculiar behavior of an increase and then a decrease in grafting with the total dose was not observed with isotactic polypropylene (IPP) fiber^{12,13} and film.¹⁴ The difference in the behavior of the backbone polymers IPP and PE toward grafting may be explained on the basis of their morphological structures. For IPP, being a highly crystalline polymer, grafting occurs on the surface with the expulsion of tertiary hydrogen, providing

a site for grafting after the formation of hydroperoxide.

In the case of PE as the backbone polymer, some of the free radicals produced by ionizing radiations are trapped mainly in the crystalline region, where the diffusion of oxygen as well as of the monomer is slow. On the other hand, free radicals formed in the amorphous region easily come in contact with the monomer, owing to the facile segmental motion of the backbone polymeric chain. Similar observations were made by Gupta and Chapiro¹⁵ during the grafting of acrylic acid onto the PE film. The higher efficiency for grafting at low doses was explained as being due to the mechanochemical grafting during the initial stages of the reaction when grafting is limited to the amorphous domains of the polymeric matrix. This creates polar grafted zones in the nonpolar matrix. After the grafting in the amorphous region, grafting then starts at the surface of the film, where a decrease in the percentage of grafting is observed. The grafted zones during this period swell in the aqueous medium, which strains the polymer and leads to the rupture of polymeric chains. New polymeric radicals are thus created and enhancement in grafting is again observed. Grafting into crystalline regions can occur only when some oxygen diffuses through the rigid structure which undergoes rupture, producing active sites where grafting can occur, as indicated by the small increase in the P_g after the second increase and decrease of the P_g .

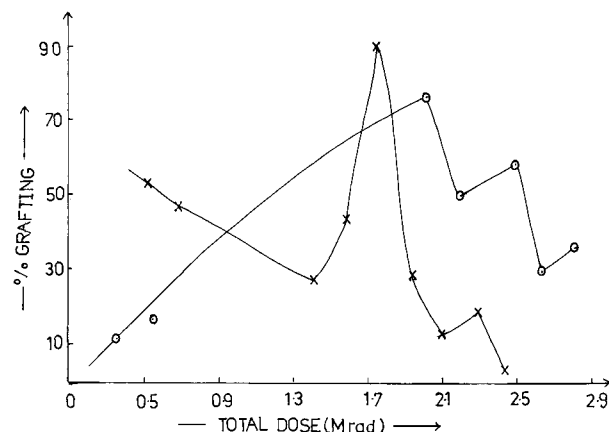


Figure 1 Effect of total dose on P_g of (—x—x—) MA and (—o—o—) 4-VP. PE film = 2 × 4 cm; dose rate = 0.088 Mrad/h; [MA] = 1.1 mol/L; water = 10 mL. PE film = 2 × 4 cm; dose rate = 0.092 Mrad/h; [4-VP] = 0.23 mol/L; water = 20 mL.

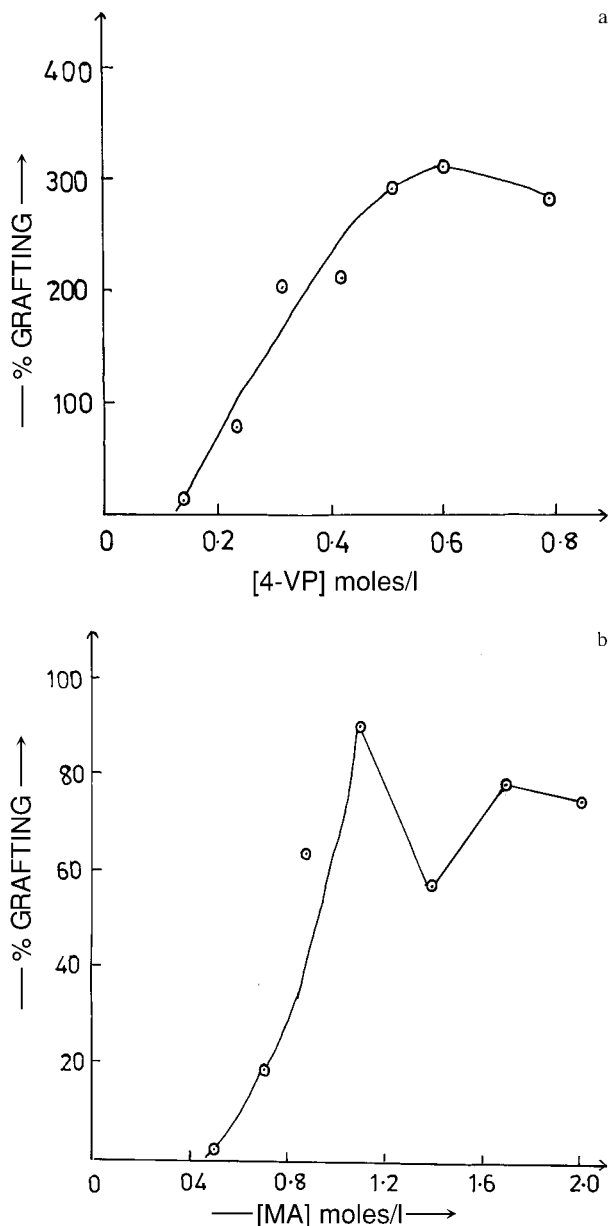


Figure 2 (a) Effect of [4-VP] on P_g of the PE film = 2×4 cm; total dose = 2.02 Mrad; water = 20 mL. (b) Effect of [MA] on P_g PE film = 2×4 cm; total dose = 1.76 Mrad; water = 10 mL.

