

Graft Copolymerization of Acrylonitrile and Its Binary Mixture with 4-Vinyl Pyridine onto Isotactic Polypropylene Powder by Preirradiation Method

INDERJEET KAUR,* RAGHUVIR BARSOLA, and B. N. MISRA

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171 005, India

SYNOPSIS

Graft copolymerization of acrylonitrile (AN) and its binary mixture with 4-vinyl pyridine (4-VP) onto isotactic polypropylene powder in aqueous medium, using γ -rays as an initiator, was studied. Optimum conditions for affording maximum percentage of grafting were evaluated. Rate of grafting (Rg) of AN and binary mixture (4-VP + AN) was determined as a function of total initial monomer concentrations. The graft copolymers were characterized by IR spectroscopy and thermogravimetric analysis. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Isotactic polypropylene (IPP) is a useful thermoplastic and has a wide range of uses such as film, fiber, molding resin, etc. However, being a non-functional polymer, IPP lacks properties that require chemical affinities such as dyeability, printability, paintability, etc. Introduction of various functional groups in the backbone polymer can, however, improve these properties. Different groups of workers¹⁻³ have reported grafting of various vinyl monomers onto IPP fiber and have observed improvement in thermal and dyeing properties. Misra and coworkers⁴⁻⁷ have successfully grafted different vinyl monomers such as acrylic acid, acrylamide, acrylonitrile (AN), 4-vinyl pyridine (4-VP) etc. onto IPP fiber by the preirradiation method. In the present communication we report on graft copolymerization of AN and a binary mixture of (4-VP + AN) onto IPP powder by the preirradiation method in order to study the effect of acceptor monomer, AN, onto percentage of grafting of donor monomer, 4-VP.

EXPERIMENTAL

Materials and Method

IPP in the form of beads was received from Indian Petrochemical Corporation Ltd., Baroda (India).

The beads were recrystallized from *p*-xylene, converted into powder, and used in all grafting reactions. 4-VP (Fluka) was used as received; AN (Fluka) was freshly distilled and the middle fraction was used. Distilled water was used as a reaction medium in all reactions.

Irradiation of IPP was carried out from a 2100 Ci Co⁶⁰ γ -ray source housed in a Gamma Chamber-900 at a constant dose rate of 0.164 Mrad/h for different time periods.

Graft Copolymerization

Irradiated IPP powder (50 mg) was suspended in a known amount of water in a reaction flask fitted with a long water condenser. To it was added an appropriate amount of monomer [AN, (4-VP + AN)] and the flask was placed in an oil bath maintained at a constant temperature between 90 and 120°C. The reaction was allowed to proceed for different time periods. After the completion of the reaction, the reaction mixture was filtered and the residue thoroughly washed with water and then extracted with appropriate solvent (acetic anhydride for polyacrylonitrile, PAN, and methanol for poly(4-VP-co-AN) to ensure complete removal of the homopolymer and copolymer. The grafted IPP was dried at 50°C until constant weight was obtained; percentage of grafting was calculated as follows:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

* To whom correspondence should be addressed.

