

# Radiation-Induced Graft Copolymerization of Methylmethacrylate onto Poly(tetrafluoroethylene-*co*-ethylene) Film

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**ABSTRACT:** Modification of poly(tetrafluoroethylene-*co*-ethylene), Tefzel (ETFE), film has been carried out by grafting methylmethacrylate (MMA) by radiation method including preirradiation and double-irradiation methods. Percentage of grafting has been determined as a function of the (i) total dose, (ii) monomer concentration, (iii) amount of liquor ratio, (iv) reaction time, and (v) temperature. The effect of different alcohols such as methanol, ethanol, 2-propanol, *n*-butanol, *n*-pentanol, and 2-ethoxy ethanol on percentage of grafting of MMA was also studied. The graft copolymers were characterized by IR spectroscopy and thermogravimetric analysis (TGA).

Methylmethacrylate produces higher percentage of grafting by preirradiation method than double-irradiation method. MMA-grafted ETFE films ( $S_{irr}$ ), i.e., prepared by preirradiation involving single irradiation show better thermal stability than MMA-grafted ETFE films ( $D_{irr}$ ), i.e., prepared by double irradiation and unmodified ETFE film. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2238–2244, 2009

**Key words:** graft copolymerization; ETFE film; MMA; pre-irradiation; double irradiation; thermal analysis and swelling behavior

## INTRODUCTION

Poly(tetrafluoroethylene-*co*-ethylene) and ETFE ( $-\text{CF}_2-\text{CF}_2-\text{co}-\text{CH}_2-\text{CH}_2-$ ), possess excellent properties such as strength and toughness, electric properties, weatherability, etc., which make this polymer useful in many diverse applications. However, lack of functional moieties in the polymer makes ETFE chemically inert. Functionalization of the polymer by graft copolymerizing various vinyl monomers with different pendant functional groups imparts many additive and desired properties, which make the polymer useful in the areas where the chemical interactions are required specially in the membrane processes such as the separation of liquid solvent mixtures, desalination processes, etc. Irradiating of PE hollow fiber membrane with an electric beam and grafting with GMA and divinyl benzene followed by the treatment with  $\text{H}_3\text{PO}_4$  gave a membrane with good ion-absorption properties.<sup>1,2</sup> Proton-exchange membranes were prepared by the simultaneous radiation grafting of styrene onto poly(tetrafluoroethylene-*co*-hexafluoroethylene) films.<sup>3</sup> Radiation-induced graft copolymerization and sulfo-

nation of GMA onto porous hollow-fiber membranes of polyethylene with different pore sizes were carried out by Kim and Saito.<sup>4</sup> An increase in the  $\text{SO}_3\text{H}$  group density of the graft chain decreased the permeability of pure water. Cation-exchange membranes were prepared by the radiation-induced graft copolymerization of styrene onto Teflon-PFA.<sup>5</sup> Synthesis of perfluorinated cation exchange membranes was carried out by grafting acrylic acid onto ETFE films by preirradiation method.<sup>6</sup> Graft copolymerization of styrene and methacrylonitrile has been successfully carried out onto preirradiated ETFE film and preirradiated and monomer-swollen Tefzel film by Kaur et al.<sup>7</sup> Successful grafting of acrylate monomers, such as ethylacrylate and methylacrylate, has been achieved, and the dependence of reaction conditions on percent grafting was evaluated.<sup>8</sup> In the present manuscript, we report on grafting of acrylate monomer, MMA, onto ETFE film by preirradiation and double-irradiation methods. During double irradiation, the film was irradiated twice with a gap of 4 h. The objective of double irradiation was that during the gap period, the radicals generated in the bulk of the polymer, i.e., the trapped radicals may shift to the surface or within the bulk through inter- or intramolecular hydrogen-abstraction reactions. These processes might increase the number of active sites or evenly distribute them on the polymer backbone. This change might affect the grafting yield.

