Gamma Preirradiation and Grafting of 2*N*-Morpholino Ethyl Methacrylate onto Polypropylene Fabric

S. M. GAWISH,[1] A. KANTOUCH,[1] A. M. EL-NAGGAR,[2,*] and S. MOSLEH[1]

[1]Textile Division, National Research Center, Tahrir Str., Dokki, Cairo, Egypt; [2]National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

SYNOPSIS

The radiation-induced grafting of 2*N*-morpholino ethyl methacrylate (MEMA) in aqueous solution onto polypropylene fabric by a preirradiation technique has been investigated. Among the most important factors affecting the graft yield are monomer concentration, irradiation dose, reaction temperature, and time. It was found that the graft yield increased with increasing monomer concentration, grafting temperature, and preirradiation dose. The kinetic studies showed that the dependence of the grafting rate on monomer concentration is of 1.1 order. Moreover, the calculated overall activation energy was 14.2 kcal/mol. The grafted PP fabric shows an increase in moisture regain with increasing graft yield. Also, the dyeability with acid dye was significantly increased due to grafting with MEMA. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Today, polypropylene (PP) is interesting because of its wide industrial applications, cheapness, low density, and excellent mechanical properties. On the other hand, PP fibers possess some drawbacks such as a hydrophobic nature with poor water absorption, development of static electricity, and a greasy feel and exhibit a low sticky temperature. Also, the absence of hydrophilic reactive groups in PP macromolecules prevents its dyeability.

To improve these disadvantages, PP fibers are modified by graft copolymerization of suitable vinyl monomers onto the polymer backbone without affecting most of the original properties. Mutual and preirradiation grafting techniques have been adopted for this purpose using γ-rays, UV, ozone, or electron beam as initiators.

A literature review revealed that Mehta et al.[1] graft-copolymerized soluble vinyl monomers such as acrylic acid and acrylamide (in water or methanol) onto isotatic PP by a gamma preirradiation method. Sugo et al.[2] irradiated nonwoven PP fabric by a 20 Mrad electron beam, then immersed it into a chloromethyl styrene solution and heated it *in vacuo* at 50°C for 1.5 h. This method gave an evenly grafted fabric with 146% graft yield vs. 68% of unevenly grafted product when using gas-phase polymerization without soaking in the monomer solution. It has also been reported that PP fibers can be grafted with various monomers[3] by both mutual and preirradiation methods using an electron-beam accelerator. It was observed that greater dye penetration depths were attained by the preirradiation method. Crosslinking of acrylic-grafted PP fibers with metal salts increased both thermal stability and the melting point of the fiber. The dyeability of PP fibers with disperse dyes was enhanced by grafting vinylamides, especially vinyl pyrrolidone and vinyl caprolactam. PP for biomedical application[4] was also produced by gamma irradiation and grafting of 2-hydroxyethyl methacrylate.

In a previous work, Gawish et al.[5] grafted 2-*N*-morpholino ethyl methacrylate (MEMA) onto electron-beam-irradiated PP fabric. The physical properties of the fibers were determined including melting point, crystallinity, and decomposition temperatures by the DSC method. The dynamic mechanical thermal properties of the fibers were also measured. In the present investigation, we proceeded to graft the same

* To whom correspondence should be addressed.

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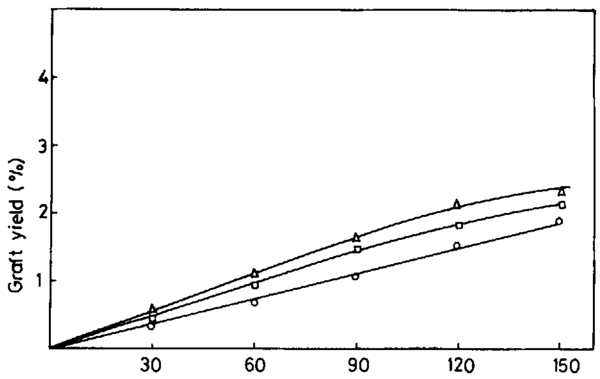


Figure 1 Effect of reaction time on the degree of grafting different MEMA concentrations onto 0.5 Mrad preirradiated PP fabric: (○) 10%; (□) 15%; (△) 20%. Grafting temperature, 50°C; liquor ratio, 1:30.

previous monomer by the gamma preirradiation method to create active hydrophilic sites onto the polymer chains. Moreover, the properties of the grafted PP with MEMA in terms of dye affinity for acid dye and moisture regain are taken into consideration.

