Graft Copolymerization of Methacrylic Acid onto Isotactic Polypropylene by Radiochemical Methods

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ABSTRACT: Graft copolymerization of methacrylic acid onto isotactic polypropylene has been studied in water–methanol medium using γ-rays as the source of initiation. Graft copolymerization has been conducted by (1) mutual irradiation, (2) preirradiation, and (3) double irradiation methods. All of the reaction parameters that seem to influence grafting have been studied, and the optimum conditions leading to maximum percentage of grafting have been evaluated. A plausible mechanism for radiation-induced grafting of methacrylic acid onto polypropylene has been suggested, and the results have been explained on the basis of the proposed mechanism. A comparative study of graft copolymerization by different radiation methods has been made, and it was observed that the preirradiation method affords the best results. Evidence of grafting has been obtained from differential scanning calorimetric analysis and the dyeing behavior of the grafted material. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 143–152, 1998

Key words: graft copolymerization; mutual irradiation; preirradiation; double irradiation; isotactic polypropylene; methacrylic acid

INTRODUCTION

Polypropylene (PP) is an important thermoplastic material that finds widespread uses in commerce and industry in the forms of fiber, films, and plastics. Being a hydrocarbon polymer, it is resistant to chemicals at/or near ambient temperature and is stable to air and sunlight. This inertness excludes its applications in various fields where affinity toward chemicals is required. It cannot be used under conditions that require high temperatures. These drawbacks can be removed by effecting functionalization of the backbone polymer through grafting. Photografting of methacrylic acid (MAAc) and acrylamide using benzophenone as photosensitizer has been attempted by Gao and colleagues.[1] Taher and colleagues[2] studied the effect of different solvents on the swelling and grafting of MAAc onto isotactic polypropylene (IPP) films. The copolymers of MAAc and ω-caprolactam were grafted to PP and the graft showed good adhesion to metals and afforded coating materials.[3] 4-Vinyl pyridine was grafted onto IPP using trihexylboron in benzene by Kirshenbaum and colleagues.[4] Canterino[5] grafted a mixture of acrylic monomers onto PP using benzoyl peroxide as a radical initiator. Graft copolymer of PP fiber and MAAc were used as fibrous ion exchangers by Savchenko and colleagues.[6] Misra and colleagues[7] and Mehta and colleagues[8] have successfully grafted acrylonitrile, 4-vinyl pyridine, and a mixture of acrylonitrile and 4-vinyl pyridine[9] onto preirradiated IPP fiber. In this article, we report on the grafting of MAAc onto IPP fiber using different radiation methods.

EXPERIMENTAL

Materials and Methods

IPP was received from the National Rayon Corporation (Bombay, India) in the fiber form. MAAc

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(Merck, Germany) was freshly distilled, and the middle fraction was used. Double distilled water and freshly distilled methanol were used as solvents.

Irradiation of IPP was conducted using 2100 Ci of ^{60}Co source in the air at a constant dose rate of 0.128 Mrad h^{-1} for different time periods.

Graft Copolymerization

Preirradiation Method

Preirradiated fiber (100 mg) was suspended in a known amount of water–methanol solvent system in a flask fitted with a long water condenser, and then a definite amount of MAAc was added. The flask was placed in an oil bath maintained at a constant temperature, and the reaction was allowed to continue for different time periods. After the specified time, the grafted fiber was filtered, washed thoroughly with an excess of water, and then extracted with water for 48 h to ensure complete removal of the homopolymer formed during the reaction. The fiber was dried in a vacuum oven at 40°C until constant weight was obtained.

Mutual Method

To a suspension of IPP fiber (100 mg) in a definite amount of water–methanol mixture a known amount of monomer (MAAc) was added. The reaction mixture was irradiated by γ-rays from a ^{60}Co source for different time periods at a dose rate of 0.128 Mrad h^{-1}. After definite time periods, the reaction flask was removed from the chamber, and the grafted fiber was washed and extracted with water for 48 h to ensure complete removal of the homopolymer, dried, and weighed until constant weight was obtained.

Double Irradiation Method

IPP fiber (100 mg) was irradiated in air by a ^{60}Co source at a constant dose rate of 0.128 Mrad h^{-1}. The irradiated fiber was suspended in a definite amount of water–methanol solvent mixture, and a known amount of monomer was added. The reaction mixture was placed in the gamma chamber and irradiated for different time periods. The reaction mixture was worked up as described.