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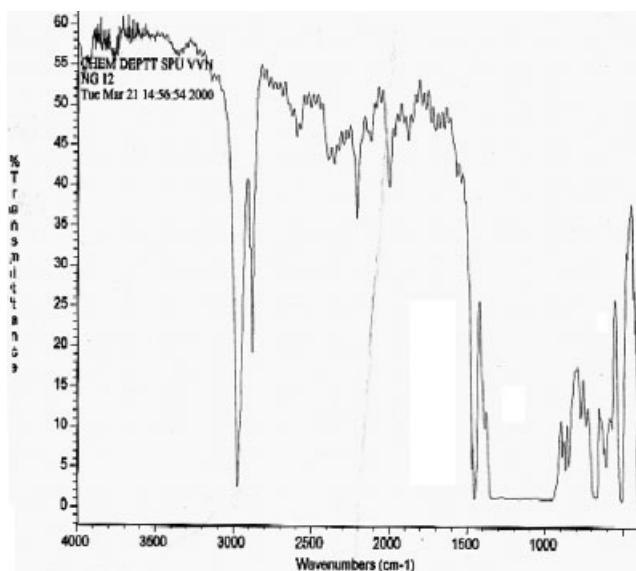


Figure 1 IR spectrum of Tefzel film.

## EXPERIMENTAL

### Materials and methods

ETFE film (127 mu), obtained as a gift from E.I. Dupont de Nemours, USA, was washed with methanol and dried in vacuum oven at 50°C. Methyl methacrylate (MMA; Merck) was purified by washing with 0.5% NaOH solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, distilled, and the middle fraction was used. All alcohols (reagent grade) were distilled before use. Distilled water was used as the reaction medium.

### Irradiation of Tefzel film

1. For the preirradiation method, the methanol-washed and -dried ETFE film (4 cm × 2 cm) was irradiated in air from Co<sup>60</sup> source, housed in "Gamma Chamber-900" at a constant dose rate of 0.50 kGy/h for different time periods that determine different total dose given to the sample. The irradiated film was used for the grafting of MMA. The film is referred to as single irradiated (S<sub>irr</sub>).
2. For the double-irradiation method, the methanol-washed and -dried ETFE film (4 cm × 2 cm) was irradiated in air from Co<sup>60</sup> source at a constant dose rate of 0.50 kGy/h for a particular time period. The film was removed from the Gamma Chamber, wrapped in a carbon paper, and kept at room temperature for 4 h. The film was then again irradiated for the same time period as used for the first irradiation. The double-irradiated (D<sub>irr</sub>) film was used for the grafting of MMA.

### Graft copolymerization

Irradiated and weighed ETFE film (4 cm × 2 cm) were suspended in a definite amount of reaction solvent, water-methanol, keeping the amount of methanol fixed at 5 mL the amount of water was varied between 5 and 25 mL. A known amount of the monomer, MMA, (0.4–3.49 mol) was added to the reaction flask, and the flask was placed in an oil bath maintained at a constant temperature (100°C). The reaction mixture was then refluxed for 180 min. After the stipulated time, the film was removed from the flask and washed thoroughly with acetone to remove poly(MMA) formed during the reaction till constant weight of the grafted film was obtained. The grafted ETFE film, free from homopolymer, was dried in vacuum oven at 50°C and weighed. Percentage of grafting (Pg) was calculated as follows:

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

where  $W_0$  and  $W_1$  are the weights of original and grafted films after the complete removal of the homopolymer.

### Evidence of grafting

#### IR spectral analysis

IR spectra for ETFE (Fig. 1), ETFE-g-poly(MMA)S<sub>irr</sub> (Fig. 2), and ETFE-g-poly(MMA)D<sub>irr</sub> (Fig. 3) were obtained by Beckman Spectrophotometer. On comparison with the IR spectra of these films, it was observed that the grafted ETFE film, i.e., ETFE-g-poly(MMA) shows a peak at 1720 cm<sup>-1</sup> due to >C=O group of the grafted MMA, which was found absent in the ungrafted ETFE film there by confirming the formation of the graft.

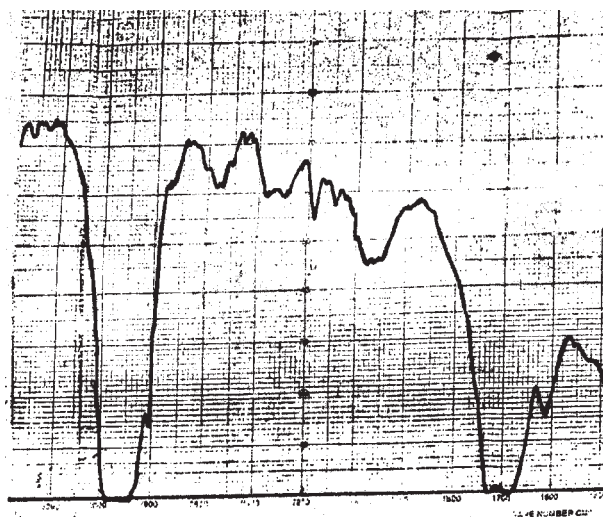


Figure 2 IR spectrum of ETFE-g-poly(MMA) S<sub>irr</sub>.