EXPERIMENTAL

PP fabric (100%) used in this work was obtained from Montedison Co., weaved from highly isotatic fibers with the specifications of warp 238 dtex and fill 251 dtex. The monomer MEMA, purity 97.8%, stabilized by 50 ppm methyl hydroquinone was supplied by the Geraman Rohm Co. and used without further purification. The acid dye Irganol yellow 5GLS was supplied by Ciba Geigy, and the nonioning wetting agent, Hostapal CV. ET, obtained from Hoechst Co. was used during the dyeing process.

Technical Procedures

Fabric Washing

Before irradiation, the fabric was throughly washed to remove PP additives such as a UV stabilizer and antioxidants considered as inhibitors for the grafting process. The washing solution was first prepared by dissolving sodium chloride (2.5% mg/L) and ammonium bifluoride (1.9 gm/L) in hot water. The cold mixture was then added to sodium nitrate (1.25 gm/L) and potassium nitrate (1.5 gm/L) and the overall mixture was heated to 90°C. The PP fabric was introduced into the prepared washing solution at a liquor ratio of 1 : 60 and allowed to rotate for 2.5 h. At the end, the contents were cooled to room temperature, throughly washed several times with running tap water, and air-dried.

Preirradiation Grafting of MEMA onto PP

Irradiation to the required doses was carried out in the cobalt-60 gamma source of the National Center of Radiation Research and Technology, Cairo, Egypt. The preirradiation method was adopted, in which the dry PP fabric was exposed to irradiation over a dose levels of 0.5, 0.75, and 1 Mrad in the presence of air (dose rate 0.55 Mrad/h). The irradiated samples were weighed and immersed into hermetically closed Pyrex tubes containing aqueous MEMA solution at different concentrations (5–20%). Nitrogen gas was purged into the solution for 5 min to ensure an oxygen-free solution. The tubes were thermostated at different temperatures (50, 75, 98°C) for specific periods. The grafted samples were throughly washed with warm and cold water and then extracted with acetone to remove any residual homopolymer to a constant weight. The degree of grafting was calculated as follows:

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

where W_0 and W_g are the initial weight and the grafted weight, respectively.

Dyeing Procedure

The dye concentration (0.5 g/L) was made into a smooth paste by a suitable amount of a nonionic wetting agent and sufficient boiling water was added to dissolve it completely. The dissolved dye

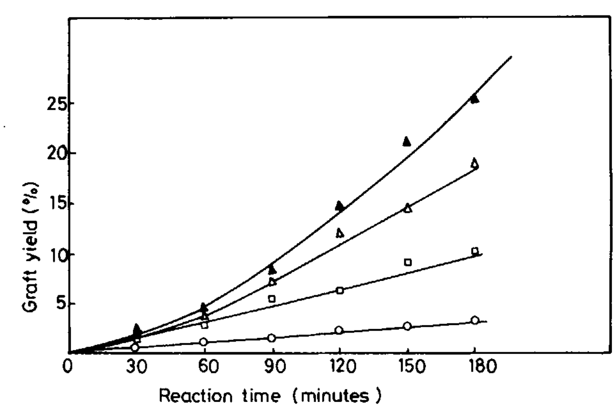


Figure 2 Effect of reaction time on the degree of grafting different MEMA concentrations onto 0.5 Mrad preirradiated PP fabric: (○) 5%; (□) 10%; (△) 15%; (▲) 20%. Grafting temp, 75°C.

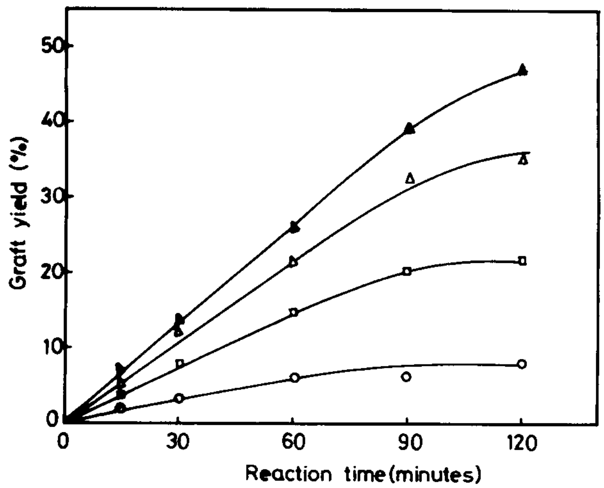


Figure 3 Effect of reaction time on the degree of grafting different MEMA concentrations onto 0.5 Mrad preirradiated PP fabric: (○) 5%; (□) 10%; (△) 15%; (▲) 20%. Grafting temp, 98°C.

was then added to the dye bath such that the fabric-to-liquor ratio was 1 : 100 and the pH was adjusted to 5.5. The dyeing was started at 50°C and the temperature was gradually increased to boiling over 0.5 h and maintained at this temperature for another 0.5 h. The dyed sample was washed with fresh water to remove the unreacted dyestuff.