The percentage of grafting of MAAc onto IPP by all of the methods described has been determined from an increase in the weight of the original IPP fiber as follows:

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

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

Evidence of Grafting

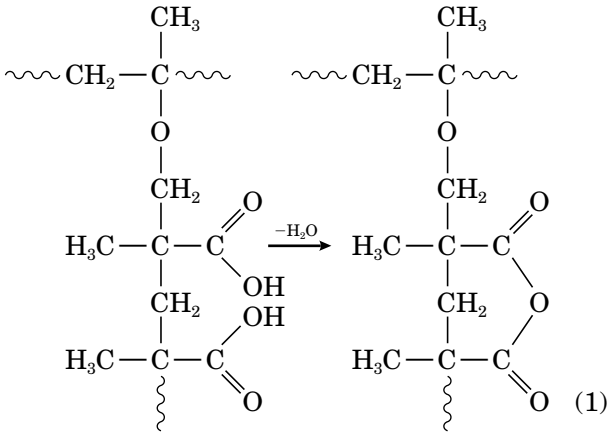
Isolation of Poly(MAAc) from IPP-g-Poly(MAAc)

The grafted Poly(MAAc) chains were separated from the graft copolymer, IPP-g-Poly(MAAc), by the method reported previously.[9] Isolation of the grafted polymer provides an evidence for the formation of the graft copolymer.

Differential Scanning Calorimetric (DSC) Analysis

DSC analysis of IPP-g-Poly(MAAc) was performed on a Differential Calorimeter (Perkin-Elmer, Norwalk, CT) type DSC-205. Results are presented in Table I.

It is observed from Table I that the grafted IPP fiber, IPP-g-Poly(MAAc)—prepared by mutual, preirradiation, and double irradiation methods—showed endothermic peaks at 159.8°, 149°, and 145.3°C, respectively, that may arise due to melting of the grafted Poly(MAAc) chains, whereas the exothermic peaks at 198.4°C and 187.3°C—observed for the grafted products obtained by preirradiation and double irradiation methods, respectively—are attributed to the anhydride formation between the pendant carboxylic groups in the following manner:

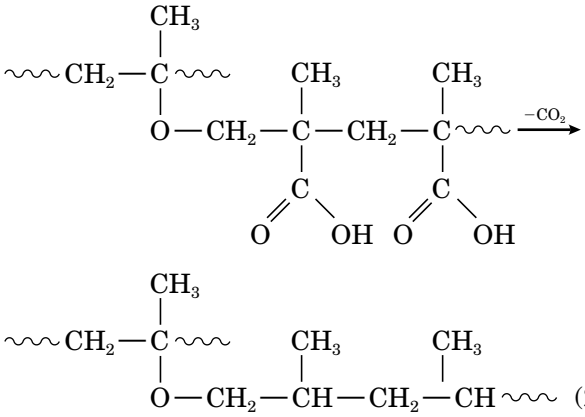


(1)

Table I DSC Data of IPP-g-Poly(MAAc)

Method	% Grafting	Endothermic Peak (°C)	Endothermic ΔH (J g^{-1})	Exothermic Peak (°C)	Exothermic ΔH (J g^{-1})	Exothermic Peak (°C)	Exothermic ΔH (J g^{-1})	Exothermic Peak (°C)	Exothermic ΔH (J g^{-1})
Double irradiation method	37	145.3	261, 07	187.3	641, 95	401.8	811, 71	460.4	798, 15
Preirradiation method	51	149.0	39, 601	198.4	2043, 8	355.6	1899, 2	498.7	4389, 4
Mutual method	40	159.8	234, 70	—	—	407.6	1977, 8	489,5	1022, 2

The other exothermic peaks at 355.6°, 401.8°, and 407.6°C in the graft obtained by preirradiation, double irradiation, and mutual methods may correspond to the decarboxylation reactions of the carboxylic groups of Poly(MAAc)-grafted chains.



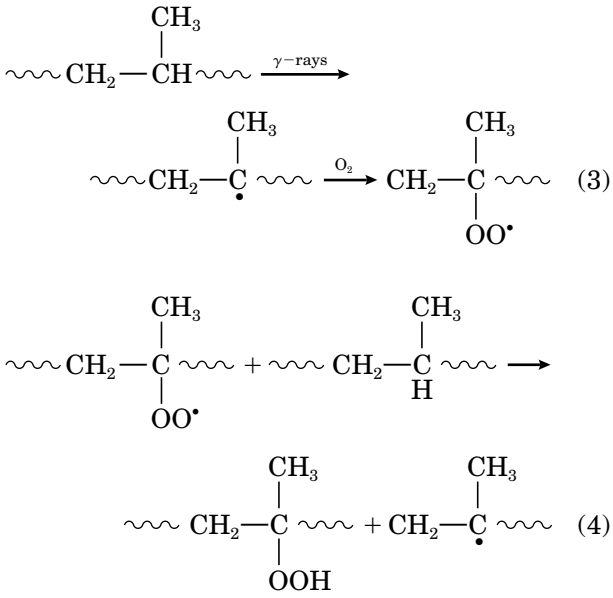
The exothermic peaks at 498.5°, 498.7°, and 460.7°C in the DSC curves of IPP-g-Poly(MAAc) prepared by mutual, preirradiation, and double irradiation methods, respectively, may arise due to the C—C bond scission.

