Radiochemical Graft Copolymerization of Methacrylonitrile and Binary Mixture of Methacrylonitrile with 4-Vinylpyridine onto Isotactic Polypropylene Fiber

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SYNOPSIS

Graft copolymerization of methacrylonitrile (MAN) and its binary mixture with 4-vinylpyridine (4-VP) onto isotactic polypropylene (IPP) fiber has been studied in aqueous medium by the preirradiation method. Optimum conditions for obtaining the maximum percentage of grafting have been evaluated. Rate of grafting (Rg) has been determined as a function of total initial monomer concentration. The graft copolymers are characterized by IR spectroscopy, by thermogravimetric analysis, and by isolating the polymer from the graft copolymer. The effect of MAN, an acceptor monomer, on percentage of grafting of 4-VP, a donor monomer, has been discussed in the light of the mechanism proposed for grafting by the radiochemical method. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) is a highly useful thermoplastic and is broadly used as a molding resin as well as in many extruded forms including film, fiber, and monofilaments. However, it cannot be used under conditions that require high temperature and chemical interactions such as dyeing and paintability because of its low heat resistance and lack of any functionality in the polymer backbone. These drawbacks have been successfully removed by chemical modification of PP involving oxidation, chlorination, sulfonation, nitration, and various other reactions. Modification of PP has also been achieved by graft copolymerization of various vinyl monomers using chemical and radiation methods. *N*-2-Vinylpyrrolidone and acrylic acid were grafted onto PP by Heisti.[1] Garnett and Yen[2] reported the effect of acids during grafting of styrene onto PP using γ and UV radiations. Misra et al.[3-5] successfully grafted vinyl monomers onto isotactic polypropylene (IPP) fiber by the preirradiation method. Masuda and Schimizu[6] manufactured polystyrene-grafted PP particles with improved rigidity, adhesion, and printability. PP fiber grafted with acrylonitrile (AN), methyl acrylate (MA) and methyl methacrylate (MMA) by the corona discharge method showed higher dyeability to disperse and basic dyes as compared to the original fiber.[7] Chapiro and Gupta[8] were successful in preparing permselective membranes from polyethylene by incorporating polar groups by radiation-induced grafting. PP grafted with polar vinyl monomers may find applications as ion exchangers and permselective membranes. To explore the possibility of preparing ion exchangers and permselective membranes from PP, an attempt was made in the present study to graft-copolymerize methacrylonitrile and AN and a binary mixture of methacrylonitrile (MAN) and 4-vinylpyridine (4-VP) onto preirradiated IPP fiber as a function of different reaction parameters that influence grafting reactions. In earlier paper, we discussed the graft copolymerization of 4-VP and its binary mixture with AN onto preirradiated IPP fiber.[9] It would be interesting to study the effect of the methyl group in MAN on graft copolymerization of MAN and a binary mixture of MAN + 4-VP. The presence of the pendant nitrile groups and the C=N in the pyridine rings of the grafted polymethacrylonitrile Poly(MAN) and poly(4-vinylpyridine) Poly(4-VP), respectively, may improve the binding of the

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Journal of Applied Polymer Science, Vol. 51, 329-336 (1994)
 CCC 0021-8995/94/020329-08

dye molecule to the fiber. The thermal behavior of the IPP fiber is also expected to improve after graft copolymerization.

EXPERIMENTAL

Materials and Method

IPP fiber was received from the National Rayon Corp., Bombay. 4-VP was freshly distilled and the fractions boiling at 59°C (14 mmHg) were collected and used immediately. MAN was freshly distilled before use. Distilled water was used as the reaction medium in all the experiments. IPP fiber was irradiated in air from a 2100 Ci ^{60}Co γ-radiation source housed in a Gamma Chamber-900, supplied by BARC, Bombay, India, at a constant dose rate of 0.164 Mrad/h for different time periods.