Testing

Color Strength

The color strength (K/S) of the dyed sample before and extraction with 50% aqueous solution DMF was determined using a spectrophotometer (Perkin-Elmer Lambda 3B) and applying the Kubelka–Munk equation[6] as follows:

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0}$$

where K is the absorption coefficient; S, the scattering coefficient; and R and R_0, the decimal fractions of the reflectance of the dyed and undyed samples, respectively.

Moisture Regain

The samples were conditioned at room temperature for four dyes in a desiccator containing a saturated solution of sodium nitrite to achieve a relative humidity of 65%. The samples were weighed and dried and the moisture regain was calculated as follows:

$$\text{Moisture regain } (\%) = (W - W_0/W_0) \times 100$$

where W and W_0 are the conditioned and dry weights of the sample, respectively.

IR Spectroscopic Analysis

The infrared analysis was carried out using an FTIR spectrophotometer (Model PU 9700) by Philips. The samples were ground to a very fine powder, mixed with highly dried KBr powder, and pressed to transparent disks.

RESULTS AND DISCUSSION

Factors Affecting Grafting

Effect of MEMA Concentration

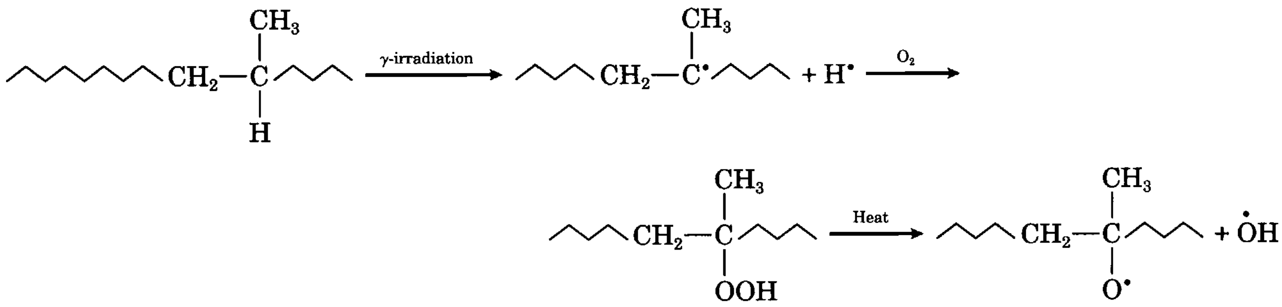
The effect of reaction time on the degree of grafting different aqueous concentrations of MEMA onto preirradiated PP fabric at 0.5 Mrad and carried out at 50, 75, and 98°C is shown in Figures 1–3. At 50°C, the reaction was very slow and the maximum graft yield does not exceed 2.3%, as shown in Figure 1. At 75°C, an induction period of 60 min was observed for all monomer concentrations (5–20%); then, the grafting yield increased lineary with time (Fig. 2). As shown in Figure 3, for MEMA concentrations, there is a linear increase in graft yield with increasing reaction and then the graph tends to level off in a period of 90–120 min. In general, at a given reaction temperature, the graft yield for all MEMA concentrations increases with increasing grafting time. However, the higher the monomer concentration, the higher the graft yield. Also, increasing grafting temperature from 50 to 98°C causes a significant increase in the graft yield.

The enhancement in the graft yield associated with increasing MEMA concentration could be attributed to the diffusion of excess monomer into the PP matrix. On the other hand, the fast homopolymerization of MEMA, at longer grafting time and higher temperature, will eventually increase the viscosity of the grafting solution. This process can reduce the diffusion of the monomer inside the PP matrix and may account for the leveling-off of the graft yield observed in Figure 3. The lifetime of the formed active center may be also an additional reason for this leveling.

Figure 4 and Table I show the logarithmic relationship between the grafting rate and MEMA concentration based on the results shown in Figure 3. The dependence of the grafting rate on monomer concentration was found to be of 1.12 order. Thus, the grafting reaction of MEMA onto gamma-irradiated PP depends entirely on the monomer concentration.