Dyeing Behavior of IPP-g-Poly(MAAc)

IPP fiber and IPP-g-Poly(MAAc) fiber were dyed in a 0.1% aqueous solution of crystal violet. The dyeing procedure and the quantitative determination of the total dye uptake by the grafted fiber has been discussed in an earlier article.[10] The total dye uptake by IPP-g-Poly(MAAc) determined from the standard curves is presented in Table II. It is observed from Table II that the total dye uptake by the grafted PP shows little change, with an increase in percentage of grafting. At higher grafting levels (92% and 137%), the concentration corresponding to the total dye uptake becomes constant. The pendant carboxylic groups in the graft seem to have been involved in the binding of the dye molecule to the grafted fiber.

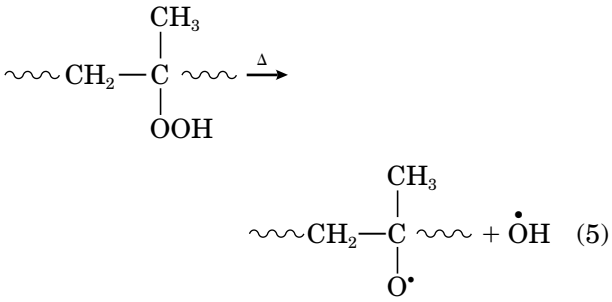
RESULTS AND DISCUSSION

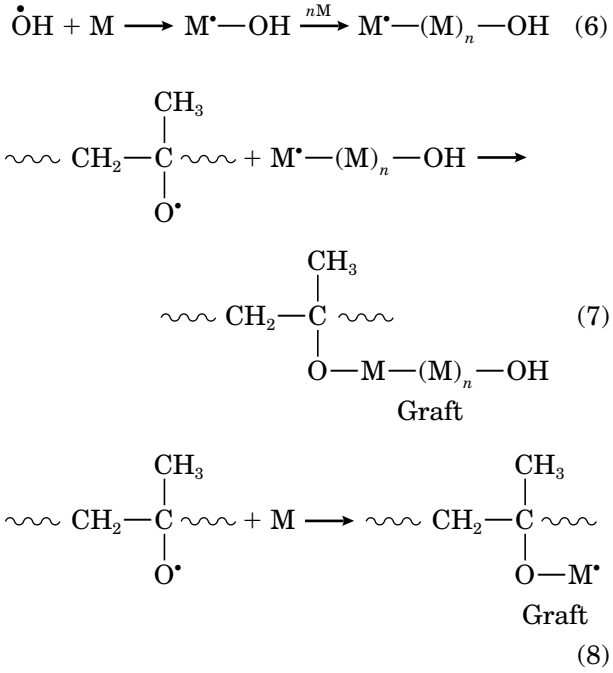
When PP is irradiated in the presence of air, PP hydroperoxides (PP—OOH) are preferentially formed because of the presence of a large number of labile tertiary hydrogens.



Hydroperoxide upon decomposition generates an hydroxyl radical and the polypropyleneoxy (PP—O•) radical, where grafting of vinyl monomers can take place. Afterward, a tentative mechanism is proposed to explain the grafting of MAAc onto IPP by different radiation methods.