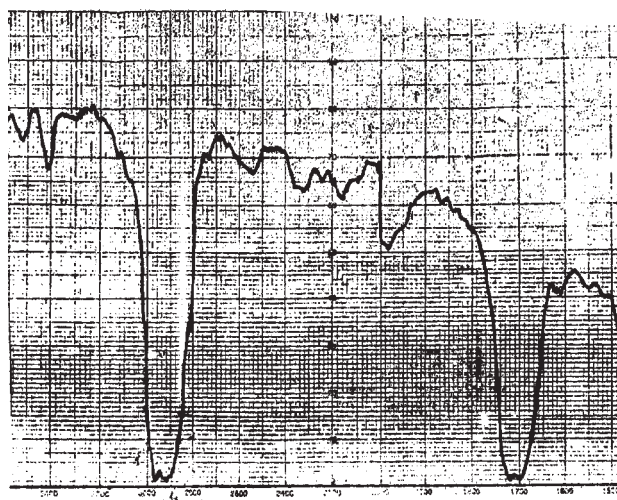
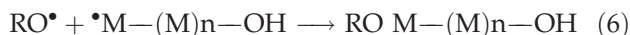
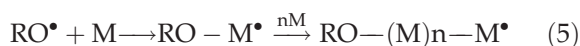
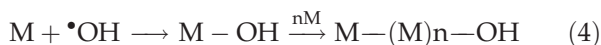
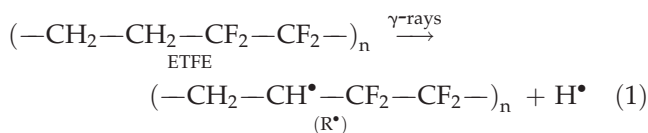


Figure 3 IR spectrum of ETFE-g-poly(MMA)  $D_{irr}$ .

## RESULTS AND DISCUSSION

Irradiation in air introduces hydroperoxide groups in the ETFE film following the cleavage of the C—H/C—F bonds.<sup>9</sup> These groups offer sites for the grafting of vinylic monomers. The following mechanism is suggested to explain the grafting of MMA onto ETFE film.



where  $R$  represents all carbon-free radicals on the polymer backbone. Percentage of grafting has been studied as a function of various reaction parameters, and the results are discussed in the light of the proposed mechanism.

### Effect of total dose

Percentage of grafting of MMA onto ETFE film was determined as a function of total dose, and the results are presented in Figure 4. It is observed from the figure that the percentage of grafting of MMA onto ETFE film ( $S_{irr}$ ) increases continuously with the

increase in the total dose giving maximum (116.4%) at 36.72 kGy. Percent grafting of MMA onto ETFE film ( $D_{irr}$ ), however, shows a slow rise in grafting with increasing total dose giving maximum (63.3%) at total dose of 30.6 kGy beyond which it decreases.

Double irradiation of the film was expected to introduce a higher number of hydroperoxide groups and as such would have given higher percentage of grafting. The lower percentage of grafting of MMA (63.3%) at total dose of 30.6 kGy in case of double-irradiated film when compared with the MMA grafting onto single-irradiated film (116.4% at 36.72 kGy) may be attributed to the reason that although the hydroperoxide groups formed during the first irradiation become well distributed during the storage time, the second irradiation might scavenge these groups via  $\beta$ -scission process as shown below:



$\beta$ -Scission of tertiary alkoxy radicals has been suggested as the major cause of chain scission during photodegradation of isotactic polypropylene<sup>10</sup> and also observed during the grafting of methacrylic acid onto isotactic polypropylene by Kaur et al.<sup>11</sup> Thus, it becomes obvious that the double irradiation of the film with a break between the two irradiations may not as such increase the number of hydroperoxide groups but instead distributes these groups evenly on the surface of the film, through intra- or intermolecular hydrogen-transfer reactions and might also decrease the active sites on the backbone polymer through such reactions.