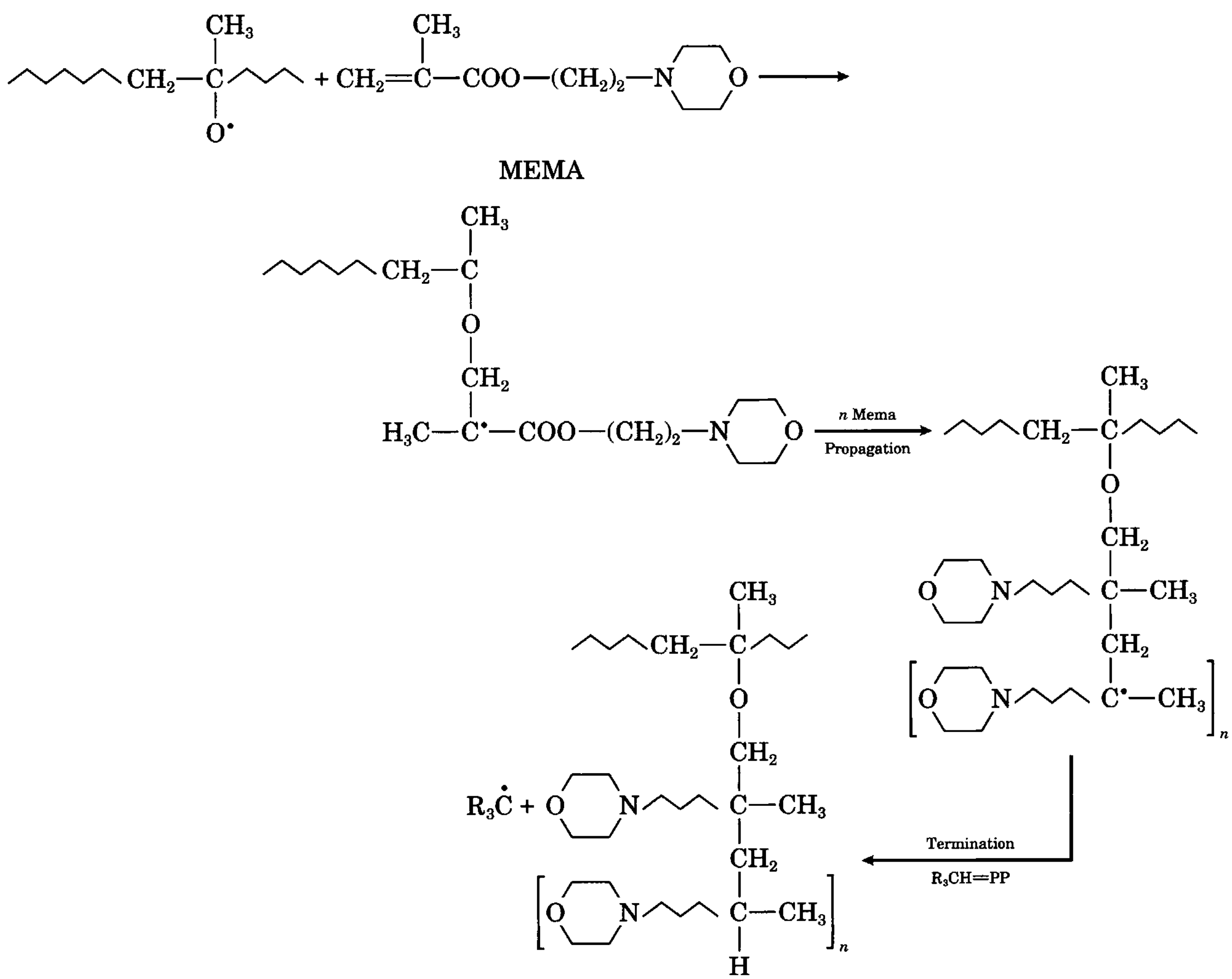
The proposed grafting reaction between the preirradiated PP fabric and the used monomer may be summarized as follows:

Gamma irradiation and free-radical formation onto PP:



(I) (II)

Grafting of 2*N*-morpholino ethyl methacrylate (MEMA) onto gamma-irradiated PP fabric:



(III)

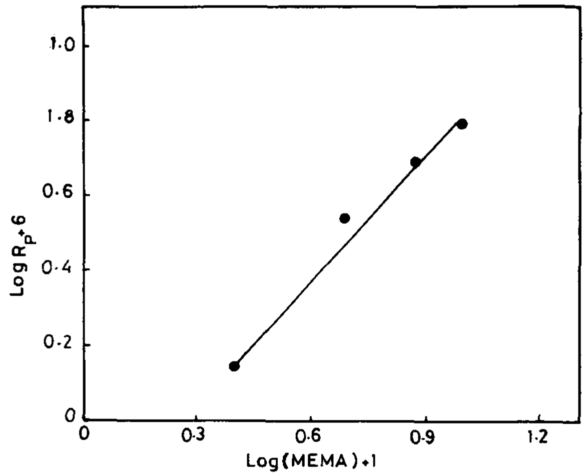


Figure 4 Logarithmic correlation between the rate of grafting (*Rp*) of MEMA onto PP fabric and MEMA concentration. Grafting temperature, 98°C.