Graft Copolymerization

Irradiated IPP fiber (100 mg) was suspended in a known amount of distilled water taken in a flask fitted with long reflux condenser. To it was added a definite amount of the monomer or monomer mixture [MAN/(MAN + 4-VP)] and the flask was placed in an oil bath maintained at a definite temperature. The reaction was allowed to continue for different time periods. After the reaction was over, the contents of the flask were filtered. The homopolymer, Poly(MAN), was removed by extraction with acetone while poly(4-VP) and the copolymer poly(4-VP-*co*-MAN) were removed by extraction with methanol. The graft copolymer, after removal of the homopolymer and copolymer, was dried at 50°C to constant weight.

Percentage of grafting of MAN and the binary mixture of (4-VP + MAN) was calculated from the initial increase in the weights of the original fiber in the following manner:

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

where W_0 and W_1 are the weights of the original IPP fiber and the grafted fiber after complete removal of the homopolymer by solvent extraction.

Isolation of the Graft Polymer

The Poly(MAN) and the copolymer of (4-VP + MA) i.e., poly(4-VP-*co*-MAN) chains grafted onto PP fiber were isolated by the treatment of the grafted PP fiber with a H_2O_2 solution of $CuCl_2$. The details of the method are reported elsewhere.[9]

IR Spectroscopic Analysis

The fiber sample was cut into small pieces and converted into KBr pellets. The IR spectra was run on Perkin-Elmer Model 983 spectrophotometer.

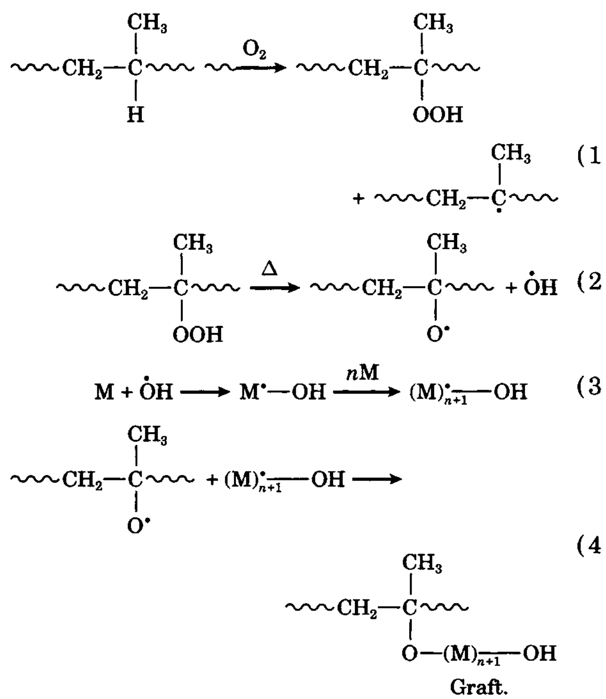
IR spectra of IPP-*g*-Poly(MAN) and IPP-*g*-poly(4-VP-*co*-MAN) showed peaks at 2230 cm^{-1} assigned to —C≡N of MAN and 1580 and 2940 cm^{-1} assigned to —C=N and —CH stretching of 4-VP, respectively. These peaks are absent in the IR spectrum of IPP fiber, which suggests that these monomers are grafted onto IPP fiber.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the IPP fiber and grafted fiber was performed using DuPont thermal analyzer in air using a heating rate of 10°C/min, and the results are presented in Figure 1.

RESULTS AND DISCUSSION

Irradiation of IPP in air is known[10] to form hydroperoxide groups on the backbone polymer because of the presence of tertiary hydrogen atoms. These hydroperoxide groups, on heating, may decompose to generate the polypropylene oxide macroradical (IPP—Ȯ) and the hydroxy radical (ȮH) that can initiate polymerization of the monomer. The growing polymeric chains thus produced can either attach to the polymer backbone to give the graft copolymer (step 4) or terminate to give the homopolymer (step 3):



