

Study of Thermal and Dyeing Behavior of Isotactic Polypropylene Fiber Graft Copolymerized with Acrylate Monomers Using Preirradiation Method*

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SYNOPSIS

In an attempt to modify isotactic polypropylene (IPP) fiber, grafting of acrylate monomers such as methyl acrylate (MA) and ethyl acrylate (EA) onto IPP has been carried out by preirradiation method in aqueous medium. Percentage of grafting has been determined as a function of various reaction parameters. Rate of grafting (R_g) and induction period (I_p) have been evaluated as a function of total initial monomer concentration. Methyl acrylate was found to be more reactive than ethyl acrylate toward grafting. Thermogravimetric analysis (TGA) indicates that the thermal stability of polypropylene fiber is significantly improved upon grafting. While polypropylene fiber could not be dyed by crystal violet, the grafted fiber was dyed with crystal violet, and the dye uptake has been quantitatively determined by spectrometric method. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene has a number of desirable properties that make it a versatile material among modern thermoplastic polymers. It is made from cheap raw materials and was commercialized in 1958 for the first time. Since then, it has become one of the biggest growing plastics due to its low cost, versatility, and wide applicability. It is used broadly as molding resin as well as in many extruded forms including films, fibers, and monofilaments. Its copolymers with ethylene possess good low-temperature impact resistance. It can be alloyed with a variety of polymers for a wide spectrum of purposes, such as improvement in impact resistance and dyeability. Filled up to 40% mineral fillers, polypropylene (PP) can be used for high structural rigidity and can be formulated for fire retardancy. Polypropylene when properly stabilized is inert to most chemicals at or near ambient temperature. It possesses useful resistance

to alteration by the environment. This inertness excludes its application from the field where chemical affinities or penetration of components is necessary, e.g., dyeing of fiber, printing of films, etc. However, PP, when modified either by oxidative treatment of the surface or through chemical reaction, possesses superior properties. Modification of PP by graft copolymerization of a variety of vinyl monomers has been studied by different groups of workers. The chemical modification of PP by grafting may occur by chain transfer using benzoyl peroxide, dicumyl peroxide, and di-tertiary butyl peroxide as initiators. Canterino¹ grafted a mixture of acrylate monomers onto PP using benzoyl peroxide as initiator. Grafting of styrene and methyl acrylate onto PP has been reported in the presence of butylamine, pyridine, and formamide.² The photochemical graft copolymerization of PP³ has been studied using benzophenone as sensitizer. Tazuke et al.⁴ reported photografting of acrylic acid onto PP in acetone in the presence of a sensitizer. Lapcik et al.⁵ have recently reported on the grafting of acrylate monomers onto PP using low-pressure plasma. Peroxidized PP has been used for graft copolymerization. The decomposition of preirradiated PP by γ -rays in air in the presence of monomer initiated graft copolymeriza-

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tion. Chapiro⁶ studied the kinetics of the graft copolymerization of acrylonitrile onto radiation-peroxidized PP films. Sobue et al.⁷ studied the influence of dosage on percent grafting at particular preirradiation intensities, confirming the occurrence of chain reaction in the formation of hydroperoxides. They observed that grafting rate increases with increase in the time of reaction. Decrease in the grafting rate with increase in preirradiation dose has been observed by O'Neill.⁸ In our laboratory, we have studied the modification of isotactic polypropylene (IPP) fiber by γ -rays-induced graft copolymerization of acrylonitrile,^{9,10} acrylic acid,¹¹ and acrylamide,¹¹ using preirradiation technique. Effects of a variety of solvents on percentage of grafting have been studied. Water was found to enhance the grafting rate. Similar result has been reported by Torikai et al.¹² Mikulasova et al.¹³ studied the effects of solvents upon graft copolymerization of methyl methacrylate onto PP by mutual γ -radiation *in vacuo*. Garnett and coworkers^{14,15} studied the effect of acids and other additives on the ultraviolet (UV) and γ -rays-induced grafting of vinyl monomers onto PP. The present article describes studies on the graft copolymerization of methyl acrylate (MA) and ethyl acrylate (EA) onto PP preirradiated by γ -rays in air. Optimum conditions for affording maximum percentage of grafting have been evaluated and an attempt has been made to compare relative reactivity of MA and EA toward radiation-induced grafting onto PP. Thermal behavior and dyeability of the grafted PP have also been studied.