### Effect of monomer concentration

Figure 5 describes the effect of concentration of MMA on the percentage of grafting of MMA onto ETFE film. It is observed from the figure that the  $P_g$  of MMA onto ETFE ( $S_{irr}$ ) increases sharply with the

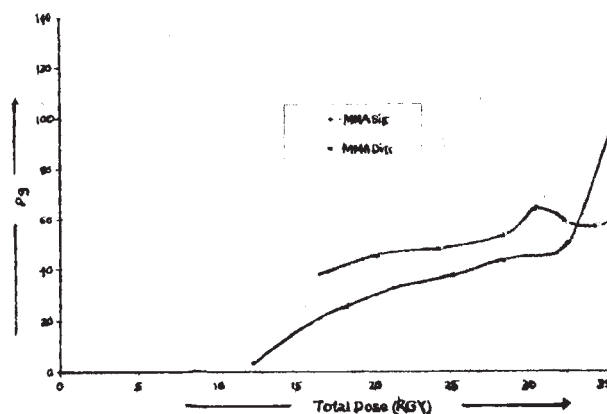
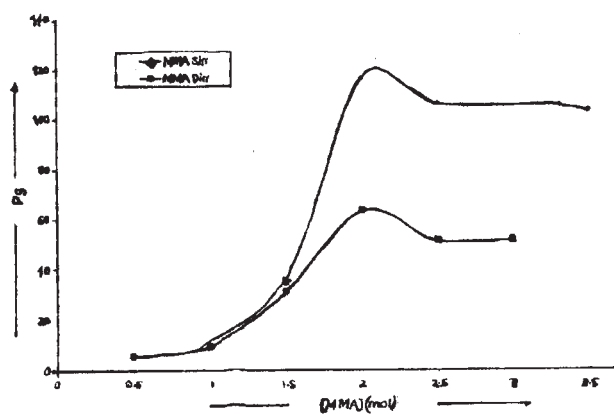


Figure 4 Effect of total dose on  $P_g$  of MMA using single and double irradiation onto ETFE.

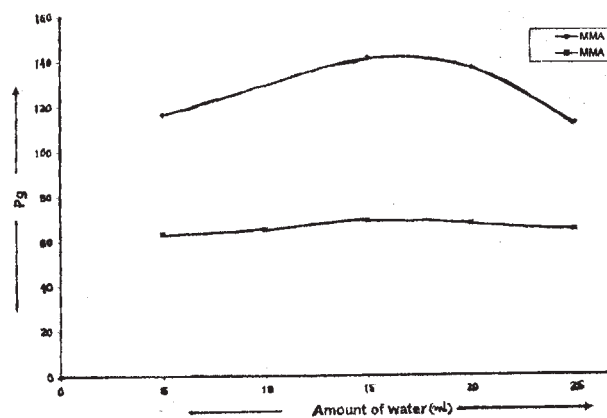


**Figure 5** Effect of [MMA] on Pg using single and double irradiation onto ETFE.

increasing [MMA], giving maximum (116.4%) at [MMA] = 0.306 mol decreases slightly and then levels off. However, in case of grafting of MMA onto double-irradiated ETFE film, the rise in grafting percentage is smooth and gradual, giving maximum (63.2%) at the same [MMA], i.e., 0.306 mol, decreases a little and becomes constant. Higher Pg for single-irradiated ETFE when compared with double-irradiated film is maybe due to the reason that in the single-irradiated film, grafting also occurs in the bulk wherein some radicals are trapped. Huglins and Smith<sup>12</sup> have investigated the grafting by trapped radicals and trapping of the growing grafts in the crystalline region. In case of double-irradiated film, as discussed earlier, these trapped radicals either shifts toward the surface or are decomposed during the second irradiation through  $\beta$ -scission thus decreasing the number of active sites.

#### Effect of liquor ratio

Effect of the amount of water on the percentage of grafting of MMA onto ETFE film was studied, and the results are presented in Figure 6. It is observed from the figure that the percentage of grafting of MMA onto single- and double-irradiated films show slight increase in the percentage of grafting with increasing amount of water in water-methanol binary system, the amount of methanol being fixed at 5 mL. Maximum Pg (141.3% and 68.95%) of MMA onto single- and double-irradiated film, respectively, is obtained using 15 mL of water. Increase in the percentage of grafting with an increased amount of water is due to the increased swelling of the peroxidized ETFE film and hence more exposure of the active sites where grafting can occur. Swelling of the backbone polymer, PP, in the presence of the solvents was also observed by Burchill et al.<sup>13</sup> during