Effect of Monomer

Figure 2(a,b) describes the effect of the variation in the monomer concentration on the P_g of 4-VP and MA, respectively. It is observed from the figure that the P_g of 4-VP increases with increasing concentration of 4-VP, giving a maximum (309.2) at [4-VP] = 0.60 mol/L and then decreases. The P_g of MA, on the other hand,

shows a sharp increase with increasing [MA], giving a maximum (90.3%) at [MA] = 1.10 mol/L, then decreases to 57.7% at [MA] = 1.4 mol/L. Further increase in the concentration of MA leads to a slight increase in P_g , and beyond [MA] = 2.0 mol/L, P_g decreases. Such a peculiar behavior of 4-VP and MA toward grafting onto PE can be explained by considering the polymerizability of the monomers being grafted. The k_p values of 4-VP (ref. 16) and MA (ref. 17) are of the order 12 and 1580 L mol⁻¹·s, while k_t values for 4-VP and MA are 3×10^6 and 55×10^6 L mol⁻¹·s, respectively. The polymerizability ($k_p/k_t^{1/2}$) values for MA and 4-VP are 213×10^{-3} and 7×10^{-3} , respectively. This indicates that the higher ($k_p/k_t^{1/2}$) value for MA is responsible for more homopolymer formation than for grafting as compared to 4-VP. 4-VP, being more soluble than MA in aqueous medium, produces higher grafting owing to its greater accessibility to the active sites.

Effect of Amount of Water

The effect of varying amounts of water on the P_g of 4-VP and MA has been studied and the results are presented in Figure 3(a,b). It is observed from the figures that the P_g for both the monomers increases with an increasing amount of water. The maximum P_g of 4-VP (521%) and MA (90%) is obtained using 10 mL of water. Further increase in the amount of water decreases the P_g of 4-VP up to 25 mL and of MA up to 30 mL of water. With further increase in the amount of water, the P_g increases slightly with both monomers. Increase in the P_g with an increased amount of water is explained by assuming that, in the presence of excess water, the swelling of the peroxidized PE backbone polymer occurs to some extent, thus exposing the active sites where grafting can occur. The decrease in grafting, beyond an optimum amount of water, is attributed to the formation of large amounts of hydroxyl ($\dot{O}H$) radicals arising from the radiolysis of water, which lead to preferential homopolymer formation at the expense of the graft. Further increase in the amount of water leading to an increase in the P_g is explained by the fact that the homopolymer [Poly(4-VP)], being soluble in water, decreases the viscosity of the medium and this will enhance the accessibility of the growing polymeric

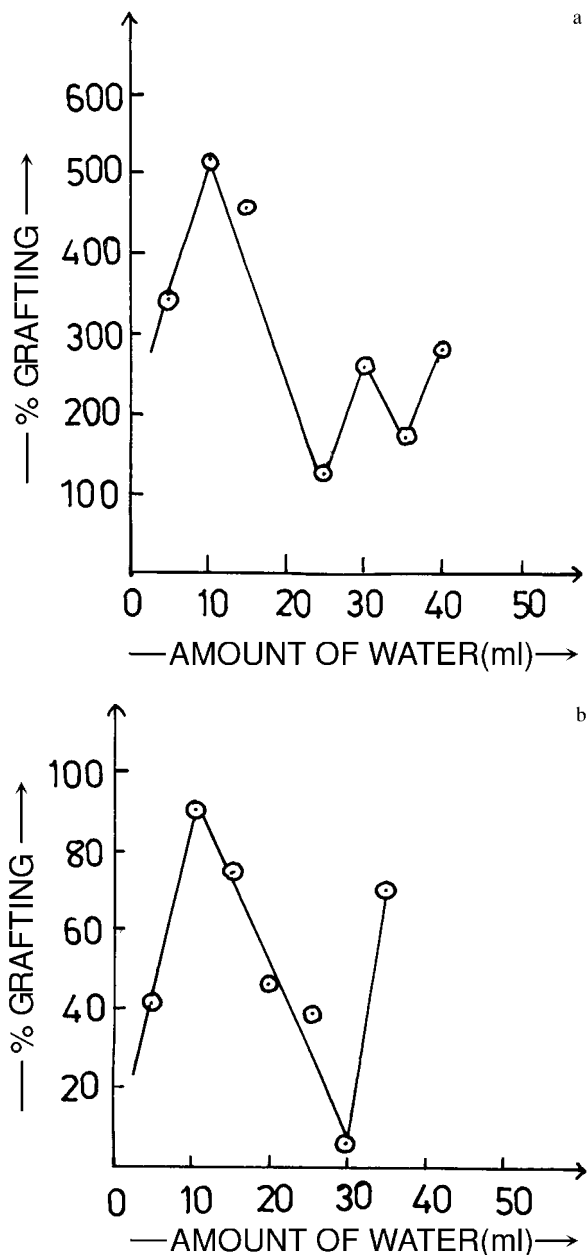


Figure 3 (a) Effect of water on P_g of 4-VP. Total dose = 2.02 Mrad; [4-VP] = 0.60 mol/L. (b) Effect of water on P_g of MA. Total dose = 1.76 Mrad; [MA] = 1.1 mol/L.

chains to the active sites, leading to the increase in the P_g .