EXPERIMENTAL

Isotactic polypropylene (IPP) in the form of fiber was received from National Rayon Corporation, Bombay. Methyl acrylate and ethyl acrylate were washed with 5% aqueous sodium hydroxide solution followed by washing with water and dried over anhydrous Na_2SO_4 . The monomers were freshly distilled and the middle fraction was used.

The method for γ -radiation-induced graft copolymerization of vinyl monomers to IPP fiber is similar to the one described elsewhere.^{9,10}

After the completion of the grafting reaction, the grafted fiber is extracted with acetone for 48 h to ensure complete removal of the homopolymer. Percentage of grafting has been calculated from the increase in weight of the original fiber after removal of homopolymer by solvent extraction

$$\% \text{ grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 denote, respectively, the weights of original fiber and the grafted fiber after complete removal of the homopolymer.

The percentage of grafting has been determined as a function of (a) total dose, (b) monomer concentration, (c) time of reaction, (d) temperature, and (e) amount of water used. Rate of grafting and induction period have been evaluated as a function of total initial monomer concentration. Thermal properties and dyeing behavior of IPP and grafted IPP fiber have been studied.

Evidence of Grafting

The graft copolymers obtained from grafting of PMA and PEA onto IPP showed absorption in the infrared (IR) spectrum at 1730 cm^{-1} assigned to $\text{C} = \text{O}$, which was absent in the IR spectrum of IPP.

Dyeing Behavior of IPP and Grafted IPP

In the present study, crystal violet has been used to dye IPP and grafted IPP fiber, and an attempt has been made to quantitatively determine the total dye uptake by the unmodified and the modified IPP fiber. Since the IPP grafts are insoluble in organic solvents, it becomes difficult to determine the total dye uptake quantitatively by optical methods. Alternatively, the dyed fibers could be extracted with different solvent systems such that the dye molecules absorbed or chemically bonded to the fiber are washed out. The optical densities of the extracted solvents are measured and the dye concentration in the extracts can be determined from the standard curves.

To 100 mL of 0.1% aqueous solution of crystal violet was added 100 mg of IPP and IPP grafts separately for 30 min. The fiber samples were taken out and dried at 50°C . The dried samples were treated with 100 mL of distilled water and stirred slowly on a magnetic stirrer. During stirring the dye is completely removed from the unmodified IPP indicating that the IPP fiber resists dyeing. With IPP grafts, the absorbed dye is washed out from the fiber while the chemically bonded dye remains intact. These grafted IPP samples were further treated separately with 100 mL of acetone and dimethylformamide (DMF) solvent system [comprising DMF, H_2O , and HCOOH in the ratio 60 : 39 : 1 and 4.0 g/L of aq. $(\text{NH}_4)_2\text{SO}_4$, respectively] and finally with pyridine acidified with HCOOH . The pH of DMF and pyridine solvent systems was kept con-

stant at 2.8 and 5.6, respectively. The pyridine solvent system completely removed the dye from the grafted fiber. Optical densities of the solution leached out by all the solvents mentioned above were determined by using spectronic-20 at 540 nm.

A standard curve has been obtained by plotting the concentration of dye solution prepared in water, acetone, DMF, and pyridine solvent system versus optical density. From these standard curves the concentration of the dye in each extractant obtained after treatment of the dyed grafted fiber is measured. The total concentration of the dye taken up by the grafted fiber is thus quantitatively determined and the results are presented in Table I.