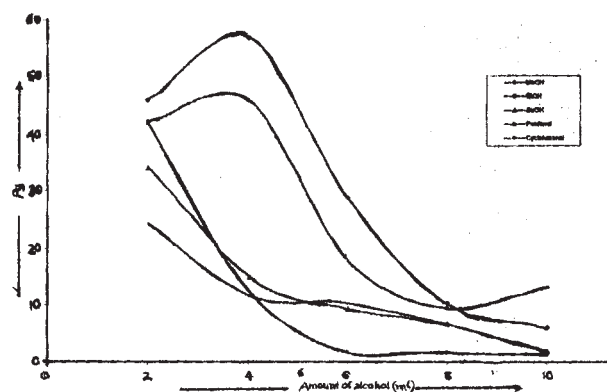
**Figure 6** Effect of amount of water on Pg of MMA using single and double irradiation.

$\gamma$ -radiation induced graft copolymerization of MMA onto PP.

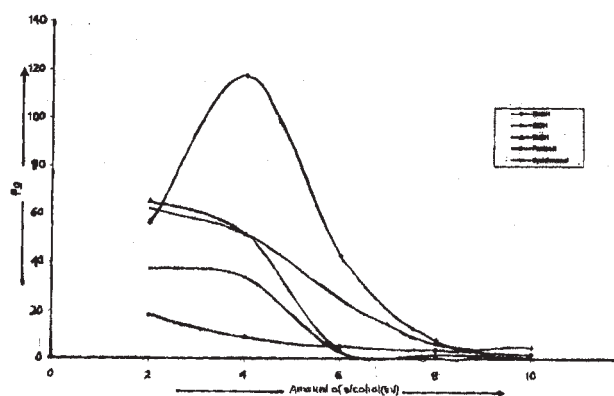
#### Effect of amount of alcohol in water-alcohol solvent system

To study the effect of the addition of primary monohydric alcohols such as methanol, ethanol, *n*-butanol, *n*-heptanol, and cyclohexanol on the percentage of grafting of MMA onto ETFE film ( $S_{irr}$  and  $D_{irr}$ ), Pg was determined as a function of amount of alcohol in water-alcohol medium, and the results are presented in Figures 7 and 8, respectively. The total volume of water-alcohol mixture was fixed at 10 mL, and the amount of alcohol was varied between 2 and 10 mL. It was observed from Figures 7 and 8 that the percentage of grafting of MMA onto Tefzel film ( $S_{irr}$  and  $D_{irr}$ ) in water-alcohol solvent system was lower than that obtained in 10 mL (5 : 5, v/v) of water-methanol system. The following reactivity order of different alcohols was obtained in water-alcohol medium influencing the grafting reaction of MMA onto single- and double-irradiated ETFE films.

Methanol > ethanol > *n*-butanol > cyclohexanol > *n*-pentanol.



**Figure 7** Effect of amount of alcohol in water-alcohol binary mixture on percentage of grafting of MMA using double irradiation.

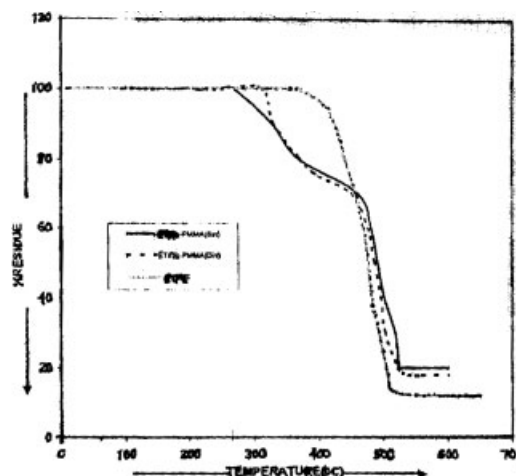


**Figure 8** Effect of amount of alcohol in water–alcohol binary mixture on percentage of grafting of MMA using single irradiation.

Decrease in the percentage of grafting in the presence of alcohols is attributed to the fact that all the alcohols have high chain transfer constants, which leads to the termination of growing polymeric chains leading to decrease in grafting. The addition of alcohols to water destroys the hydrogen-bonded structure of water with some entropy loss. Water enters into the H-bonded structure with alcohols leading to the stabilization of the structure, which is accompanied by the decreasing factor of diffusion of monomer to the active sites leading to the decrease in percentage of grafting.