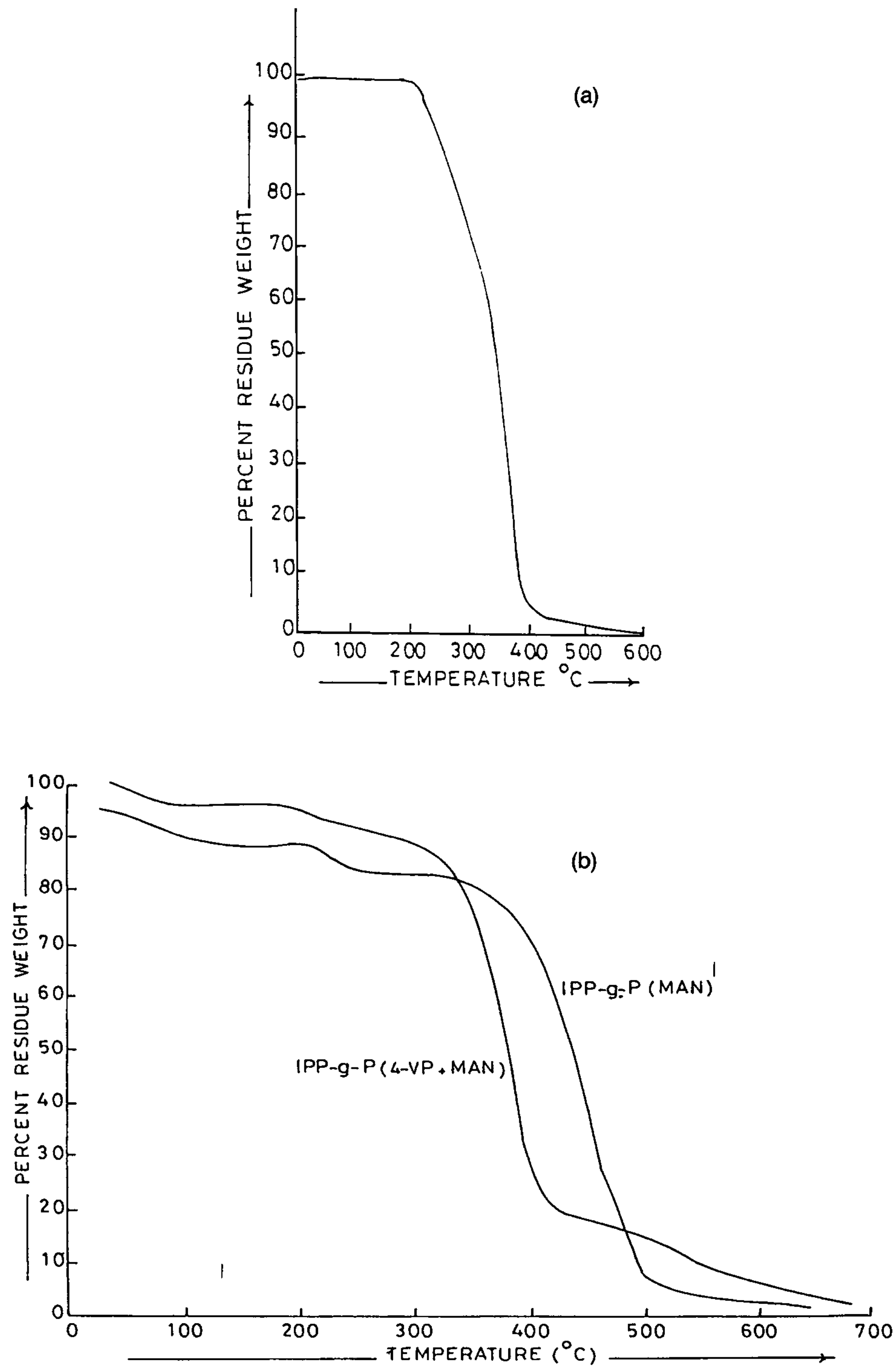


Figure 1 (a) Primary thermogram of IPP Fiber. (b) TGA of IPP-*g*-PMAN and IPP-*g*-P(4-VP + MAN).

The effect of various reaction parameters on the percentage of grafting of MAN and the binary mixture of (4-VP + MAN) has been studied and the results are discussed in the light of above-proposed mechanism.