RESULTS AND DISCUSSION

The irradiation of PP by γ -rays in air results in the formation of hydroperoxide groups on the backbone polymer. Extensive oxidative degradation of IPP was minimal when irradiation was carried out using low dose rate. The macro hydroperoxide is formed because of the presence of labile tertiary hydrogens in the IPP chain. Upon heating, the hydroperoxides thus formed undergo decomposition to generate macroradical and the hydroxyl radical ($\dot{\text{O}}\text{H}$). In the presence of vinyl monomer, $\dot{\text{O}}\text{H}$ may initiate vinyl polymerization to give a growing polymeric chains [Eq. (4)], which may attach itself to the active sites of the backbone polymer to produce the graft [Eq. (5)]. Alternatively, the vinyl monomer may directly polymerize onto the active sites to give a graft copolymer [Eq. (6)]. The following equations (1-6) illustrate the mechanism of grafting by preirradiation method.

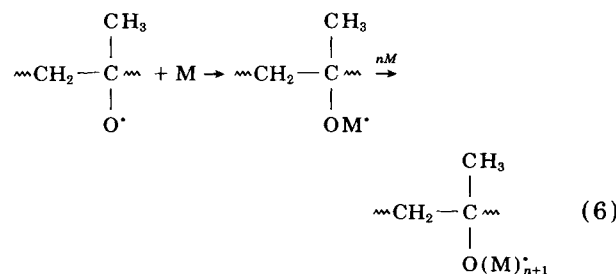
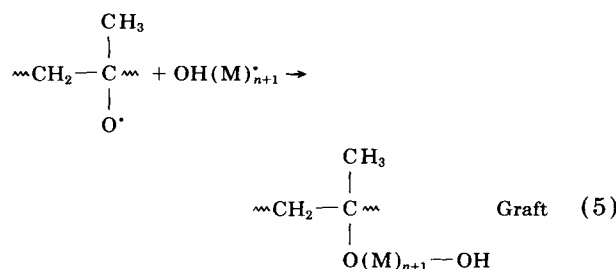
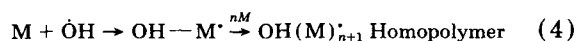
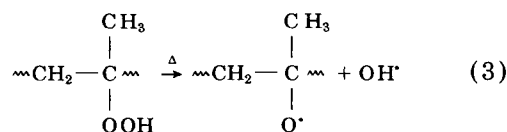
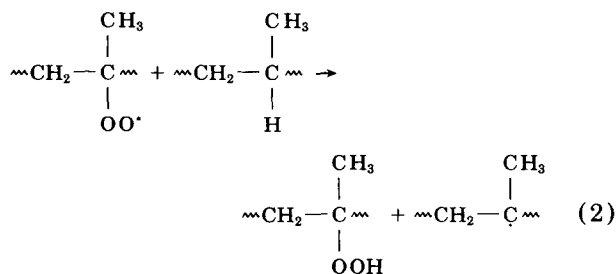
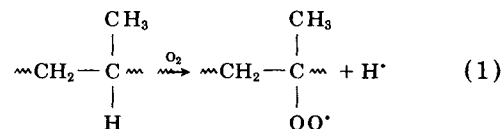


Table I Thermogravimetric Analysis of IPP, IPP-g-PMA, and IPP-g-PEA

Sample	Percent Grafting	IDT (°C)	FDT (°C)	DT (°C) at Every 10% Weight Loss									Figure
				10%	20%	30%	40%	50%	60%	70%	80%	90%	
IPP ^a	—	205	410	263	325	350	362	375	388	400	412	425	
IPP-g-PMA ^a	212	343	460	352	380	390	400	407	412	422	435	450	7
IPP-g-PMA ^b	537	345	450	362	381	391	400	408	410	418	421	430	6
IPP-g-PEA ^c	149	338	430	340	370	380	390	395	400	410	418	425	7
IPP-g-PEA ^c	287	335	460	358	371	381	390	400	402	410	420	440	6

^a IPP = 100 mg; total dose = 10.89 Mrad, [MA] = 147.2×10^{-2} mol/L, reaction time = 30 min. Temperature = 95°C, H₂O = 15 mL.

^b IPP = 100 mg; total dose = 10.89 Mrad, [MA] = 147.2×10^{-2} mol/L, reaction time = 180 min, temperature = 105°C, H₂O = 15 mL.