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) of ETFE film and ETFE-g-poly(MMA) prepared by single irradiation and double irradiation was carried out on Schimadzu Simultaneous Thermal Analyzer in air at a heating rate of 20°C/min. The respective primary thermograms are presented in Figure 9. The initial decomposition temperature (IDT), final decomposition temperature, (FDT), and decomposition temperature (DT) at every 10% weight loss of ETFE film and ETFE-g-poly(MMA) are presented in Table I. It is observed from the primary thermograms that ETFE film shows a single stage of decomposition,



**Figure 9** Primary thermogram of ETFE, ETFE-g-poly (MMA) using single irradiation, ETFE-g-poly(MMA) using double irradiation.

while ETFE-g-poly(MMA) ( $S_{irr}$  and  $D_{irr}$  films) show double-stage decomposition. The IDT values (304.5°C and 318.5°C) and FDT values (530.0°C and 509.5°C), respectively, of ETFE-g-poly(MMA) prepared by single- and double-irradiation method are lower than IDT (392.3°C) and FDT (535.0°C) of the original ETFE film. In case of MMA-grafted ETFE film ( $S_{irr}$ ), DT values are lower up to 30% weight loss beyond which these values become higher than ETFE film while in MMA-grafted ETFE film ( $D_{irr}$ ); DT values are lower upto 50% weight loss beyond that these values are higher than ETFE film. The temperature difference between every 10% weight loss is much higher for the MMA-grafted films ( $S_{irr}$  and  $D_{irr}$ ) up to 50% weight loss beyond which this difference is almost the same as that of the ETFE film indicating thermal stability of the grafted films.

The percent residue left is also higher for the grafted films ( $S_{irr}$  and  $D_{irr}$ ) (17 and 16%) when compared with 12.7% residue left for the ETFE film. Higher DT values and higher percent residues of the grafted ETFE films indicate that the thermal stability of ETFE film increased upon grafting of the acrylate monomer.

**TABLE I**  
Thermogravimetric Analysis of ETFE Film and ETFE-g-poly(MMA) ( $S_{irr}$  and  $D_{irr}$ ) Films

Sample	IDT (°C) at % residue left	FDT (°C) at % residue left	DT (°C) at every 10% wt loss										Residue left (%)
			10%	20%	30%	40%	50%	60%	70%	80%	90%		
ETFE film	392.30	535.00	425.62	440.25	458.56	469.54	476.85	484.18	493.33	510.00	–	12.70	
ETFE-g-poly (MMA) $S_{irr}$	304.50	530.00	327.00	368.00	450.00	481.00	491.00	501.00	518.00	524.50	–	17.00	
ETFE-g-poly (MMA) $D_{irr}$	318.50	509.50	330.00	370.00	400.00	450.00	476.60	486.60	496.60	503.30	532.30	16.00	

### Area change

The change in the dimensions (length and breadth) of the film upon grafting is measured in terms of percent area change and evaluated by the following equation:

$$\text{Percent area change} = \frac{A_1 - A_0}{A_0} \times 100$$

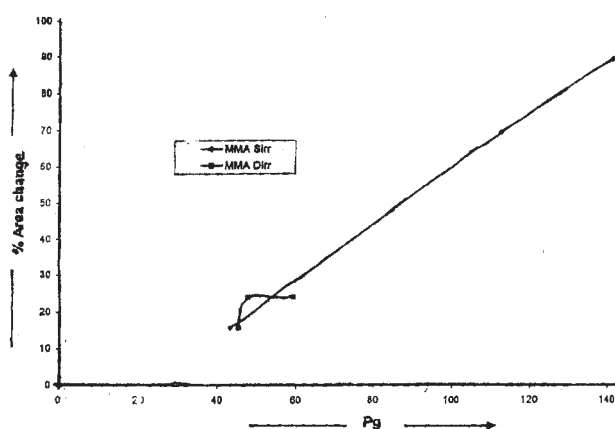
where  $A_t$  and  $A_0$  represent the area of the grafted and ungrafted films, respectively. Change in the size of the film was determined as a function of percentage of grafting, and the results are presented in Figure 10. It is observed that the percent area change for the two monomers increases with the increase in the percentage of grafting, indicating that the monomers diffuse into the bulk of the film react with the active sites to give graft copolymer leading to increase in the area of the film.