Effect of Alcohols

The P_g of 4-VP and MA was studied in alcohol-water solvent systems and the results are pre-

sented in Figure 4(a,b). Alcohols of varying chain lengths such as methanol, ethanol, isopropanol, *n*-butanol, and *n*-pentanol were used separately as components in water-alcohol mixed solvent systems. It is observed from the figure that the P_g of both monomers decreases in the alcohol-water solvent systems and maximum grafting is obtained in the water medium. Different alcohols

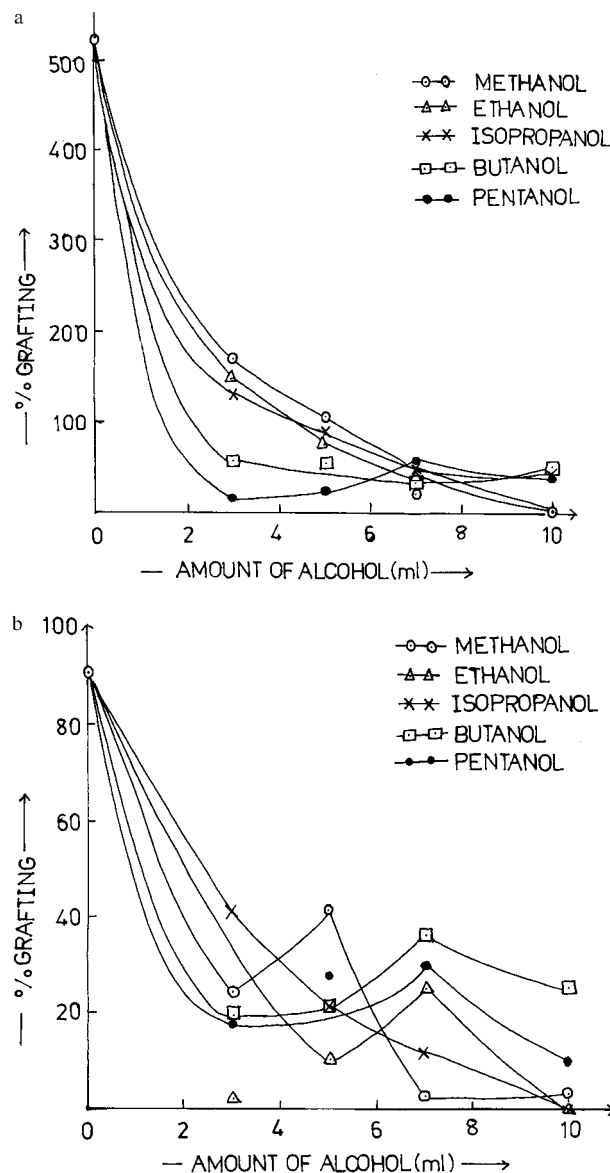


Figure 4 (a) Effect of alcohol-water binary mixtures on P_g of 4-VP onto PE film. Total dose = 2.02 Mrad; [4-VP] = 0.60 mol/L; total amount of solvent (alcohol + water) = 10 mL. (b) Effect of alcohol-water binary mixtures on P_g of MA onto PE film. Total dose = 1.76 Mrad; [MA] = 1.1 mol/L; total amount of solvent (alcohol + water) = 10 mL.

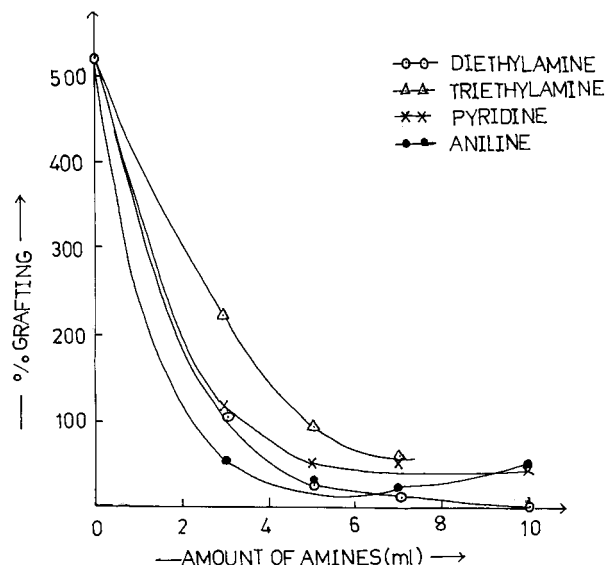
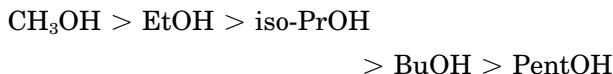
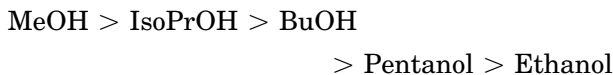


Figure 5 Effect of amine-water binary mixture on P_g of 4-VP onto PE film. Total dose = 2.02 Mrad; [4-VP] = 0.60 mol/L; total amount of solvent (amine + water) = 10 mL.