^c IPP = 100 mg; total dose = 8.68 Mrad, [EA] = 122.7×10^{-2} mol/L, reaction time = 30 min, temperature = 95°C, H₂O = 15 mL. IPP = 100 mg; total dose = 8.66 Mrad, [EA] = 366.0×10^{-2} moles/L, reaction time = 180 min, temperature = 115°C, H₂O = 5 ml.

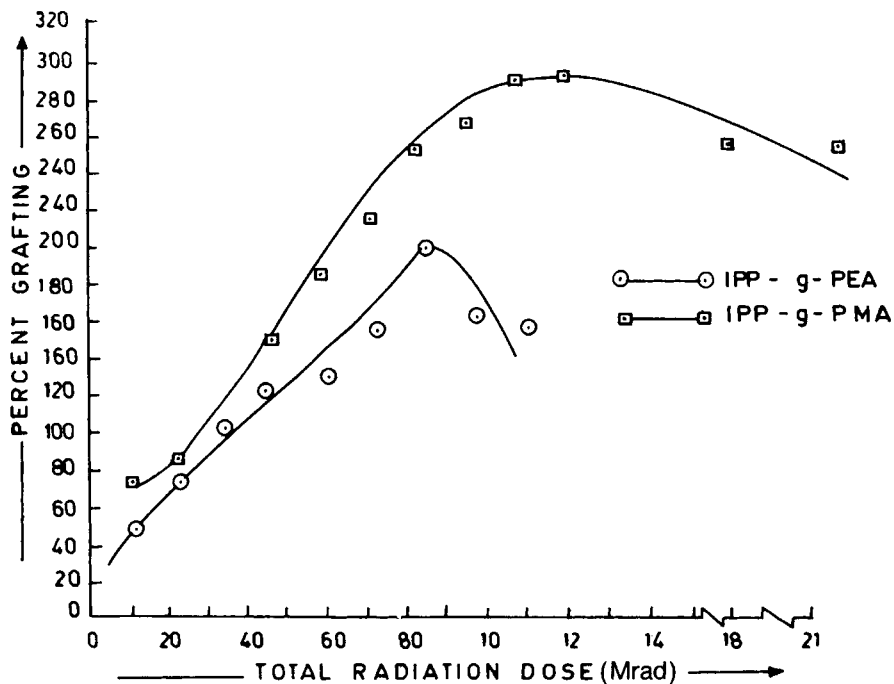


Figure 1 Effect of total dose on percentage of grafting of EA and MA.

Effect of Total Dose

Irradiation of IPP was carried at a constant dose rate of 0.31 Mrad for different time periods. Percentage of grafting of EA and MA onto preirradiated IPP has been studied as a function of total dose and the results are presented in Figure 1. It is observed from the figure that the percentage of grafting increases with increase in total dose with both EA and MA, reaches maximum, and then decreases. The rate of grafting is found to be higher with MA than EA. The maximum grafting (287 and 195%) was ob-

tained for MA and EA at a total dose of 12.10 Mrad and 8.68 Mrad, respectively, under optimum conditions.

Effect of Monomer Concentration

Figure 2 represents the effect of concentration of monomer (MA and EA) on percentage of grafting. It is observed that with increasing [MA] percentage of grafting increases giving maximum (578%) at 147.2×10^{-2} mol/L whereas in the case of EA, percentage of grafting reaches maximum with increas-

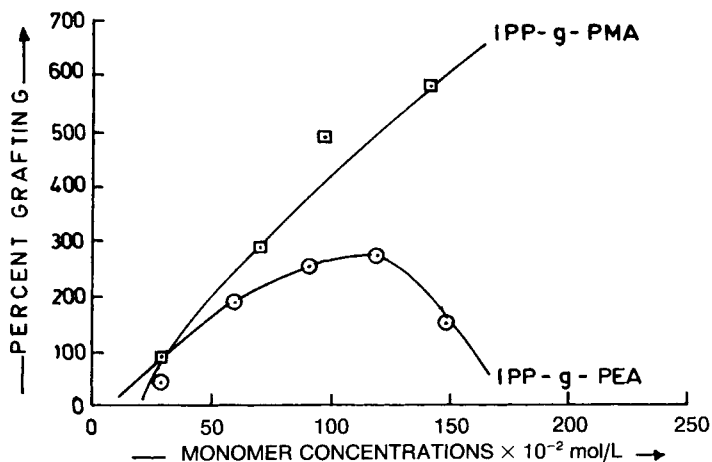


Figure 2 Effect of [EA] and [MA] on percentage of grafting.