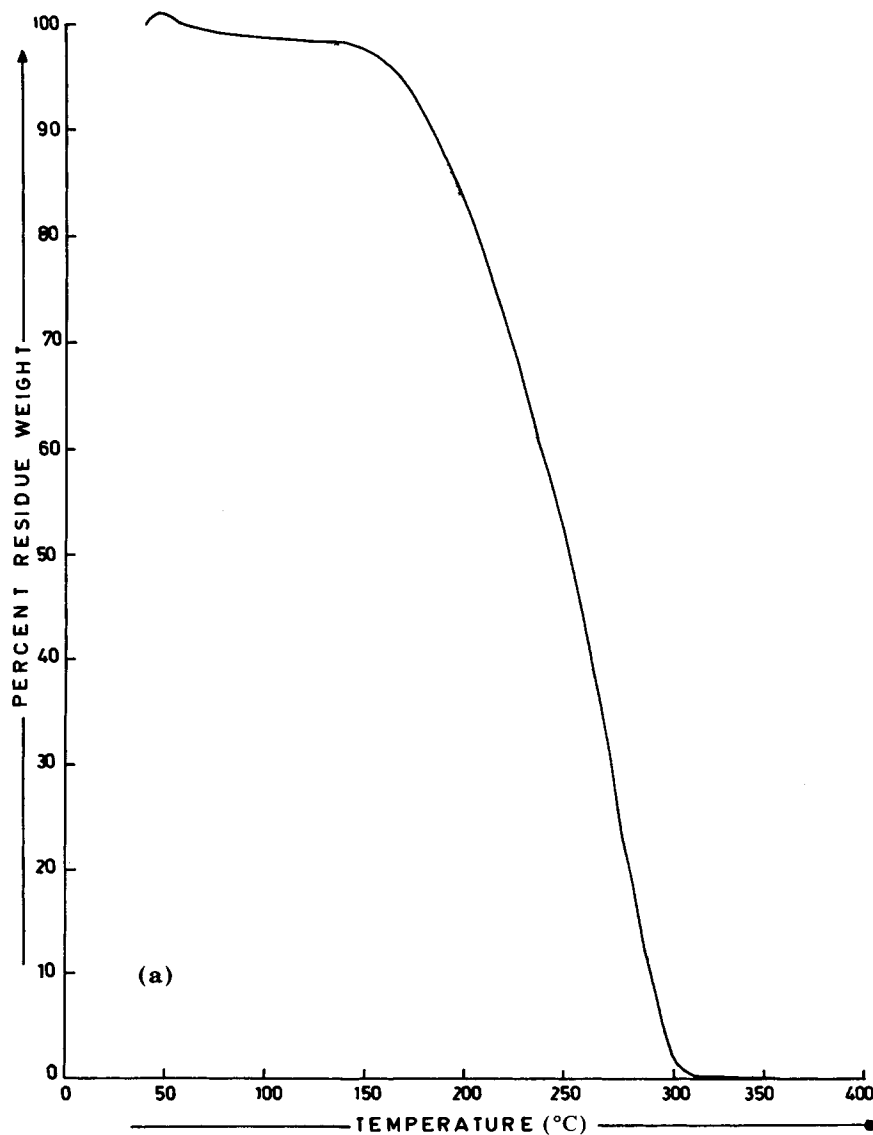


Figure 1 Primary thermogram of (a) IPP powder and of (b) IPP-*g*-poly(AN) (%*G* = 1200%) and IPP-*g*-poly(4-VP-*co*-AN) (%*G* = 286%).

where W_1 and W_2 are the weights of original IPP and grafted IPP after complete removal of the homopolymer and copolymer, respectively.

Evidence of Grafting

IR spectra of IPP-*g*-PAN and IPP-*g*-poly(4-VP-*co*-AN) showed peaks at 2260 cm^{-1} due to $\text{—C}\equiv\text{N}$ of PAN; 1580 cm^{-1} due to $\text{—C}=\text{N}$ of pyridine ring; and 2940 cm^{-1} due to —CH stretching of pyridine indicating that the grafted polymer is attached to the backbone polymer by a covalent bond.

Solvent Extraction

A physical mixture of IPP and PAN was prepared by mixing IPP in a solution of PAN in acetic an-

hydride. The mixture was stirred thoroughly with acetic anhydride and filtered. The residue was then extracted with acetic anhydride and dried. IR spectrum of the residue did not show any peak due to $\text{—C}\equiv\text{N}$ indicating that acetic anhydride completely removes the homopolymer (PAN) from the mixture. A similar experiment was performed for the removal of poly(4-VP-*co*-AN) from the physical mixture of IPP and poly(4-VP-*co*-AN) using methanol as a solvent.

Isolation of Grafted Polymer

Grafted polymeric chains [PAN and poly(4-VP-*co*-AN)] were separated from the respective graft copolymers by the method reported earlier.⁷