showed the following reactivity order toward the grafting of 4-VP:



Toward the grafting of MA, different alcohols showed the following reactivity order:

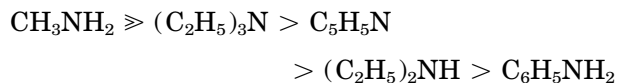


Both CH_3OH and EtOH , being polar, promote grafting more than do the relatively less polar pentanol and butanol. Isopropanol, having a higher chain-transfer constant value, should have afforded less grafting than did n -BuOH and pentanol, but the reverse is true. This may indicate that both n -BuOH and n -pentanol, being relatively less polar than isopropanol, are more efficient in breaking the associated structure of water, leading to poor accessibility of the active sites. Consequently, the P_g is higher in isopropanol than in n -BuOH or n -pentanol.

Effect of Amines

The grafting of 4-VP was studied in the presence of water-amine solvent systems and the results are presented in Figures 5 and 6. It is observed

from the figures that, with the exception of methylamine, all other amines decrease the P_g . Different amines showed the following reactivity order toward grafting:



It appears that the macropoly(ethylene oxide) radical ($\text{PE}\dot{\text{O}}$) is swelled considerably in highly nucleophilic methylamine, leading to the enhancement of grafting. In the presence of other amines, chain-transfer reactions may be accelerated, leading to a decrease in grafting.

Evidence of Grafting

Spectral Analysis

Comparison of the IR spectra of the PE film, PE- g -poly(4-VP), and PE- g -poly(MA) shows peaks at 1575 and 1730 cm^{-1} , respectively, due to the $-\text{C}=\text{N}$ of pyridine of grafted 4-VP in PE- g -poly(4-VP) and the $\text{C}=\text{O}$ of grafted MA in PE- g -poly(MA) that were absent in the IR spectra of PE film (Fig. 7). The appearance of additional

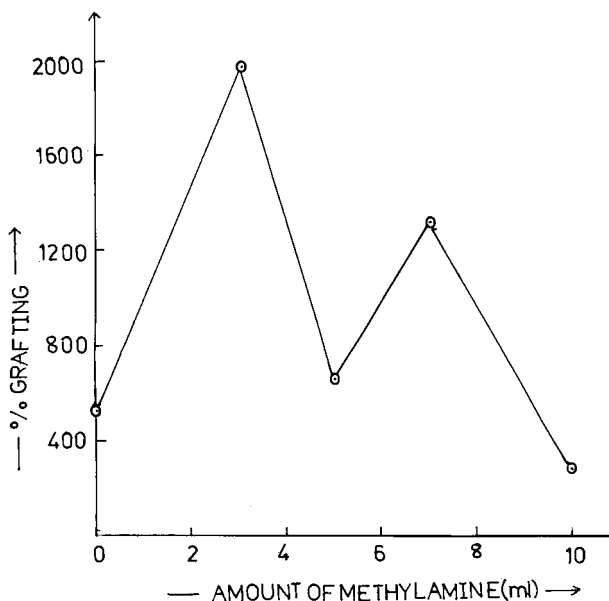


Figure 6 Effect of methylamine on P_g onto PE film. Total dose = 1.76 Mrad; [4-VP] = 0.60 mol/L; total amount of solvent (amine + water) = 10 mL.