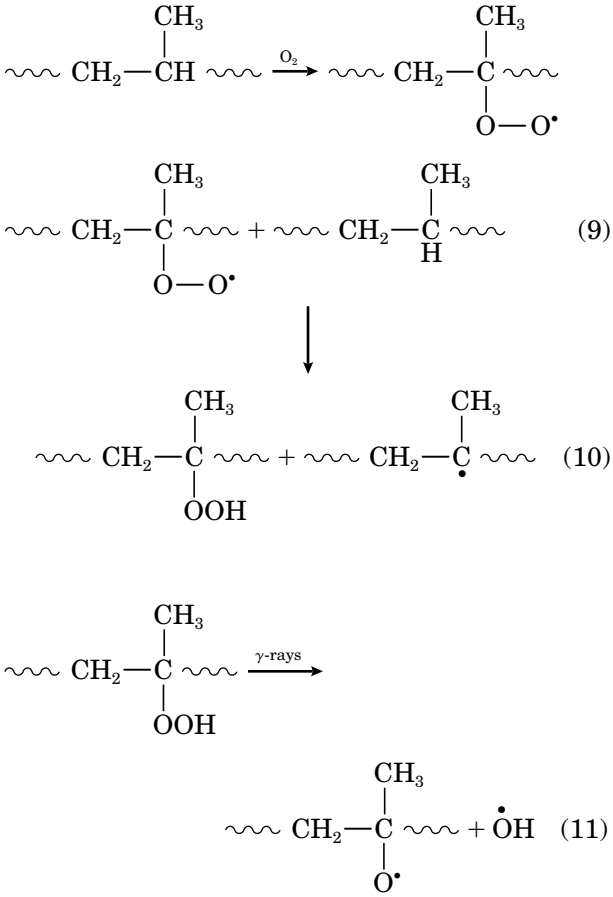
Preradiation Method



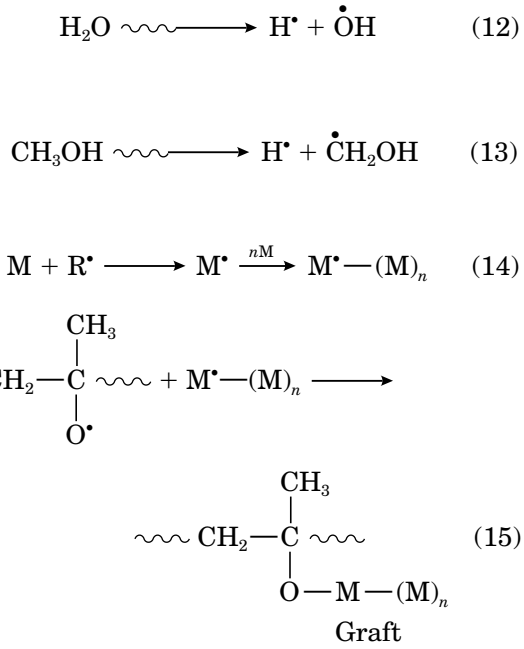


(6)–(8)

Mutual and Double Irradiation Methods



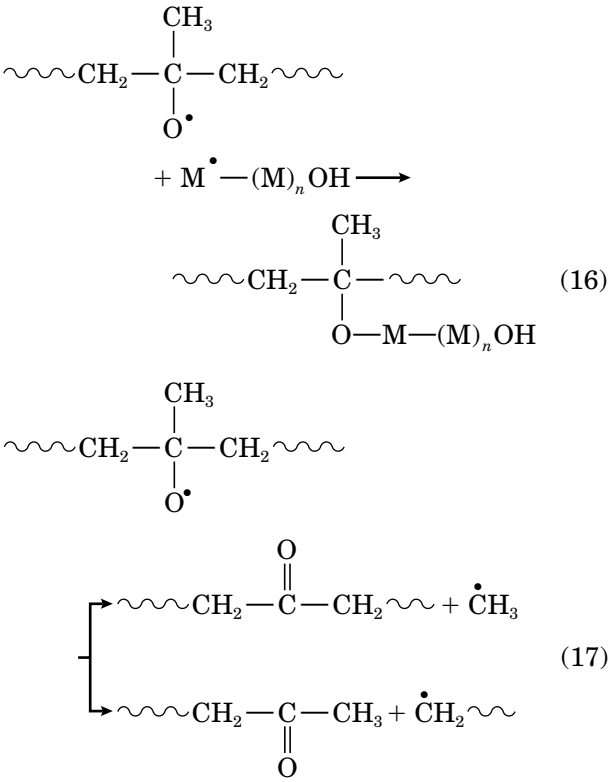
(9)–(11)



(12)–(15)

where R• represents the various radical species arising from irradiation of solvents, monomer, and backbone.

Termination



(16)–(17)

Table II Total Dye Uptake [Strength (% Concentration)] for IPP-g-Poly(MAAc)

		H_2O System 590 nm		Acetone System 590 nm		DMF-H_2O-HCOOH 590 nm		
Graft Copolymer	% Grafting	O.D.	Conc. (%)	O.D.	Conc. (%)	O.D.	Conc. (%)	Total Concentration (%)
IPP-g-Poly(MAAc)	32	0.25	0.00009	0.25	0.00009	0.28	0.00014	0.00032
IPP-g-Poly(MAAc)	92	0.32	0.000115	0.30	0.00011	0.27	0.000135	0.00036
IPP-g-Poly(MAAc)	137	0.34	0.00012	0.28	0.0001	0.28	0.00014	0.00036

O.D. = optical density; conc., concentration; DMF = Dimethyl formamide.

The extent of formation of graft copolymer is very much dependent on reaction conditions. Therefore, the percentage of grafting of MAAc has been studied as a function of different reaction parameters, and the results are explained in light of the proposed mechanism.

Effect of Total Dose

Figure 1 illustrates the plot of percentage of grafting of MAAc onto IPP by the preirradiation method as a function of total dose. It is observed from the figure that the percentage of grafting increases with increasing total dose, reaches maximum (96%), and then decreases. When grafting of MAAc is attempted by the mutual method (curve II, Fig. 2) and the double irradiation method (curve I, Fig. 2), the percentage of grafting increases with increasing total dose; after attaining a maximum value (44 and 71%, respectively), it levels off during the mutual method, whereas it decreases in the double irradiation method. The maximum percentage of grafting (96%, 44%, and 71%) of MAAc by preirradiation, mutual, and double irradiation methods is obtained at optimum total doses of 7.68, 1.28, and 1.02 Mrad, respectively. The preirradiation method affords the maximum percentage of grafting at a much higher total dose (7.68 Mrad), compared with two other methods. This is attributed to the maximum hydroperoxidation of the backbone polymer during preirradiation. This is further confirmed when grafting of MAAc is conducted by the double irradiation method. In the double irradiation method, preirradiated PP sub-

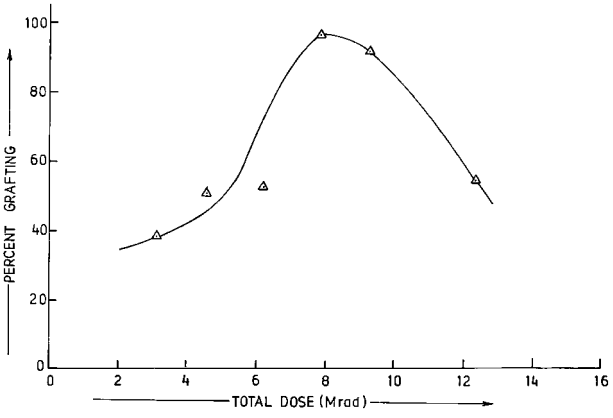


Figure 1 Effect of total dose on percent grafting of MAAc by the preirradiation method. *Preirradiation method:* IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); [MAAc] = 23 mol L^{-1}; reaction time = 180 min; reaction temperature = 100°C.