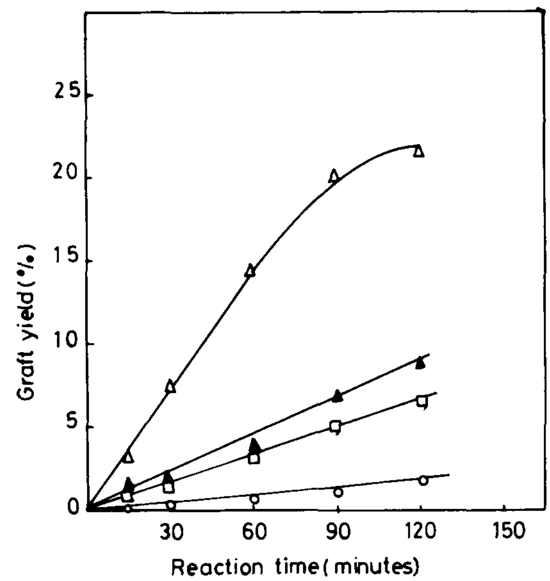


Figure 5 Effect of reaction time on the degree of grafting 10% MEMA onto 0.5 Mrad preirradiated PP fabric at different reaction temp: (O) 50°C; (□) 75°C; (▲) 80°C; (△) 98°C.

Irradiation of PP fabric forms active free-radical centers on the labite tertiary hydrogen atoms of PP chains. These modicals will immediately react with air oxygen, leading to the formation of hydroperoxides (I) at ambient temperature. They are decomposed by heat in the presence of an inert atmosphere to give alkoxide radicals (II) where grafting can take place. It is to noted that the formation of the MEMA homopolymer is due to the reaction of OH˙ radicals (III) with the monomer.

Effect of Grafting Temperature

It has been proven that the reaction temperature has a significant effect on the grafting process due to its influence on the diffusion of the monomer into the polymer matrix. Moreover, it greatly affects both the lifetime of the trapped radicals and their decomposition in the preirradiated polymer. Figure 5 and Table II show the grafting-rate graphs for the grafting of aqueous MEMA onto PP fabric at various reaction temperatures. It is clear that the rate of grafting increases with increasing reaction temperature. However, the rate of grafting is greatly enhanced at higher reaction temperature. Moreover, the graft yield is found to increase by increasing monomer concentration. These trends indicate that the diffusion of the monomer and the decay of the trapped peroxy radicals increase at elevated reaction temperatures.

It has been reported[7] that the reaction rate of grafting at a definite temperature and concentration can be represented by

$$\text{Grafting rate, } Rp = KC$$

where K is the rate constant and is function of the absolute temperature in Arrhenius the equation

Table I Dependence of Rate of Grafting (*Rp*) onto PP Fabric on MEMA Concentration

MEMA Concn (mol/L)	log MEMA Concn	log MEMA + 1	Rate (*Rp*) (mol L^{-1} s^{-1})	log (*Rp*)	log (*Rp*) + 1
0.25	−0.6020	0.398	0.13×10^{-5}	−5.886	0.144
0.50	−0.3030	0.699	0.34×10^{-5}	−5.468	0.531
0.75	−0.1249	0.875	0.48×10^{-5}	−5.319	0.681
1.01	4.3214×10^{-3}	1.004	0.62×10^{-5}	−5.208	0.792

Grafting conditions: temperature 98°C; reaction time 30 min; liquor ratio 1 : 30.

Table II Dependence of Rate of Grafting (*Rp*) of MEMA onto PP Fabric on Reaction Temperature

Temp (°C)	$10^3/T$	*Rp* (mol L^{-1} s^{-1})	*ln Rp*	*ln Rp* + 16
50	3.09	0.2×10^{-6}	−15.4249	0.5751
75	2.87	0.8×10^{-6}	−14.0386	1.9614
80	2.83	1.1×10^{-6}	−13.7202	2.2798
98	2.69	3.3×10^{-6}	−12.6216	3.3784

Grafting conditions: MEMA concn 0.502 mol/L; liquor ratio 1 : 30; time 60 min.

$$d \ln K/dT = E/RT$$

$$K = Ae^{-E/RT}$$

$$\ln K = \text{constant} - E/RT$$

where $\ln K = \ln Rp$. A is a constant having the same units as the rate constant and is proportional to the frequency of collisions between the reacting molecules and is called the preexponential factor; R is the universal gas constant, with the same energy units used for E and is equal to 1.987 cal mol^{-1} K; and E is the activation energy of the reactants required for the reaction.

On plotting ln Rp vs. $(1/T)$, a straight line of slope $-E/R$ will be obtained. Figure 6 shows the Arrhenius plot for the grafting of MEMA onto the PP under investigation. The calculated overall activation energy from this plot was found to be 14.19 kcal/mol.