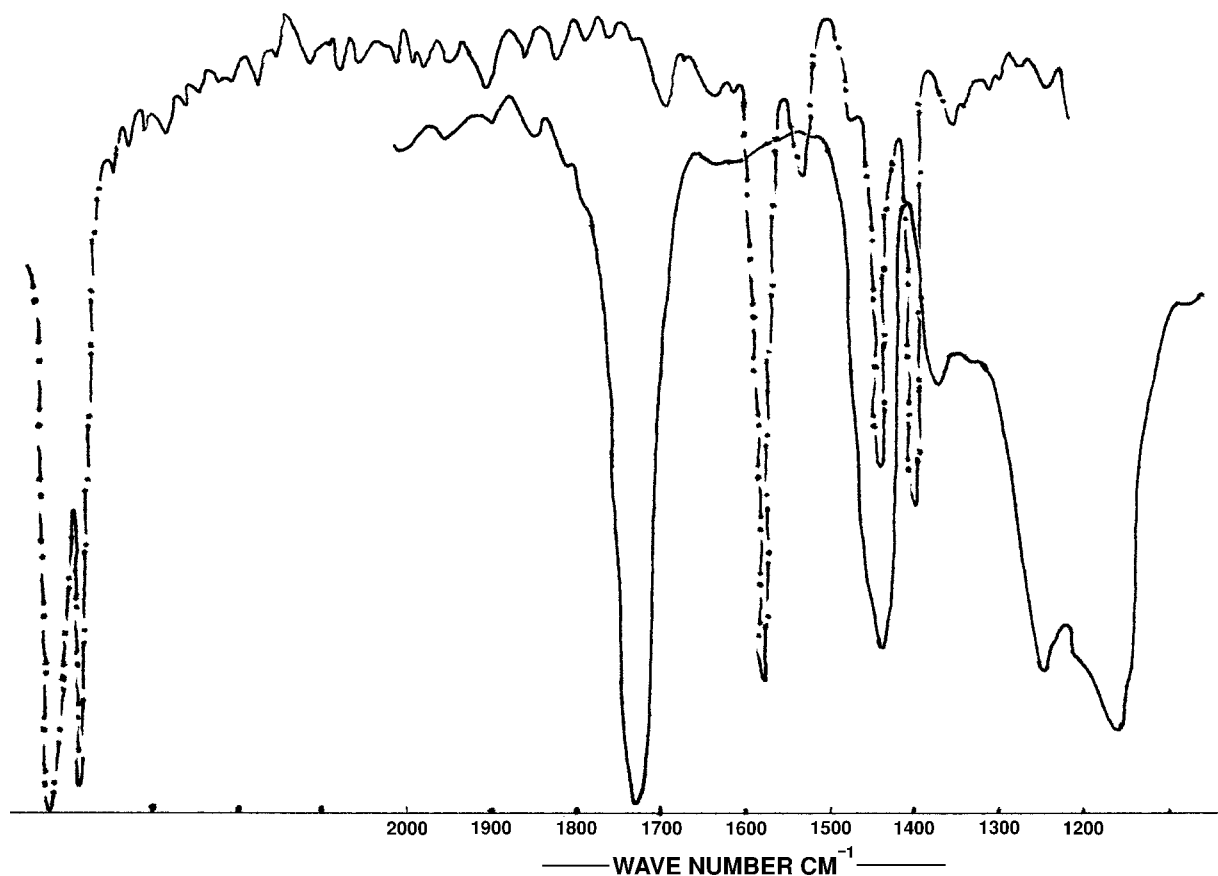


Figure 7 IR spectrum of PE-*g*-poly(4-VP).

peaks in the IR spectra of the grafted PE indicates that both 4-VP and MA are grafted onto PE.

Isolation of the Grafted Poly(4-VP) and Poly(MA) from PE-*g*-poly(4-VP) and PE-*g*-poly(MA)

PE-*g*-poly(4-VP) and PE-*g*-poly(MA) copolymers were separately treated with 0.01 g of cupric chloride in 50 mL of 30% (v/v) hydrogen peroxide at room temperature and kept for about 1 week. Considerable amounts of the grafted polymer, poly(4-VP), and poly(MA) were isolated and their identity was established by IR spectroscopy. The same procedure was used for the separation of grafted polystyrene from poly(ethylene oxide)-*g*-poly(sty).¹⁸

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the PE, PE-*g*-poly(4-VP), and PE-*g*-poly(MA) films

was carried out on a TGA-7 (Perkin-Elmer) in air, at a 20°C/min heating rate. Figures 8–10 represent the primary thermograms of the PE and the grafted PE films. The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperature (DT) at every 10% weight loss are presented in Table I. It is observed from the table that the IDT and DT at every 10% weight loss of PE are higher than those of the grafted samples. For PE, being a straight-chain hydrocarbon polymer, no final decomposition is observed. However, in the grafted samples, the final decomposition is observed at 477.5°C for PE-*g*-poly(MA) and 434.5°C for PE-*g*-poly(4-VP). The low values of the IDT and DT of the grafted PE film is due to the disturbances in the structure of PE caused by the grafting. Since grafting occurs not only on the surface but also in the bulk of the film both in the amorphous and crystalline regions, it causes an overall decrease in thermal stability of the PE film.

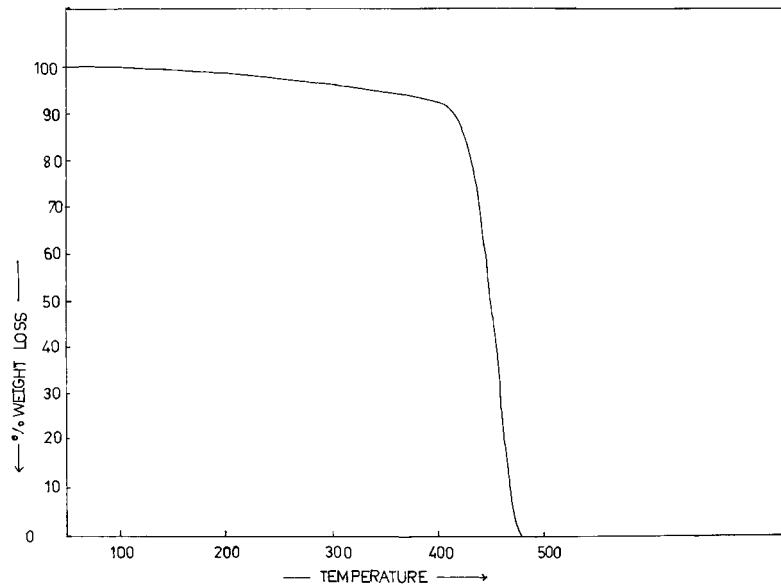


Figure 8 Primary thermogram of PE film.