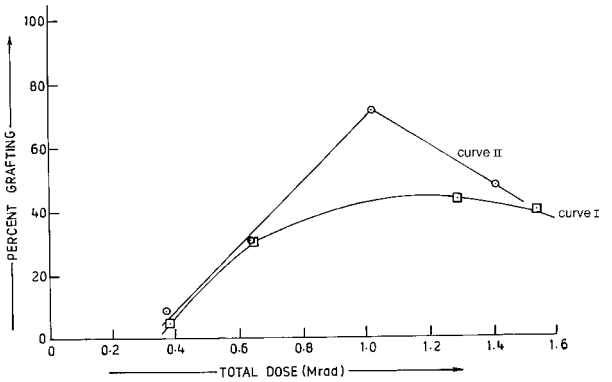


Figure 2 Effect of total dose on percent grafting of MAAc by the mutual (⊡ — ⊡) and double irradiation (⊙ — ⊙) methods. *Mutual method:* IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); [MAAc] = 35 mol L^{-1}. *Double irradiation method:* IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); total dose during preirradiation = 7.68 Mrad; [MAAc] = 35 mol L^{-1}.

strates were prepared using different total doses (Fig. 3). Maximum grafting (30%) by the double irradiation method was obtained when preirradiation of PP was conducted using 7.68 Mrad, confirming that maximum hydroperoxidation of PP occurred at 7.68 Mrad. During the mutual and double irradiation methods, the maximum percentage of grafting was obtained at a much lower total dose, compared with the preirradiation method. This is explained by the fact that, in both the mutual and double irradiation methods, irradiation is performed in the presence of a monomer, and hence more homopolymer is formed at the expense of the graft. A decrease in grafting beyond optimum total dose may be due to the chain scission or induced decomposition at higher total doses.

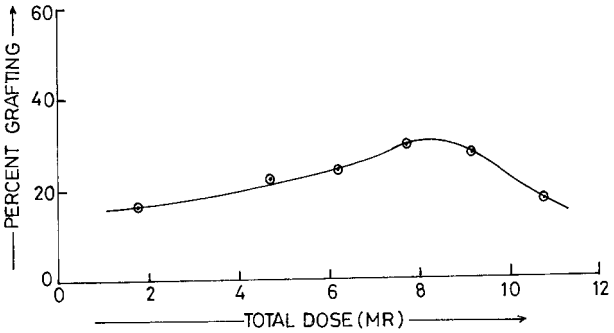
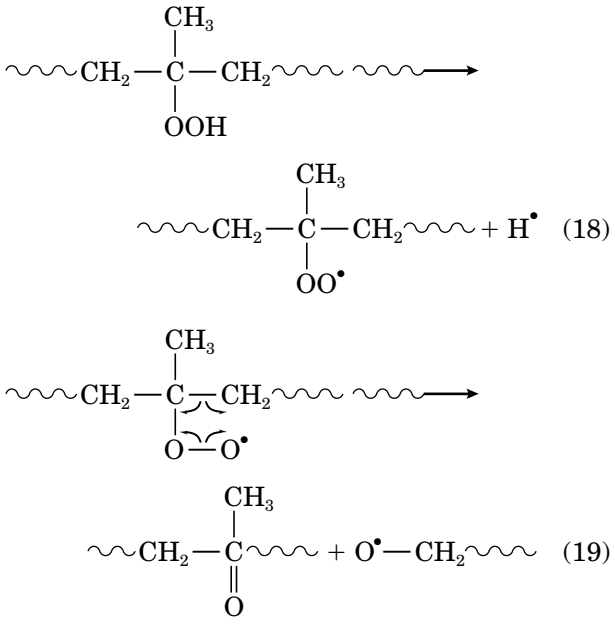
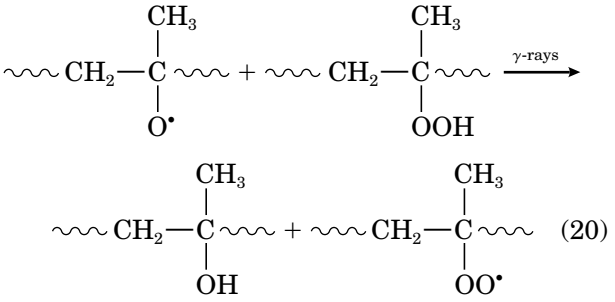


Figure 3 Effect of total dose on percent grafting of MAAc during preirradiation of the IPP fiber. *Double irradiation method:* IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); total dose during mutual irradiation = 0.64 Mrad; H_2O : CH_3OH = 5 : 5 (ml); [MAAc] = 35 mol L^{-1}.