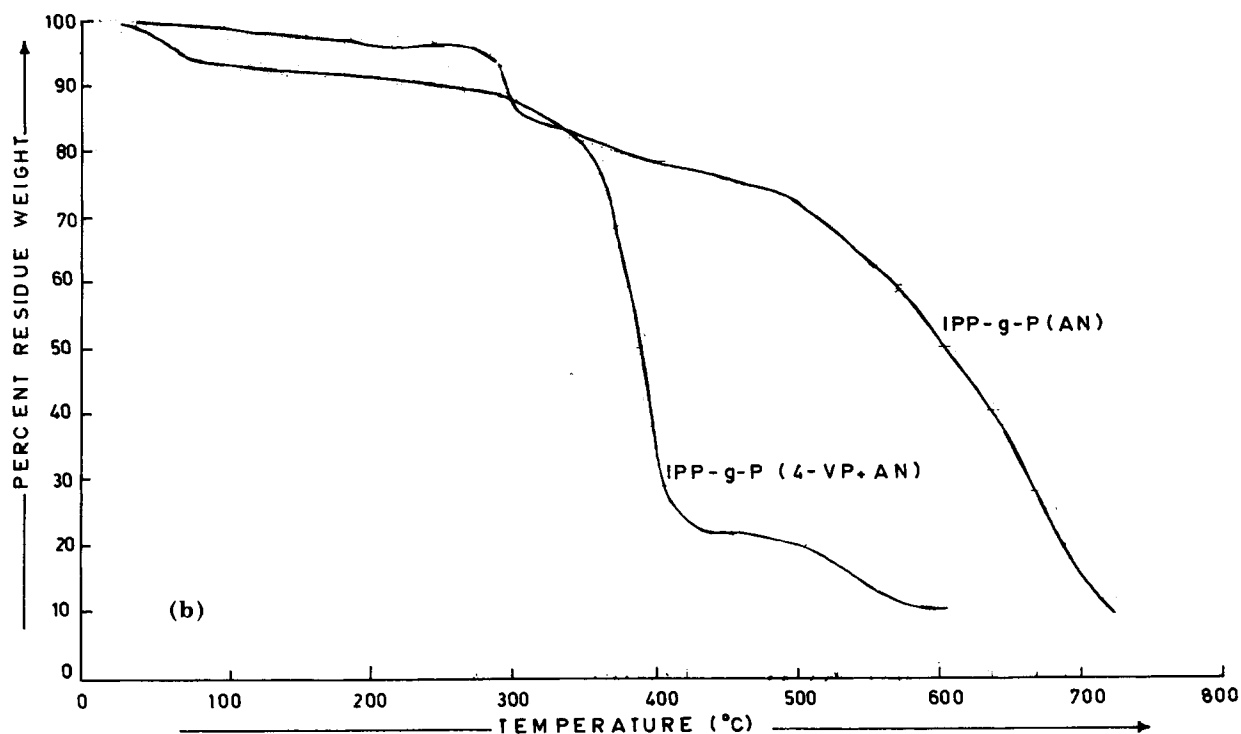


Figure 1 (Continued from the previous page)

Thermogravimetric Analysis

The primary thermograms of IPP [IPP-*g*-PAN, and IPP-*g*-poly(4-VP-co-AN)] are presented in Figure 1(a) and 1(b), respectively. It is observed from the figure that the initial decomposition temperature (IDT) (165°C) and final decomposition temperature (FDT) (307.5°C) of IPP are much lower than those of IPP-*g*-PAN (272.1 and 720.7°C) and IPP-*g*-poly(4-VP-co-AN) (300 and 420.7°C, respectively). The decomposition temperature (DT) at every 10% weight loss is also higher for the grafted samples than unmodified IPP powder. The IDT, FDT, and DT values at every 10% weight loss are presented in Table I. It is further observed that the IDT of IPP-*g*-poly(4-VP-co-AN) is higher than that of IPP-*g*-PAN; but the FDT and DT values are much lower than those of IPP-*g*-PAN suggesting that AN im-

parts better thermal properties than the binary mixture of (4-VP + AN).

RESULTS AND DISCUSSION

Irradiation of IPP powder leads to the formation of hydroperoxide groups on the polymeric backbone. These groups, on decomposition, form polymeric macroradical (IPP \dot{O}) where grafting of various vinyl monomers can take place. The detailed mechanism for radiation-induced graft copolymerization of vinyl monomers onto IPP was reported earlier.^{4,5}

Percentage of grafting of AN and the binary mixture (4-VP + AN) has been studied as a function of various reaction parameters and the optimum conditions for affording maximum percentage of graft-

Table I Thermogravimetric Analysis of IPP and Grafted IPP Powder

Sample	Percentage of Grafting	IDT (°C)	FDT (°C)	DT (°C) at Every 10% Wt Loss								
				10	20	30	40	50	60	70	80	90
IPP	—	165	307.5	182.5	205	225	237.5	252.5	265	275	285	295
IPP- <i>g</i> -PAN	1200	272.1	720.7	279.6	400	520.6	572.1	600	637.7	669.1	689.7	720.7
IPP- <i>g</i> -poly(4-VP-co-AN)	286	300	420.7	272.1	358.6	372.4	382.4	391.8	400	408.2	510.3	