Area Change

Upon grafting, the dimensions of the PE film increased tremendously, indicating that grafting occurs, not only on the surface, but also in the bulk of the film. The percent area change was determined from the increase in the area of the original film after grafting as follows:

$$\% \text{ Area change} = \frac{\text{final area} - \text{initial area}}{\text{initial area}} \times 100$$

Tables II and III and Figures 11 and 12 provide the percent area change as a function of the P_g of 4-VP and MA, respectively. It is observed from the tables that the percent area change increases

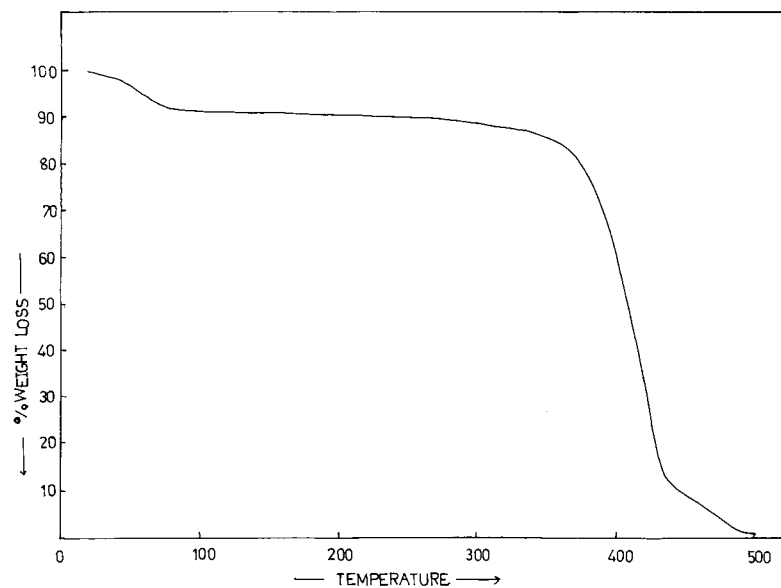


Figure 9 Primary thermogram of PE-g-poly(4-VP).

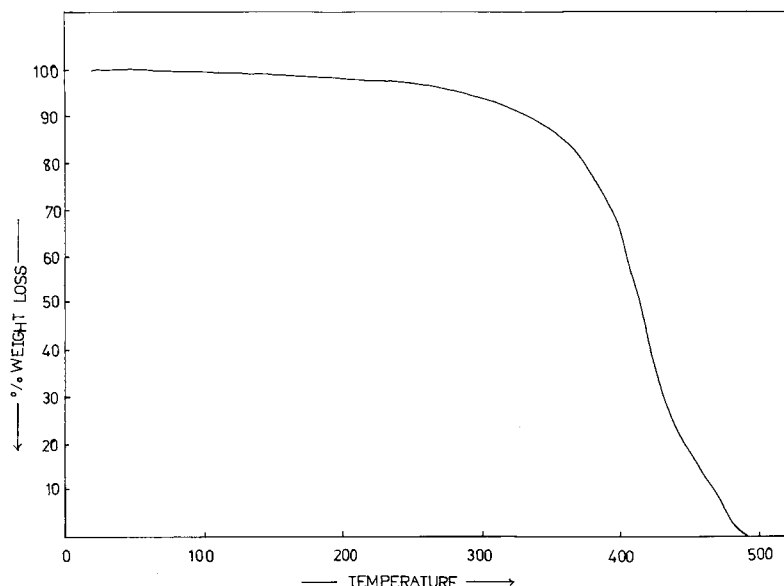


Figure 10 Primary thermogram of PE-*g*-poly(MA).

with increasing *P_g*, suggesting that after the maximum surface grafting proceeds into the bulk of the film, thereby increasing the area of the film.

Swelling Behavior

PE, PE-*g*-poly(4-VP), and PE-*g*-poly(MA) were treated with polar and nonpolar solvents such as water, MeOH, pyridine, DMSO, DMF, and benzene overnight for 24 h. The films, after being removed from the solvent, were pressed between the folds of filter paper two to three times to remove the adhered solvents and were immediately weighed. From the increase in the weight of the film, the percent swelling was calculated as follows:

$$\% \text{ Swelling} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100$$

The percent swelling of PE-*g*-poly(4-VP) and PE-*g*-poly(MA) was determined as a function of the *P_g* and the results are presented in Figures 13 and 14, respectively. The percent swelling of PE-*g*-poly(4-VP) increases with increasing *P_g* in the presence of polar solvents (Fig. 13) In the case of water, the percent swelling is much less and becomes almost constant with increasing *P_g*, while in the nonpolar solvent, benzene, the percent swelling decreases with increase in the *P_g*, but beyond approximately 340% grafting, an increase in percent swelling is observed. These results indicate that there is an interaction between pendant pyridine groups of grafted poly(4-VP) with the polar solvents, resulting in an increase of the swelling of the films.

When the swelling behavior of PE-*g*-poly(MA) in these solvents was studied (Fig. 14), the reverse trend was observed. Swelling in all the

Table I Thermogravimetric Analysis of PE, PE-*g*-poly(MA), and PE-*g*-poly(4-VP)

| Sample | IDT (°C) | FDT (°C) | Decomposition Temperature (<i>DT</i>) (°C) at Every 10% Weight Loss | | | | | | | | |
|--------------------------|----------|----------|---|-----|-----|-----|-------|-----|-------|-----|-------|
| | | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| PE | 409 | — | 411 | 431 | 440 | 446 | 450 | 453 | 457 | 462 | 470 |
| PE- <i>g</i> -poly(MA) | 360 | 477.5 | 332.5 | 376 | 393 | 405 | 412.5 | 420 | 430 | 446 | 467.5 |
| PE- <i>g</i> -poly(4-VP) | 363 | 434.5 | 282.5 | 375 | 390 | 400 | 407.5 | 415 | 422.5 | 429 | 451 |