Table II Rate of Grafting (R_g) and Induction Period (I_p) as a Function of Total Initial Monomer Concentration^a

Sample	[EA] × 10 ² (mol/L)	[MA] × 10 ² (mol/L)	R_g (% min)	I_p (min)
1	122.0	—	5.17	7
2	183.0	—	4.84	1
3	244.0	—	5.54	2
4	—	147.2	6.19	1
5	—	220.8	6.33	0
6	—	294.4	8.03	0

^a Reaction conditions: PP = 100 mg; H₂O = 15 mL, Temp. = 95°C. Total dose = 8.68 Mrad (EA); 10.89 Mrad (MA).

ing [EA] and then decreases. Maximum grafting (272%) was obtained at [EA] = 122.6 × 10⁻² mol/L.

The rate of grafting (R_g) and induction period (I_p) as a function of total initial monomer concentration of EA and MA have been calculated from the plot of percentage of grafting versus reaction time and the values are presented in Table II. It is observed from the table that R_g of both EA and MA increases with increasing monomer concentration while I_p of both monomers decreases. R_g of MA is higher than that of EA indicating that MA is more reactive than EA.

The higher rate of grafting observed with MA as compared to EA may be explained by the facts that MA being more soluble in water (5 parts/100 parts of H₂O at 25°C) than EA (1.5 parts/100 parts of H₂O at 25°C)¹⁶ easily comes in contact with the active sites of the polymeric backbone in aqueous medium resulting in higher percentage of grafting.

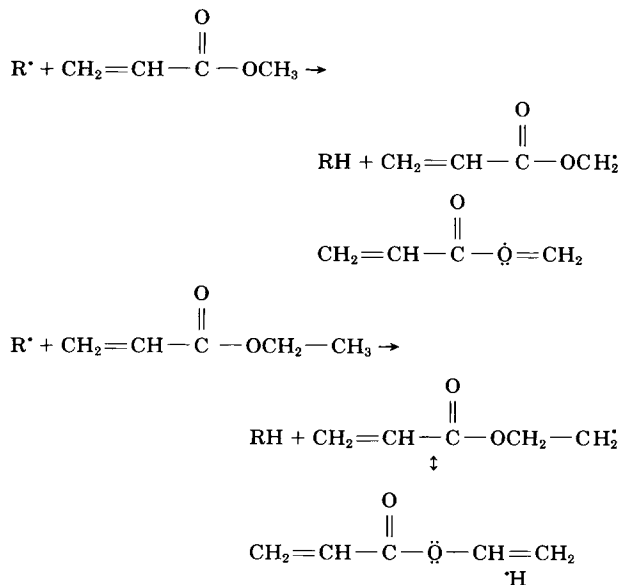
Table III Dye Uptake (Percent Strength) for Graft Copolymers of Acrylate Monomers onto Polypropylene^{a,b}

Graft Copolymer	Percent Grafting	Water System		Acetone System		DMF-H ₂ O System		Pyridine System		Total Conc. (%)
		O.D.	Conc. (%)	O.D.	Conc. (%)	O.D.	Conc. (%)	O.D.	Conc. (%)	
IPP-g-PMA	72	0.01	0.0001	0.06	0.006	0.05	0.0015	0.01	0.0003	0.0079
IPP-g-PMA	148	0.06	0.004	0.07	0.007	0.03	0.0007	0.01	0.0003	0.0084
IPP-g-PMA	262	0.08	0.00048	0.13	0.0125	0.03	0.0006	0.03	0.003	0.0166
IPP-g-PMA	287	0.04	0.0003	0.04	0.004	0.03	0.0007	0.01	0.0003	0.0073
IPP-g-PEA	122	0.06	0.0004	0.04	0.004	0.05	0.0015	0.01	0.0003	0.0062
IPP-g-PEA	152	0.3	0.00895	0.055	0.00575	0.04	0.0012	0.02	0.0012	0.0171
IPP-g-PEA	188	0.05	0.0004	0.03	0.003	0.02	0.003	0.01	0.0003	0.0040
IPP-g-PEA	237	0.07	0.00045	0.02	0.002	0.07	0.002	0.01	0.0003	0.00475

^a Graft copolymer used = 100 mg.