Effect of Total Dose

Graft copolymerization of MAN and its binary mixture with 4-VP has been studied as a function of total dose, and the results are presented in Figure

2(a) and (b), respectively. The percentage of grafting of MAN [Fig. 2(a)] increases with increasing total dose, reaches maximum (139%), and then decreases. It is observed from the figure that the percentage of grafting experiences a jump at an optimum total dose of 5.71 Mrad due to the onset of Tromdorff's effect, similar to that observed during grafting of AN onto preirradiated PP by Misra et al.[3] During grafting of the binary mixture of (4-VP + MAN), the percentage of grating is found to increase with increasing total dose and then decreases [Fig. 2(b)]. The maximum percentage of grafting (265%) is obtained at a total dose of 4.89 Mrad. The optimum dose (4.89 Mrad) required for maximum grafting of the binary mixture is less than that required for the maximum grafting of MAN alone (5.71 Mrad). A similar trend was observed[9] during grafting of AN and binary mixture (4-VP + AN) where optimum total dose of 6.68 Mrad for AN was reduced to 5.26 Mrad for (4-VP + AN). This suggests that the acceptor monomers, MAN and AN, influence the grafting of donor monomer, 4-VP. Also, in the presence of less acceptor monomer, MAN, as

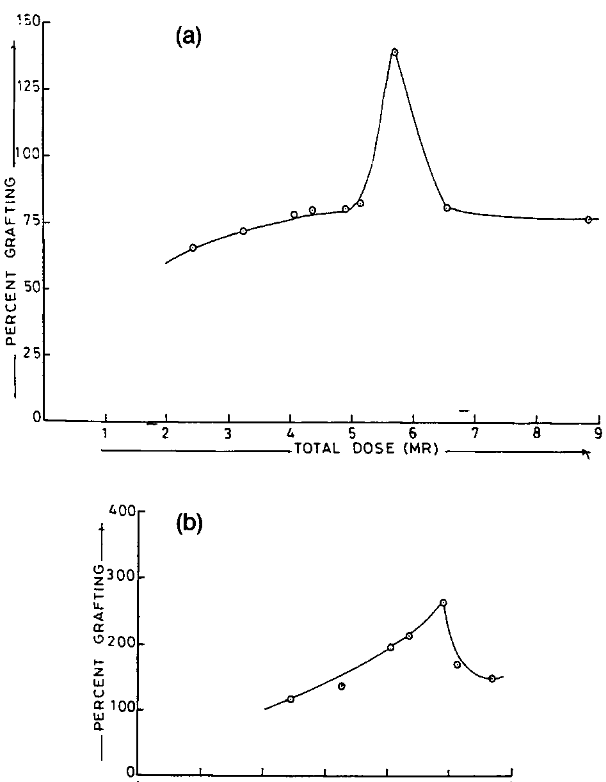


Figure 2 (a) Effect of total dose on percentage of grafting of MAN. (b) Effect of total dose on percentage of grafting of 4-VP + MAN.