Chain Scission



Induced Hydroperoxide Decomposition



Effect of Monomer Concentration

The percentage of grafting of MAAc by three radiation methods has been studied as a function of monomer concentration, and the results are presented in Figure 4. The maximum percentage of grafting 137%, 44%, and 71% was obtained at 41 mol L^{-1}, 35 mol L^{-1}, and 35 mol L^{-1} of methacrylic acid (MAAc), respectively, by preirradiation, mutual, and double irradiation methods. A further increase in monomer concentration beyond optimum leads to a decrease in grafting in all of the methods. An increase in grafting with increasing MAAc concentration is because MAAc, being soluble both in water and methanol, is easily accessible to the active sites. At higher monomer concentrations, homopolymer formation becomes the preferred process. Furthermore, the homopolymer, being soluble in the reaction medium, increases the viscosity of the medium, thereby restricting the mobility of the growing polymeric chains leading to a decrease in grafting.

Rate of grafting (Rg) of MAAc by all three methods has been determined as a function of total initial monomer concentration, and results are presented in Table III. It is observed from the table that the Rg of MAAc during mutual and double irradiation methods increases with increasing monomer concentration and then decreases; whereas, during the preirradiation method, Rg goes on increasing with increasing MAAc concentration. Maximum Rg (0.73, 0.127, and 0.203% min^{-1}) was obtained using 59, 47, and 35 mol L^{-1} of MAAc, respectively, in preirradiation, mutual, and double irradiation meth-

ods of grafting. The plot of log *Rg vs.* log[*M*] during grafting by the preirradiation method bears a linear relationship, and the monomer exponent value is found to be 0.2 (Fig. 5).

Effect of Reaction Time

Figure 6 represents the plot of percentage of grafting as a function of time of reaction by the preirradiation method. It is observed from Figure 6 that the percentage of grafting increases with increasing reaction time and reaches maximum (137%) within 180 min, beyond which it decreases due to self-annihilation of the growing polymeric chains.

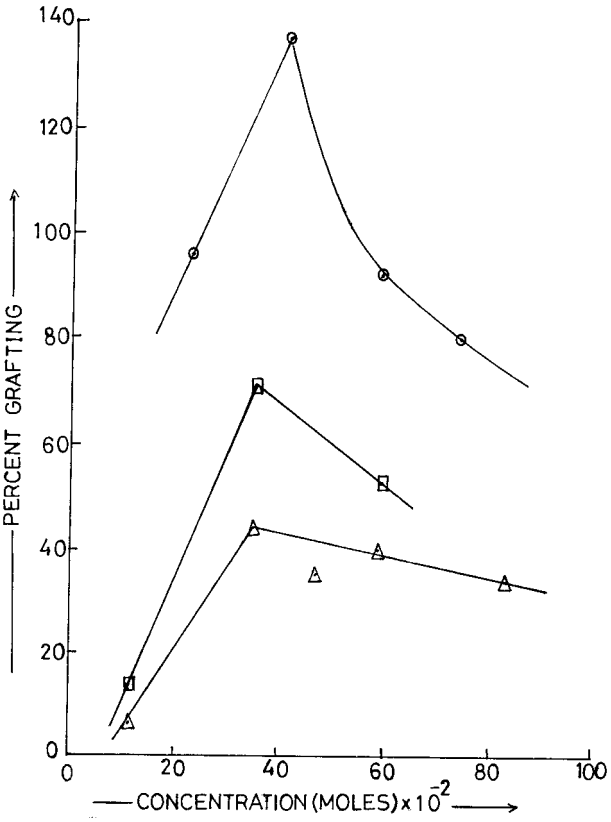


Figure 4 Effect of MAAc on percent grafting by preirradiation (⊙ — ⊙), mutual (△ — △), and double irradiation (⊡ — ⊡), methods. Preirradiation method. IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); total dose = 7.68 Mrad; reaction temperature = 100°C, reaction time = 180 min. Mutual method; IPP = 100 mg; H_2O : CH_3OH = 5 : 5 ml. Total dose = 1.25 Mrad.; Double irradiation method; IPP = 100 mg, H_2O : CH_3OH = 5 : 5 ml, total dose during preirradiation = 7.68 Mrad, total dose during mutual irradiation = 1.02 Mrad.

Table III *Rg* of MAAc as a Function Total Initial Monomer Concentration During Preirradiation, Mutual, and Double Irradiation Methods

No.	Method	[MAAc] (mol L^{-1})	*Rg* (% min^{-1})
1	Preirradiation[a]	23	0.61
		41	0.70
		59	0.73
2	Mutual[b]	35	0.116
		47	0.127
		59	0.101
3	Double irradiation[c]	11	0.055
		35	0.203
		59	0.150

[a] IPP = 100 mg; H_2O–methanol = 5 : 5 (ml); temperature = 100°C; total dose = 7.68 Mrad; dose rate = 0.128 Mrad h^{-1}.
[b] IPP = 100 mg; H_2O–methanol = 5 : 5 (ml); total dose = 1.28 Mrad; dose rate = 0.128 Mrad h^{-1}
[c] IPP = 100 mg; H_2O–methanol = 5 : 5 (ml); total dose = 1.02 Mrad; total dose for preirradiation = 7.68 Mrad; dose rate = 0.128 Mrad h^{-1}.