### Swelling behavior

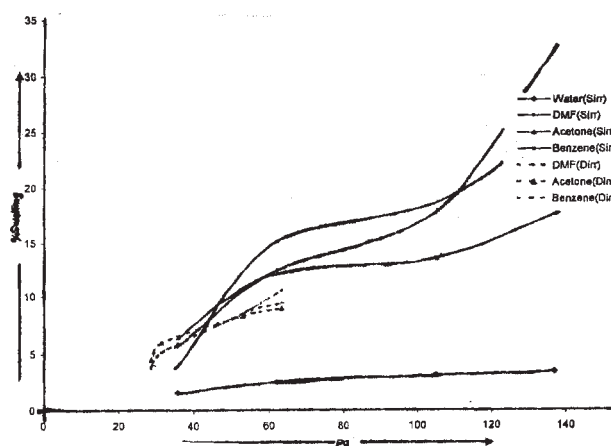
Percentage of swelling of ETFE, irradiated ETFE, and ETFE-g-poly(MMA) in polar and nonpolar solvents such as DMF, H<sub>2</sub>O, MeOH, acetone, and benzene was studied as a function of percentage of grafting. ETFE film, irradiated ETFE, and grafted ETFE film of known weights were immersed in different solvents at room temperature for 24 h. The films were removed, blotted quickly with absorbent paper to remove the liquid adhering to its surface, and weighed immediately. From the increase in the weight of the film, the percentage of swelling was calculated as

$$\text{Percent Swelling} = \frac{W_s - W_g}{W_g} \times 100$$

where  $W_s$  and  $W_g$  represent the weights of wet and dry films respectively. The results are presented in Figure 11. A continuous increase in the swelling is



**Figure 10** Effect of Pg on the percentage area change using single and double irradiation onto ETFE.



**Figure 11** Effect of Pg on percent swelling of ETFE-g-poly(MMA) in different solvents using single and double irradiation.

observed in case of ( $S_{irr}$ ) and ( $D_{irr}$ ) ETFE film grafted with poly(MMA). However, higher percent swelling is observed for single-irradiated ETFE-g-poly(MMA) film. This may be due to the reason that since grafting also occurs in the bulk of the film, solvent upon diffusion into the bulk swells the film. In case of double-irradiated film, the embedded radicals seem to shift to the surface during the gap between the two irradiations. This aspect is also substantiated from the results of percent area change, which is much higher in case of the single irradiated ETFE film (Fig. 10). Maximum percent swelling of the grafted films was observed in dipolar aprotic solvent (DMF) and minimum in water.

Following the order of swelling ability of different solvents for ETFE-g-poly(MMA), the following was observed.

DMF > benzene > acetone > water

ETFE film and irradiated ETFE films do not show any swelling in any of these solvents.

### CONCLUSIONS

From the forgoing discussion on grafting of MMA onto Tefzel film by the preirradiation method following conclusion are drawn:

1. MMA-grafted ETFE films ( $S_{irr}$ ) show better thermal stability than MMA-grafted Tefzel films ( $D_{irr}$ ) and unmodified ETFE film.
2. Graft copolymerization of MMA onto double-irradiated ETFE film although shows a smooth and gradual rise in the percentage of grafting but gives a lower percentage of grafting when compared with that obtained for single-irradiated ETFE film. This indicates that during the storage time, i.e., the time between the two irra-

diations, even the distribution of hydroperoxide groups takes place on the surface and some radicals also shift from the bulk to the surface, which helps in gradual and smooth rise in the percentage of grafting. However, during the second irradiation, these groups are scavenged via  $\beta$ -scission leading to the decrease in number of active sites and hence percentage of grafting.

3. Increase in the percent area of ETFE-g-poly (MMA) using single-irradiated film is higher than the double-irradiated film (Fig. 10). It indicates that during the grafting of MMA onto single-irradiated film, diffusion of the monomer takes place into bulk of the film wherein it reacts with the embedded free radicals producing higher percentage of grafting with higher percentage of area change when compared with grafting onto double-irradiated film, which shows even distribution of hydroperoxide groups on the surface of the film. Trapping of growing grafts in crystalline regions and or transfer from them to such regions have been postulated by Huglins and Smith during the

copolymerization of acrylic acid onto Nylon-6 by trapped radicals.<sup>12</sup>

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