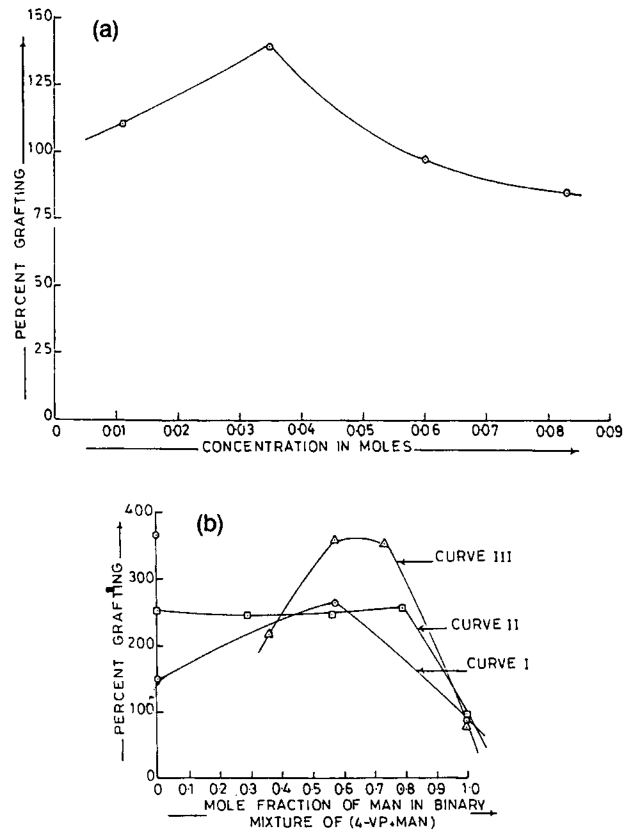


Figure 3 (a) Effect of [MAN] on percentage of grafting. (b) Effect of MAN on percentage of grafting of 4-VP in binary mixture.

compared to AN, 4-VP affords maximum grafting at a lower total optimum dose (4.89 Mrad).

Effect of Monomer Concentration

The effect of the concentration of monomer on the percentage of grafting of MAN is presented in Figure 3(a). The percentage of grafting increases with increasing concentration of MAN and produces maximum grafting (139%) at [MAN] = 3.6×10^{-1} mol and then decreases. At higher monomer concentrations, the percentage of grafting decreases, because at higher [MAN], both homopolymer formation and monomer transfer reactions [C_M at 80°C = 10.05 $\times$ 10^{-4})[11] are accelerated, leading to decrease in percentage of grafting.

Figure 3(b) represents the effect of the mole fraction of MAN on percentage of grafting of [4-VP + MAN]. It is observed from the figure that the percentage of grafting increases with increase in the mole fraction of MAN and then decreases. This pattern is observed with varying total mixed monomer concentrations of the same composition (1 : 1) (curves I, II, and III). The maximum percentage of grafting (375%) is obtained with the mole fraction of MAN in a total of 3 mL of the binary mixture (curve III). No appreciable change in the percentage of grafting is observed with increasing mole fraction of MAN in 4 mL of the binary mixture of the mixture (curve II).

An attempt has also been made to evaluate the rate of grafting (*Rg*) of MAN and the binary mixture (4-VP + MAN) as a function of total initial monomer concentration from Figure 4(a) and (b), respectively, and the values are presented in Table I. The total monomer concentration of the binary mixture is taken as the sum of total of individual concentrations of 4-VP and MAN in moles. The ratio of the monomers in the binary mixture is kept constant (1 : 1). This experiment was done to ascertain the effect of the acceptor monomer MAN on the rate of grafting of 4-VP. The rate of grafting of 4-VP by the radiation method has been reported in our earlier paper.[9] The maximum rate of grafting of 4-VP as a function of total initial monomer concentration, under optimum conditions, was reported as 6.37%/min at [4-VP] = 0.009 mol. It can be observed from the table that the maximum rate of grafting of MAN and the binary mixture (4-VP-MAN) is 0.455%/min and 2.07%/min at [MAN] = 1.2×10^{-2} mol and [4-VP + MAN] = 0.009 mol, respectively. Thus, the presence of MAN decreases the rate of grafting of 4-VP.

Effect of Reaction Time

Percentage of grafting of MAN and (4-VP + MAN) as a function of time of reaction is presented in Figure 4(a) (—⊙—⊙—) and (b) (—⊙—⊙—), respectively. It is observed from the figures that the percentage of grafting of both MAN and (4-VP + MAN) increases with increasing reaction time, producing maximum grafting of 139 and 265%, respectively, within 180 min and then decreases. The decrease in percentage of grafting beyond optimum may occur due to mutual annhilation of the growing grafted polymeric chains.

Table I Rate of Grafting (*Rg*) of MAN and 4-VP + MAN) as a Function of Total Initial Monomer Concentration

Sample No.	Monomer	[M] × 10^2 (mol)	*Rg* (%/min)
1	MAN[a]	1.2	0.455
2	MAN[a]	3.6	0.383
3	MAN[a]	5.9	0.437
4	4-VP + MAN[b]	0.9	2.07
5	4-VP + MAN[b]	2.0	0.84
6	4-VP + MAN[b]	4.1	1.14

[a] IPP = 100 mg; H_2O = 20 mL; temperature = 100°C; total dose = 5.71 Mrad.
[b] IPP = 100 mg; H_2O = 20 mL; temperature = 100°C; total dose = 4.89 Mrad.