Effect of Temperature

The percentage of grafting of MAAc by the preirradiation method has been studied as a function of temperature, and it was observed that the percentage of grafting increased with increasing temperature, giving the maximum percentage of

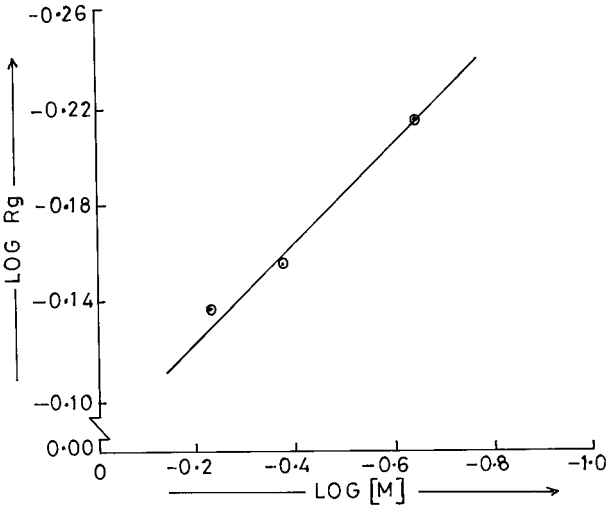


Figure 5 Plot of log *Rg vs.* log [*M*]. IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); total dose = 7.68 Mrad; reaction temperature = 100°C; [MAAc] = 41 mol L^{-1}.

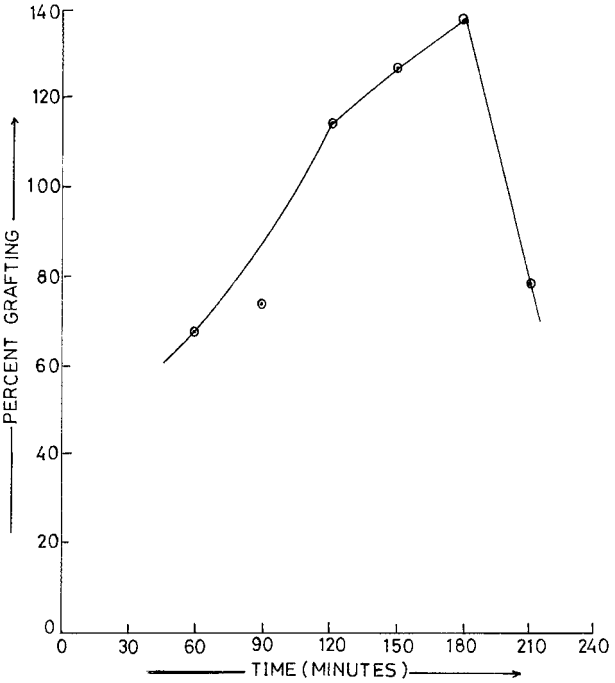


Figure 6 Effect of reaction time on percent grafting of MAAc by the preirradiation method. IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); total dose = 7.68 Mrad; [MAAc] = 41 mol L^{-1}.

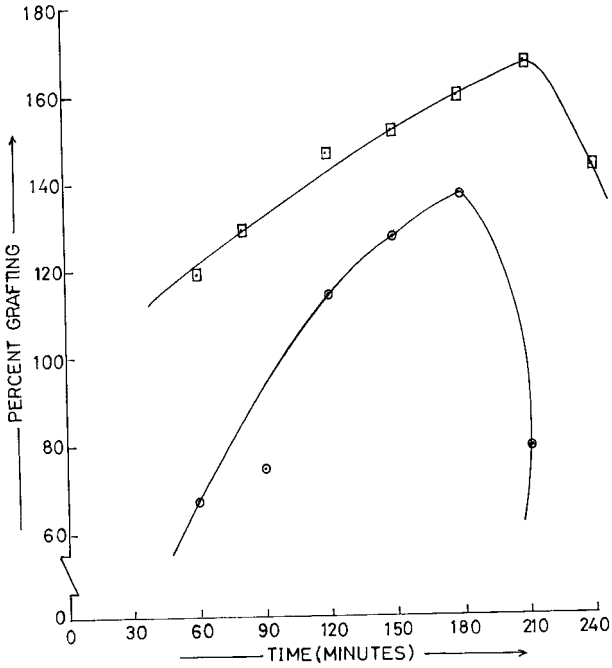


Figure 7 Percentage of grafting as a function of reaction time at 100°C (⊙ — ⊙) and 110°C (⊡ — ⊡).

grafting (167%) at 110°C. A further rise in temperature leads to a decrease in the percentage of grafting. An increase in the percentage of grafting with increasing temperature may be because at a higher temperature, mobility of the growing polymeric chains increases to produce a higher percentage of graft copolymer. A decrease in percentage of grafting beyond optimum temperature (110°C) is due to the acceleration of the various chain transfer reactions.