Table II % Area Change as a Function of P_g for PE-*g*-poly(4-VP)

| Sample | P_g | Area (sq cm) | % Area Change |
|--------------------------|---------|--------------|---------------|
| PE- <i>g</i> -poly(4-VP) | 50.20 | 9.68 | 21.00 |
| PE- <i>g</i> -poly(4-VP) | 128.49 | 12.00 | 50.00 |
| PE- <i>g</i> -poly(4-VP) | 249.55 | 14.85 | 85.62 |
| PE- <i>g</i> -poly(4-VP) | 1332.30 | 22.10 | 176.25 |

solvents showed an initial decrease, up to 28% grafting, and then increased thereafter. In case of pyridine, the percent swelling, after remaining constant up to 28% grafting, showed an increase. The decrease in percent swelling suggests that the pendant ester group of poly(MA) has too low a polarity to interact with the solvents to affect swelling. However, at a higher percentage of grafting beyond 28%, as the number of pendant ester groups increases, some increase in the percent swelling is observed.

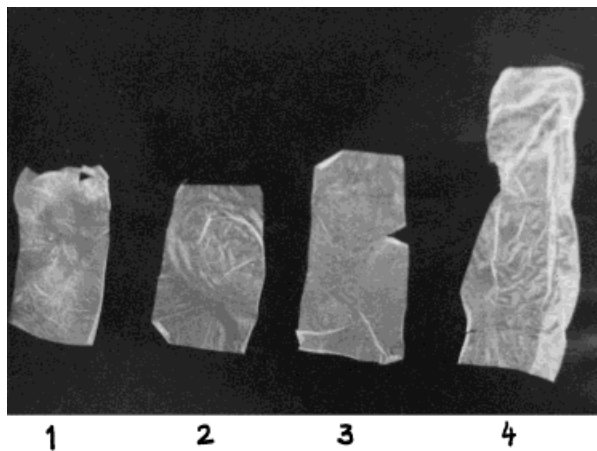
The percent swelling of the PE film in these solvents is represented in Table 4. It is observed from the table that the maximum percent swelling was observed in the nonpolar solvent, benzene. The percent swelling in polar solvents is, however, much less, as expected. Comparison of swelling behavior of grafted and ungrafted PE films shows that PE, grafted with vinyl monomers containing polar groups, swells more in polar solvents. This further confirms that grafting on the PE film has occurred.

Scanning Electron Microscopy (SEM)

The surface topography and homogeneity of PE and PE-*g*-poly(4-VP) were studied by SEM and the results are presented in Figures 15 and 16, respectively. It is observed from Figure 15 that PE

Table III % Area Change as a Function of P_g for PE-*g*-poly(MA)

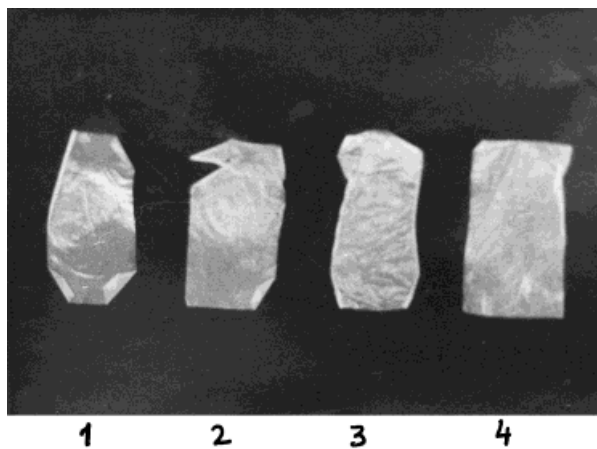
| Sample | P_g | Area (sq cm) | % Area Change |
|------------------------|-------|--------------|---------------|
| PE- <i>g</i> -poly(MA) | 18.95 | 8.40 | 5.00 |
| PE- <i>g</i> -poly(MA) | 41.55 | 8.60 | 7.50 |
| PE- <i>g</i> -poly(MA) | 47.80 | 9.45 | 18.12 |
| PE- <i>g</i> -poly(MA) | 90.30 | 9.89 | 23.62 |

**Figure 11** Photographs of PE-*g*-poly(4-VP) films with increasing P_g (Table II).

represents the unstained substrate with a smooth surface, but the grafted sample becomes rough and heterogeneous because of considerable deposition of the polymer, poly(4-VP), on the surface of the PE film (Fig. 16).