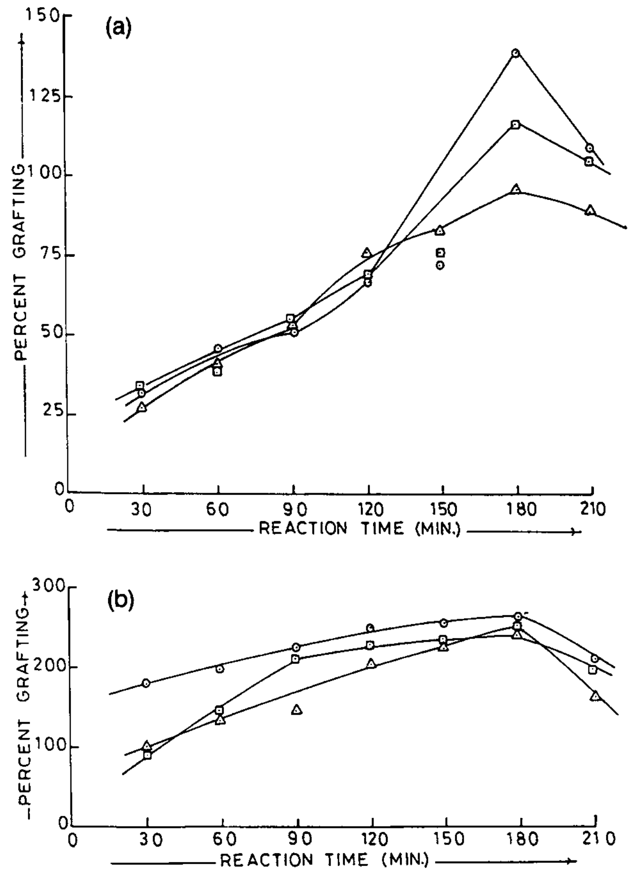


Figure 4 (a) Rate of grafting (*Rg*) as a function of initial monomer concentration of MAN: (⊡ — ⊡) 11.0×10^{-3} Mol; (⊙ — ⊙) 35.7×10^{-3} mol; (△ — △) 60.0×10^{-3} Mol. (b) Rate of grafting as a function of total initial monomer concentration of 4-VP + MAN: (⊡ — ⊡) 0.5 : 0.5; (⊙ — ⊙) 1 : 1; (△ — △) 2 : 2.

Effect of Temperature

Percentage of grafting of MAN and the binary mixture of (4-VP + MAN) has been studied as a function of reaction temperature and the results are presented in Figure 5(a) and (b), respectively. Percentage of grafting of both MAN and (4-VP + MAN) increases with increasing temperature, reaches maximum, and then decreases. MAN pro-