^b Initial dye conc. = 0.1% in each case.

Further, because of higher monomer transfer constant of EA ($C_M \times 10^{-4}$ at 70° = 0.351),¹⁷ than MA ($C_M \times 10^{-4}$ at 70°C = 0.01),¹⁸ wastage reactions involving chain transfer of growing grafted chains with monomer are greater with EA, as shown



Effect of Temperature

Percentage of grafting of EA and MA onto preirradiated IPP has been studied as a function of reaction temperature, and the results are presented in Figure 3. It is observed from the figure that maximum percentage of grafting with MA and EA is obtained at 95 and 115°C, respectively. Further increase in temperature decreases percentage of graft-

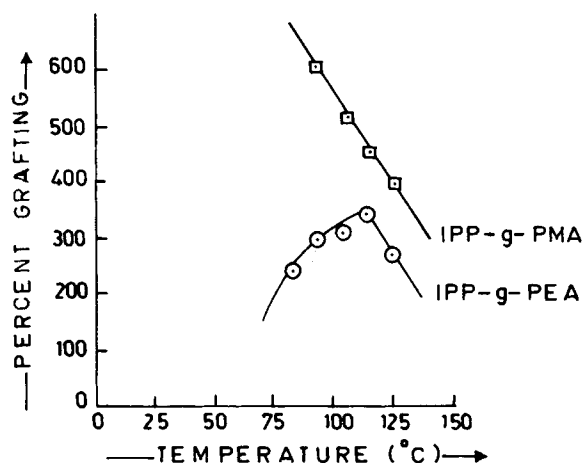


Figure 3 Effect of temperature on percentage of grafting.

ing and this is observed with both the monomers. Maximum grafting of MA (612%) under optimum conditions occurs at 95°C, whereas with EA maximum grafting (352%) occurs at 115°C. At higher temperature monomer transfer reactions of EA with growing grafted chains are accelerated leading to decrease in grafting.

Effect of Amount of Water

Figure 4 describes the effect of variation in the amount of water on percentage of grafting of MA and EA. It is observed from the figure that the percentage of grafting of both EA and MA is higher in water than in bulk. The maximum amount of grafting of both EA and MA under optimum conditions is obtained when 20 mL of water was used. Further increase in the amount of water does not signifi-

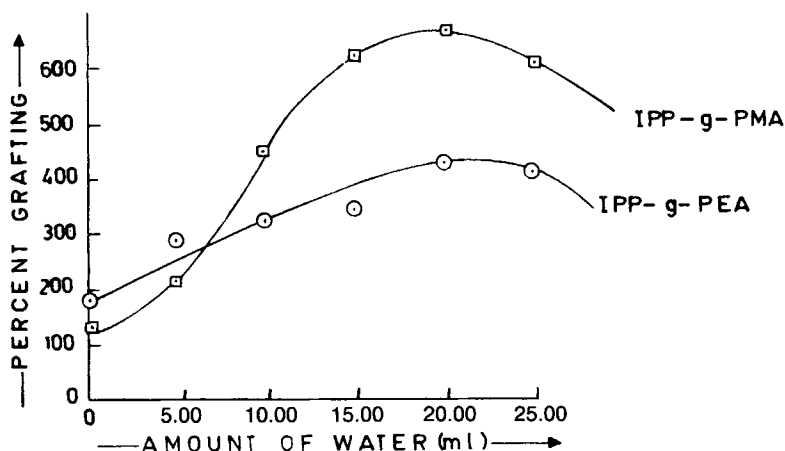


Figure 4 Effect of amount of water on percentage of grafting.

cantly affect the grafting yields. The higher percentage of grafting of MA and EA obtained in the presence of water as compared to bulk is due to the fact that water has a tendency to form hydrogen bonds with polypropylene hydroperoxide and this causes swelling of the polymer backbone which facilitates grafting.