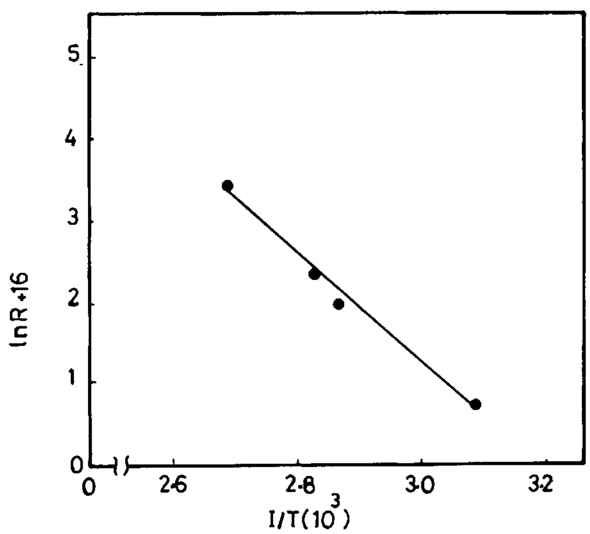


Figure 6 Arrhenius plots for graft copolymerization of MEMA onto PP fabric based on the data in Figure 5 and Table II.

Effect of Irradiation Dose

The effect of irradiation dose (0.5–1 Mrad) on the graft yield when using different MEMA concentrations onto PP fabric carried out at 75 and 98°C is shown in Figures 7 and 8. It is observed that, at a given reaction temperature, the graft yield increases with increasing irradiation dose regardless of the monomer concentration. Moreover, the graft yield increases with increasing both irradiation dose and reaction temperature due to the formation of higher amounts of hydroperoxide radicals. The rate of increase of graft yield with increase of irradiation dose depends mainly on both reaction temperature and monomer concentration. This can mean that these two factors are of much higher importance than is

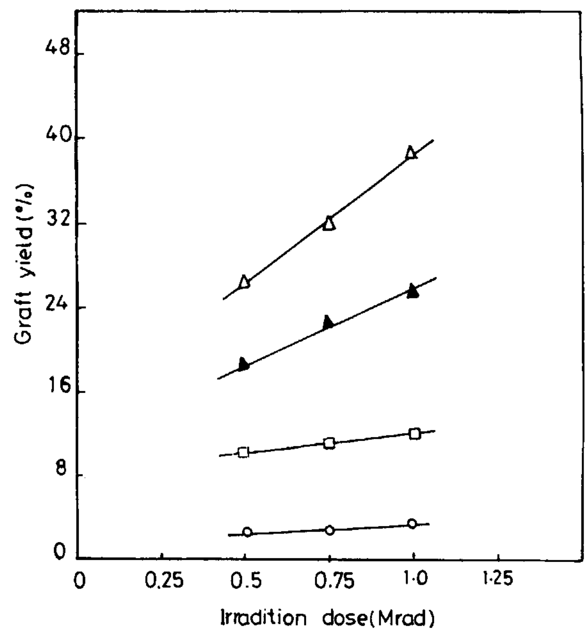


Figure 7 Effect of irradiation dose on the graft yield of different MEMA concentrations onto PP fabric: (○) 5%; (□) 10%; (▲) 15%; (△) 20%. Grafting temp: 75°C.

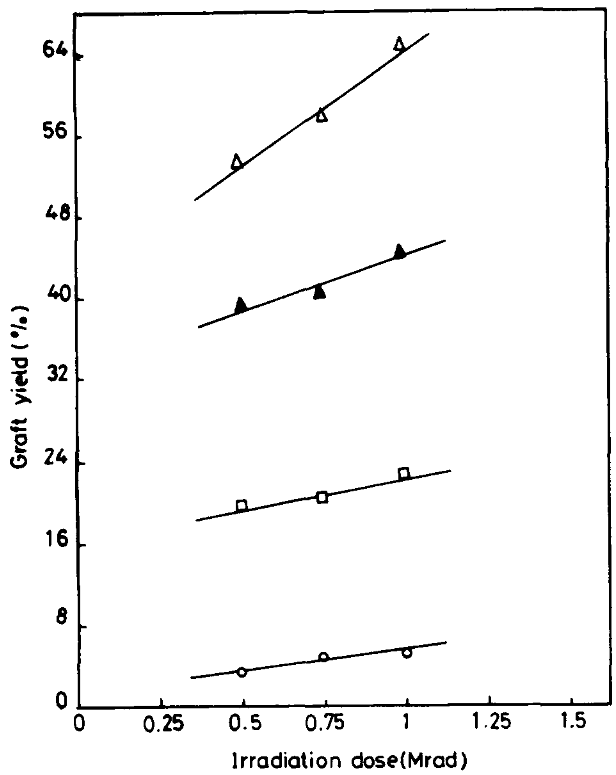


Figure 8 Effect of irradiation dose on the graft yield of different MEMA concentrations onto PP fabric: (○) 5%; (□) 10%; (▲) 15%; (△) 20%.

the irradiation dose. High irradiation dose certainly has a deteriorating effect on the mechanical properties; it is preferable to use lower irradiation doses and high temperature or high monomer concentration to obtained high graft yields.