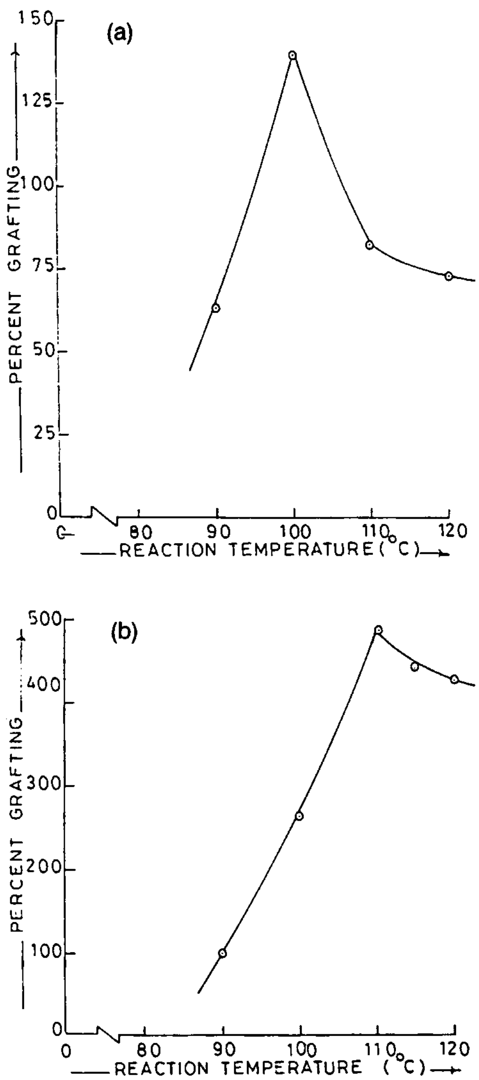


Figure 5 (a) Effect of reaction temperature on percentage of grafting of MAN. (b) Effect of reaction temperature on percentage of grafting of 4-VP + MAN.

duces maximum grafting (139%) at 100°C, whereas in the case of the binary mixture (4-VP + MAN) the maximum percentage of grafting (484%) is obtained at 110°C. A decrease in the percentage of grafting beyond optimum is due to various side reactions including monomer transfer reactions that are accelerated at higher temperatures.

Effect of Amount of Water

Figure 6(a) and (b) represent the percentage of grafting of MAN and the binary mixture (4-VP + MAN) as a function of amount of water, respectively. It is observed from Figure 6(a) that the percentage of grafting of MAN increases with increasing amount of water and reaches maximum (139%) in 20 mL of water under optimum conditions, beyond which it decreases. The maximum percentage of grafting of the binary mixture (313%) under optimum conditions is obtained using 5 mL of water, which is the same amount required for producing the maximum percentage of grafting of 4-VP also under optimum conditions. A further increase in the amount of water slightly decreases the percentage of grafting.

Thermogravimetric Analysis

The primary thermograms of IPP, IPP-*g*-MAN, and IPP-*g*-poly(4-VP-*co*-MAN) are presented in Figure 1(a) and (b). The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperatures (DT) values at ev-

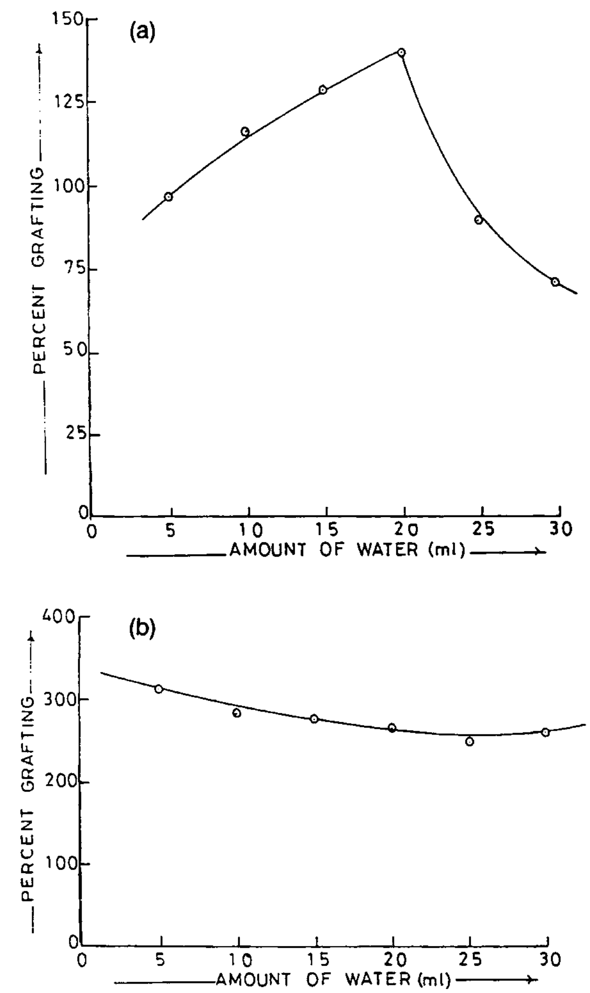


Figure 6 (a) Effect of amount of water on percentage of grafting of MAN. (b) Effect of amount of water on percentage of grafting of 4-VP + MAN.