Rg of MAAc by the preirradiation method has been determined as a function of temperature (Fig. 7) and maximum *Rg* (0.57% min^{-1}) was obtained at 100°C, beyond which it decreases to 0.36% min^{-1} at 110°C.

Effect of Solvent

The percentage of grafting of MAAc by the preirradiation method has been studied in methanol and methanol–water solvent system, and the results are presented in Table IV. It is observed from the table that the maximum percentage of grafting (532%) was obtained in 5 ml of methanol, beyond which it decreases. The maximum percentage of grafting (137%) in the water–methanol solvent system was obtained in 10 ml of 1 : 1 (v/v) water–methanol mixture. A further increase in the amount of methanol in the water–methanol system decreases the percentage of grafting. Thus, a maximum percentage of grafting of MAAc in the water–methanol system (137%) is much less than in the methanol medium (532%). A lower percentage of grafting in the water–methanol medium may be explained on the

Table IV Effect of Solvent System (H_2O : Methanol) on Percentage of Grafting of MAAc by the Preirradiation Method

No.	H_2O : Methanol (ml)	% Grafting
1	5 : 5	137
2	3 : 7	83
3	7 : 3	119
4	0 : 5[a]	532
5	0 : 10	173
6	0 : 15[b]	74

IPP = 100 mg; temperature = 100°C; reaction time = 180 min; [MAAc] = 41 mol L^{-1}; total dose = 7.68 Mrad; dose rate = 0.128 Mrad h^{-1}.

[a] [MAAc] = 82 mol L^{-1}.

[b] [MAAc] = 27.33 mol L^{-1}.

Table V Optimum Conditions for Obtaining Maximum Percentage of Grafting of MAAc by Preirradiation, Mutual, and Double Irradiation Methods

Method	Total Dose (Mrad)	[MAAc] (mol L^{-1})	% Grafting	*Rg* (% min^{-1})
Preirradiation[a]	7.68	41	137	0.73
Mutual	1.28	35	44	0.116
Double irradiation	1.02	35	71	0.203

IPP = 100 mg; H_2O : CH_3OH = 5 : 5 (ml); dose rate = 0.128 Mrad h^{-1}; total dose for preirradiation (double irradiation) = 7.68.
[a] Temperature = 100°C; time of reaction = 180 min.

basis of the studies made by Franks and Ives[11] that, in water–alcohol mixtures, the hydrogen-bonded structure of water is lost and strong, and well-organized hydrogen bonds are formed between alcohol and water. This interaction between the two solvents may inhibit the hydrogen bond formation between the hydroperoxide groups of the backbone polymer and water. This would decrease the accessibility of monomer to the active sites leading to a decrease in the percentage of grafting. Mutual grafting of MAAc onto IPP in an aqueous medium or in a methanol medium did not afford any grafting. However, when 10 ml of 1 : 1 (v/v) of methanol–water medium was used, a maximum percentage of grafting (44%) was obtained. Another change in the ratio of the solvent system did not produce any grafting. Similar observations were made by Mukherjee and Gupta[12] during MAAc grafting onto IPP by a mutual method.

Comparison of Graft Copolymerization of MAAc onto IPP by Mutual Preirradiation and Double Irradiation Methods

In the previous discussion, optimum conditions for the maximum percentage of grafting and *Rg* of MAAc onto IPP by mutual, preirradiation, and double irradiation methods have been determined, and the results are presented in Table V. It is observed from the table that the maximum percentage of grafting (137%, 44%, and 71%) and *Rg* (0.73% min^{-1}, 0.127% min^{-1}, and 0.203% min^{-1}) were obtained for grafting of MAAc onto IPP by preirradiation, mutual, and double irradiation methods. These observations can be explained by the fact that, in the preirradiation method, grafting proceeds selectively with minimum homopolymer formation, whereas in both mutual and double irradiation methods, grafting is conducted by direct irradiation of the monomer in the presence of the backbone polymer, and hence both homopolymerization and graft copolymerization occur simultaneously leading to a decrease in the formation of the graft.

In a comparison between the double irradiation and mutual methods of grafting, it is observed that the former method affords 71% of grafting at a total dose of 1.02 Mrad (with *Rg* = 0.203% min^{-1}), whereas in the mutual method 44% of maximum grafting is obtained at a higher total dose (1.28 Mrad), with *Rg* = 0.116% min^{-1}. This is explained on the basis that, during the double irradiation method, hydroperoxidized PP is the backbone that directly provides active sites for grafting; thus, *Rg* is higher at a lower total dose, compared with the mutual method.

Thus, it may be concluded that, among the three methods of grafting using γ-radiations as source of initiation, the following order is observed toward grafting of MAAc onto isotactic IPP.

Preirradiation > Double Irradiation
> Mutual Methods.

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