Effect of Time

In Figure 5 are presented the results of the effect of reaction time on percentage of grafting. It is observed from the figure that grafting of MA and EA increases with increasing reaction time reaches maximum within 180 min. This may indicate that within 180 min, all the active sites are used up in the production of graft copolymer and further increase in reaction time results in preferential formation of the homopolymer.

Thermogravimetric Analysis of IPP, IPP-g-PMA, and IPP-g-PEA

Thermogravimetric analysis was carried out in DuPont 1090 thermal analyzer with 951 modules. The heating rate was 10°C/min.

The primary thermograms of IPP, IPP-g-PMA, and IPP-g-PEA are presented in Figures 6-7. Thermal behavior of grafted IPP fiber was studied as a function of percentage of grafting. It is observed from Figures 6-8 and also from Table III that the grafted IPP fibers showed better thermal behavior as compared to unmodified IPP,⁹ also it is observed that thermal stability of grafted samples is not greatly dependent on the extent of grafting.

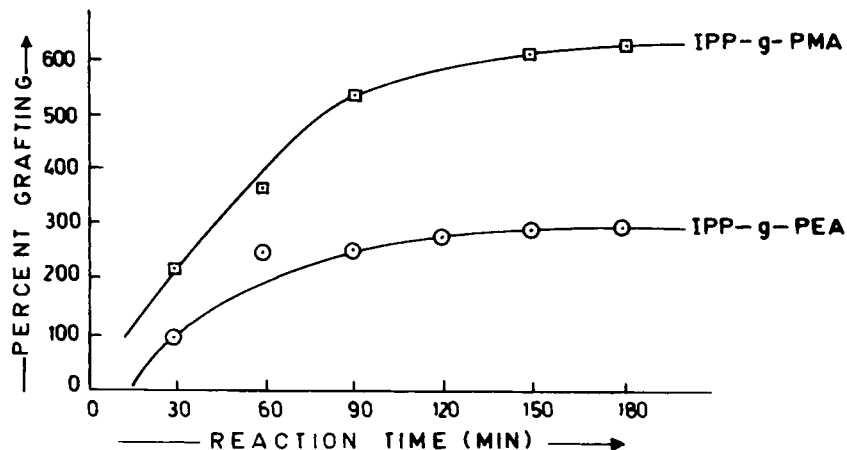


Figure 5 Effect of reaction time on percentage of grafting.

The primary thermograms of IPP⁹ and grafted IPP showed two regions of decompositions. Inflexion at 100–150°C due to presence of moisture is absent in both IPP and grafted IPP thermograms. The initial decomposition of IPP starts at 205°C, and thereafter the decomposition continues up to 410°C and then the final decomposition begins. The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperature (DT) at various weight percentage losses of IPP and IPP grafts are presented in Table III. The primary thermograms of IPP-*g*-PMA and IPP-

g-PEA show that the FDT and IDT and also the *DT* values at different weight percentage losses are higher as compared to those of IPP (Table III). Further, it is also observed from Figures 6 and 7 and Table III that IPP-*g*-PMA shows improved thermal properties than IPP-*g*-PEA.

Dyeing Behavior of IPP-*g*-Poly(MA) and IPP-*g*-Poly(EA)

Following tentative mechanism is suggested to explain the dyeing behavior of the grafted polymer with crystal violet.