Table II Thermogravimetric Analysis (TGA) of IPP and Grafted IPP Fibers

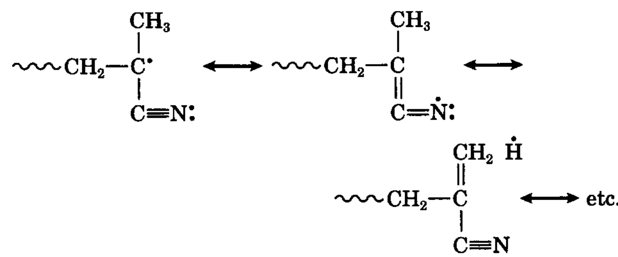
Sample	% Grafting	IDT (°C)	FDT (°C)	DT (°C) at Every 10% Weight Loss								
				10%	20%	30%	40%	50%	60%	70%	80%	90%
IPP	—	205	410	263	325	350	362	375	388	400	412	425
IPP-*g*-Poly(MAN)	95	365	495	92.5	355	400	422.5	437.5	450	457.5	475	490
IPP-*g*-Poly (4-VP-*co* + MAN)	212	325	410	275	345	365	375	382.5	392.5	400	425	550

ery 10% weight loss are presented in Table II. It is observed from the figure that the IDT and FDT values of IPP-*g*-Poly(MAN) are higher than those of IPP fiber and the residue from IPP-*g*-Poly(MAN) left at the start of final decomposition temperature is 30%, whereas for the IPP fiber, the residue left at the start of final decomposition is only 20%. Increase in IDT and FDT values show that the thermal properties of IPP fiber improve upon grafting with MAN. The IDT of IPP-*g*-poly(4-VP-*co*-MAN) is also higher than that of the original IPP fiber, but the FDT of grafted fiber (410°C) is the same as that of IPP fiber. The decomposition temperatures at every 10% weight loss of the grafted PP fiber with both monomers grafted individually and the binary monomer mixture are higher than those of IPP fiber.

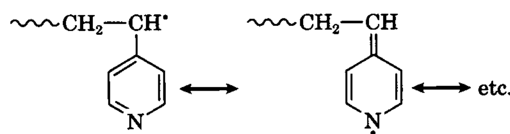
Reactivity of 4-VP and MAN

From the foregoing discussions, it is observed that under optimum conditions the maximum percentage of grafting of MAN and the binary mixture (4VP + MAN) onto preirradiated fiber is 139 and 484%, respectively. The maximum percentage of grafting (565%) of 4-VP under optimum conditions has been reported earlier.[9] This indicates that 4-VP is a more reactive monomer than is MAN toward grafting and it is also observed that the addition of MAN to 4-VP suppresses the percentage of grafting of 4-VP. This difference in reactivity of the two monomers can be explained on the basis of (i) solubility, (ii) the reactivity of the growing radical species, and (iii) monomer transfer constants. MAN has low solubility (2.57%) in water as compared to 4-VP, which is soluble in hot water. Since the reaction is carried out between 90 and 110°C, the solubility and, hence, the accessibility of 4-VP to the active sites of the backbone polymer is increased and, hence, a higher percentage of grafting of 4-VP is observed.

The stability of the growing polymeric chain radicals also affects the percentage of grafting. It is observed from the following resonance structures of the growing polymeric chains of MAN and 4-VP that the former, having more resonance stabilization than the latter, is less reactive:



Growing MAN chains



Growing 4-VP chain

Finally, MAN has a higher monomer transfer constant of the order of 10.05×10^{-4} at 80°C and some monomer is wasted in monomer transfer reactions while the monomer transfer constant of 4-VP is less ($7.0 \pm 3.2 \times 10^{-5}$ at 55°C)[12] and, consequently, 4-VP affords a higher percentage of grafting. In the binary mixture, an increasing amount of MAN is expected to decrease grafting and this is supported by experimental observation.

Financial assistance from CSIR, New Delhi, to one of the authors (R. B.) in the form of SRF is gratefully acknowledged.

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Received June 12, 1992
Accepted June 14, 1993