Permeability Behavior

PE film shows very low permeability in many solvents, but when it is grafted with vinyl monomers containing polar functional groups, the behavior of the film toward permeability changes. Upon grafting with 4-VP, the PE film becomes permeable while PE-*g*-poly(MA) behaves as an impermeable membrane. To qualitatively determine the extent of permeation, an aqueous solu-

**Figure 12** Photographs of PE-*g*-poly(MA) films with increasing P_g (Table III).

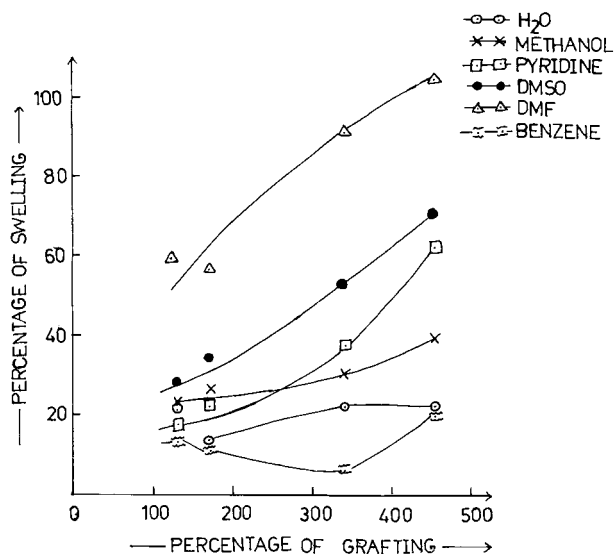


Figure 13 Effect of P_g on swelling of PE-g-poly(4-VP) in different solvents.

tion of 0.5% NaCl was made to pass through a 4-VP-grafted PE membrane placed in the microfiltration unit. A sodium chloride solution flowed through the grafted membranes at a slower rate. The conductance of the original so-

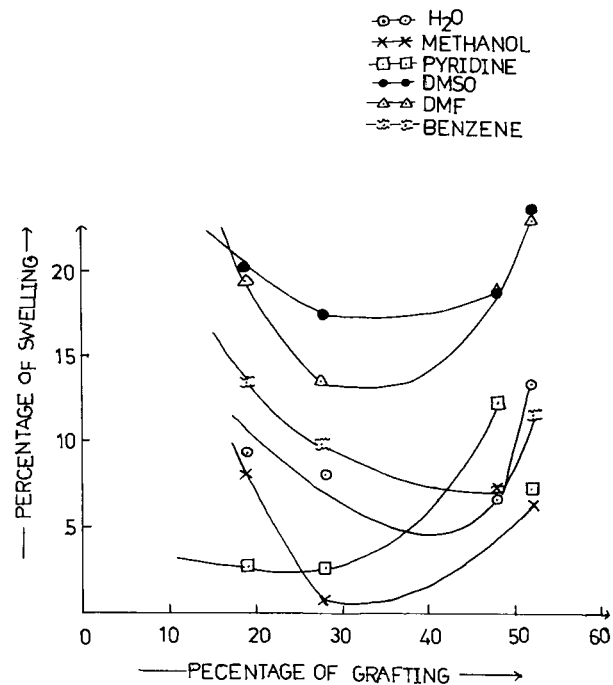
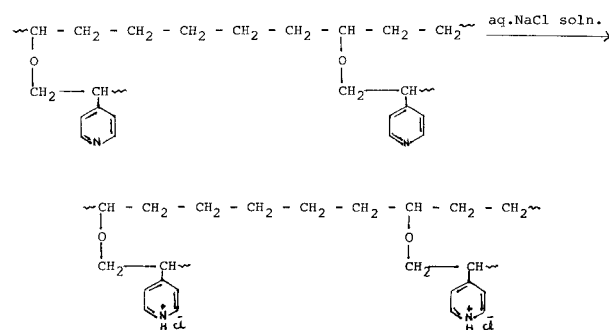


Figure 14 Effect of P_g on swelling of PE-g-poly(MA) in different solvents.

Table IV Effect of Different Solvents on Percent Swelling of PE

| Solvent | Percent Swelling |
|----------|------------------|
| Methanol | 10.65 |
| Water | 4.86 |
| DMSO | 6.11 |
| DMF | 5.99 |
| Benzene | 12.53 |

dium chloride solution and of the permeated sodium chloride solution were measured with a conductivity bridge using a cell constant of 0.268. The conductance of the permeated sodium chloride solution ($21.8 \times 10^{-3} \text{ ohm}^{-1}$) was higher than that of the original sodium chloride solution ($18.4 \times 10^{-3} \text{ ohm}^{-1}$), indicating that probably the grafted film is capable of separating chloride ions. This results in decrease in the concentration of NaCl in the permeated solution and, hence, the conductance is increased:



Similar observations were made by Jendrychowska-Bonamour and Millequent during the conductometric and dialysis studies of hydrophilic membranes, PTFE grafted with AAc and 4-VP, and they proposed that a strong counterion membrane interaction occurred (PTFE-AAc- K^+ and PTFE-4-VP- ClO_4^-).¹⁹ Thus, it is qualitatively es-

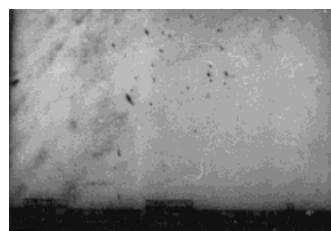


Figure 15 SEM of PE film.

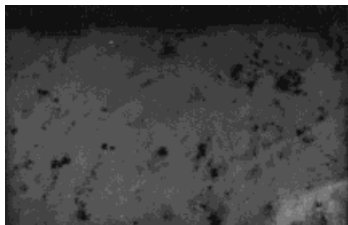


Figure 16 SEM of PE-g-poly(4-VP).

established that PE-g-poly(4-VP) is capable of effecting desalination of a brine solution.

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