Physical and Dyeing Properties

Moisture Regain

The effect of variation in graft yield of MEMA onto PP fabric on the moisture regain is shown in Figure 9. It is evident that the presence of MEMA as a graft in the molecular structure of PP improves its moisture regain to a noticeable extent. Grafting PP fabric up to 55% graft yield increased its moisture regain up to 1.9% compared to zero for the ungrafted one. The improvement in moisture regain is attributed to the hydrophilic nature of the grafted MEMA.

Affinity for Acid Dye

Table III presents the color strength (*K*/*S*) of the ungrafted as well as the grafted PP fabric (with different graft yields) before and after extraction with a 50% aqueous solution of DMF. It is clear that the color strength (*K*/*S*) of the ungrafted PP fabric is very low as compared to the grafted PP fabric with MEMA. Moreover, the increase of *K*/*S* with increasing graft yield from 4.9 to 20.9% is highly pronounced and results in higher dye absorption. After extraction of the dyed PP fabric with DMF, no change in *K*/*S* values was observed.

The above finding revealed a strong ionic bond formation between the positively charged quaternary nitrogen and the anionic part of the dye, leading to strong salt formation onto the PP fabric. Thus, the grafting of PP fabric with MEMA greatly improves its affinity for acid dye.

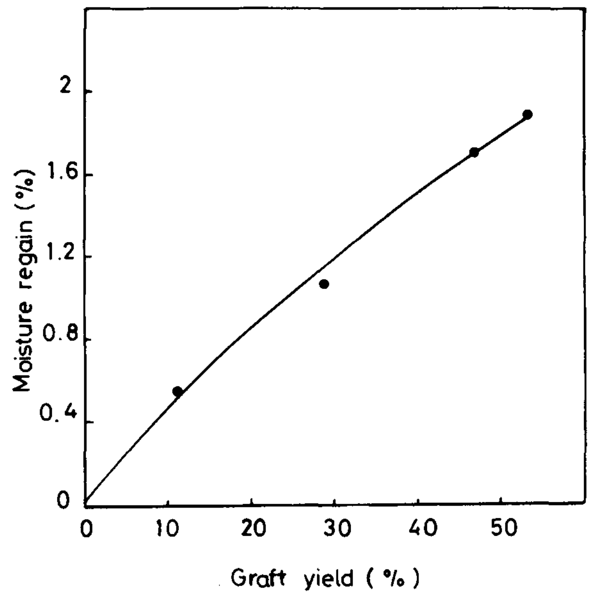


Figure 9 Effect of MEMA graft yield on the moisture regain of PP fabric.

Table III Dyeing[a] Properties of PP Grafted with MEMA

	Color Strength (*K*/*S*)	
Grafted Yield	Dyed Sample	DMF Extracted Sample
Blank	0.562	0.53
4.9	12.770	12.53
10.0	16.260	16.24
20.9	18.240	18.20

[a] Dye: Irganol yellow 5 GLS; 5% shade; reflectance measured at λ_{max} 390 nm.

Infrared Microscopic Analysis

Figure 10 shows the IR spectrum of the ungrafted and grafted PP fabric with 25% graft yield. Pure PP shows absorption bands around 2700–3000 cm^{-1}, these bands arising from C — H stretching either as — CH, CH_2, or CH_3 [Fig. 10(a)].

It can be seen from Figure 10(b) that new bands appear as a result of addition of other groups by grafting MEMA. The IR spectra of graft PP shows these extra bands:

1. An absorption band due to the C=O stretching of the ester group appears at 1727 cm^{-1}.
2. A distinctive absorption band at 1117 cm^{-1} is observed and is due to formation of the C — O group.

These data from the IR analysis confirms the presence of MEM grafts in the molecular structure of PP.

Table IV Thermochemical Properties of PP Fabrics Grafted with MEMA

PP Substrate	Melting Temperatures (°C)	Heat of Fusion (ΔHu) (J/g)
Ungrafted PP fabric	162.3	89.5
PP grafted with 12% MEMA	159.7	83.5
PP grafted with 48% MEMA	169.9	51.4

Thermal Properties of Polypropylene–MEMA Graft Copolymer

Table IV shows thermochemical features as calculated from the crystalline melting transition behavior of the first differential scanning calorimetry DSC scans of a PP fabric before and after it had been grafted with MEMA.