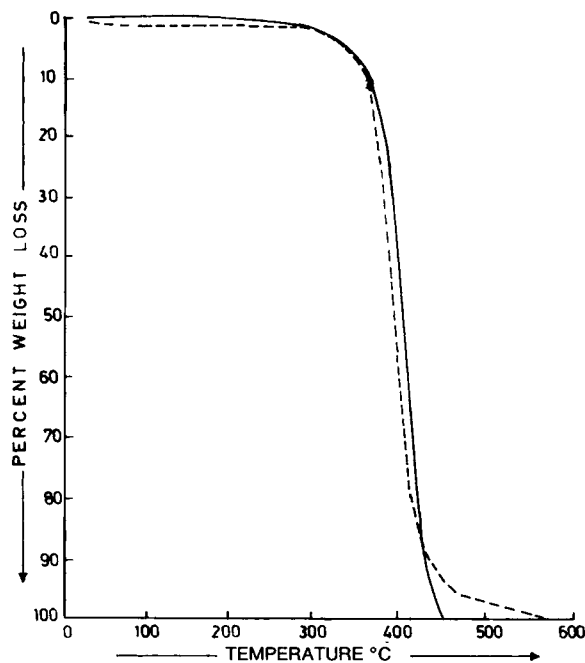


Figure 6 Primary thermogram of PP-*g*-PMA (—) and PP-*g*-PEA (-----).

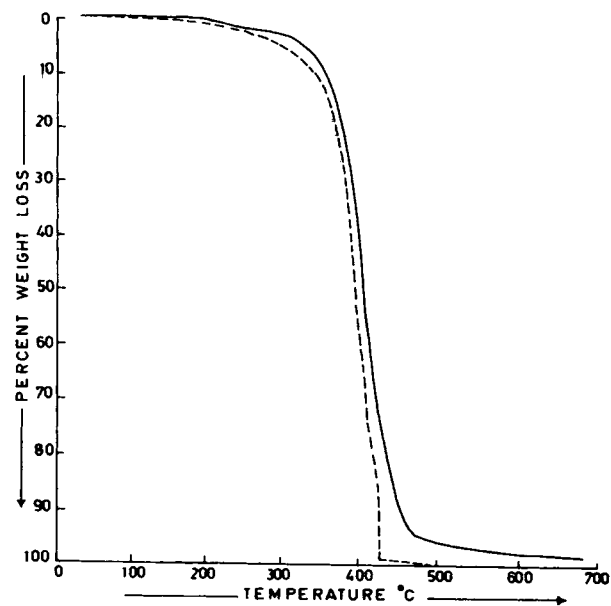
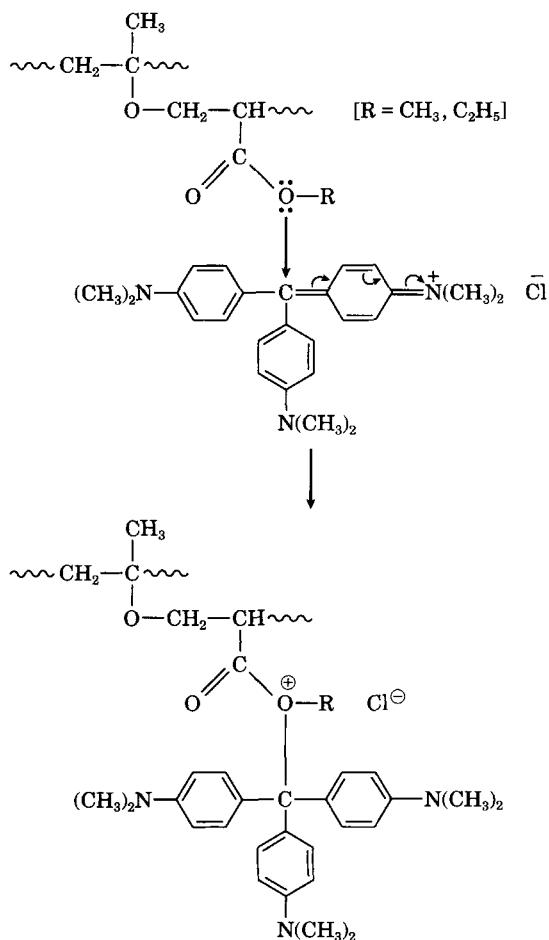


Figure 7 Primary thermogram of PP-*g*-PEA (-----) and PP-*g*-PMA (—).



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