It can be seen that the crystalline melt point and the heat of fusion of the ungrafted PP fabric are

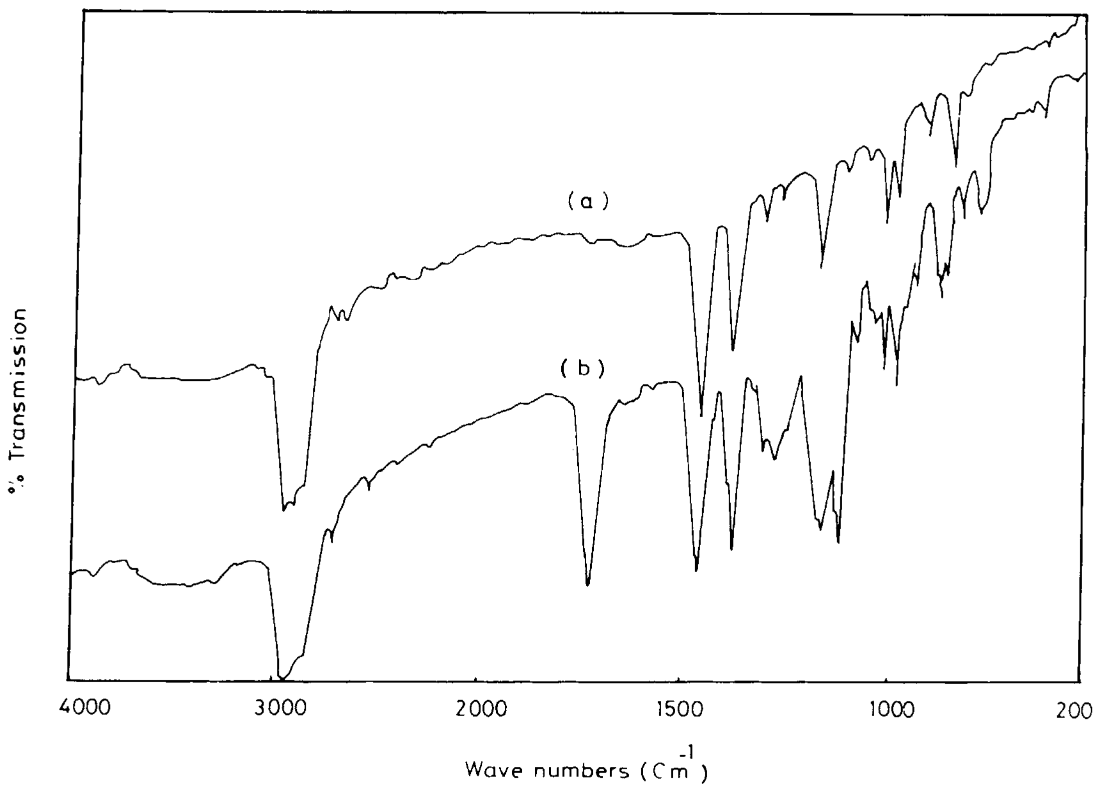


Figure 10 Infrared spectra of (a) ungrafted PP fabric and (b) PP fabric grafted with 25% MEMA.

162°C and 89.5 J/g, respectively. However, due to the introduction of 12% PMEMA, a depression of 2.6°C in the melting point and a decrease in the heat of fusion of 6°C in the melting point and a decrease in the heat of fusion of 6 J/g were measure. A further increase in the graft yield up to 48% caused a significant drop in the heat of fusion; however, an increase in the melting temperature was observed. Moreover, the obtained endothermic peak from the DSC scans becomes broader and less steep with increasing graft yield, suggesting that grafting introduces imperfection and a molecular weight increase. In addition, the observed depression in the melting point associated with the low graft yield and the abrupt decrease in the heat of fusion of the PP fabric indicate that grafting affects the crystalline structure of the fibers. This occurred in terms of the influence on structural regularity, bond flexibility, close packing ability, interchain attraction, and reduced crystallinity. The same trend was reported by Gawish et al.[5] when grafting the same monomer onto PP using electron-beam preirradiation.

For a truly random copolymer, in which a low molecular weight species was added to a high molecular polymer, a melting point depression can be approximated by using the well-known Flory relation[9] as shown by

$$1/T_m - 1/T_m^0 = (-R/\Delta Hu)\ln(Xa)$$

where T_m^0 is the melting point without noncrystallizable units in K^0 under the same melting procedure; R, the gas constant; ΔHu, the enthalpy of fusion per repeating unit in (cal/mol); and Xa, the mol fraction of the crystallizable units. A T_m of about 160°C was calculated from the above relation, showing good agreement between theory and experiment for the grafted PP fabric with 12% PMEMA. In these calculations, the quantities ΔHu, R, and Xa were substituted by 898.4 cal/mol, 1.987 cal/mol^{-1} K^{-1}, and 0.9668, respectively.

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