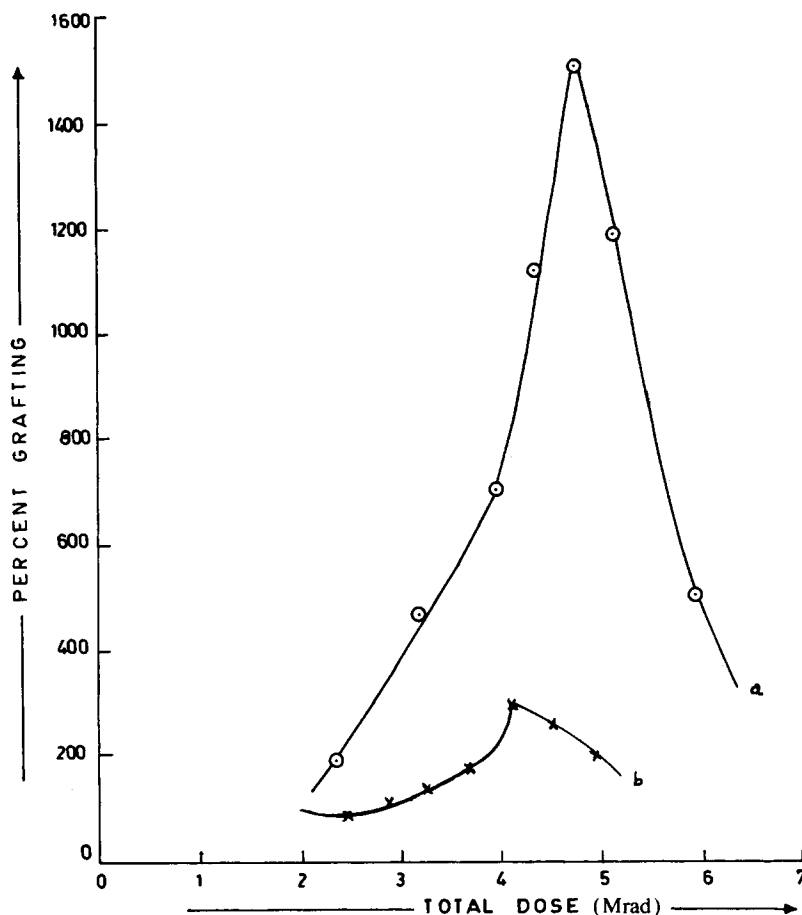


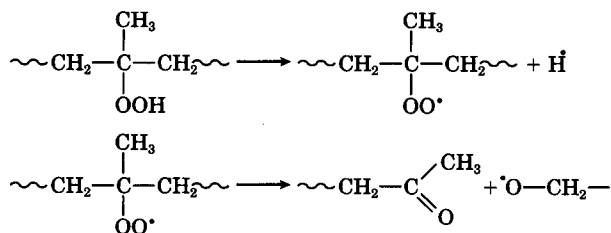
Figure 2 Curve a: IPP = 50 mg; dose rate = 0.164 Mrad/h; water = 10 mL; [AN] = 4.5×10^{-2} mol; reaction temperature = 100°C ; reaction time = 180 min. Curve b: IPP = 50 mg; dose rate = 0.164 Mrad/h; water = 10 mL; [4-VP + AN] = 2.4×10^{-2} mol; reaction temperature = 100°C ; reaction time = 180 min.

ing have been evaluated. The results are compared with those of the graft copolymerization of AN and (4-VP + AN) onto isotactic PP fiber.

Effect of Total Dose

Percentage of grafting of AN and its binary mixture with 4-VP as a function of total dose is presented in Figure 2 (curves a, b, respectively). It is observed that percentage of grafting of both AN and (4-VP + AN) increases with increase in total dose, reaches maximum (1500 and 295%) at a total dose of 4.75 and 4.08 Mrad, respectively, and then decreases. The tremendous increase in percentage of grafting of AN is attributed to the occurrence of the gel effect. These results indicate that there is a critical total dose at which maximum hydroperoxidation occurs leading to an increase in percentage of grafting. The decrease in percentage of grafting beyond optimum total dose

may be attributed to the fact that at higher doses, chain degradation of peroxidized IPP may occur in the following manner:



Comparison of these results with those of graft copolymerization of 4-VP and (4-VP + AN) onto IPP fiber reported earlier⁷ shows that AN produces a much higher percentage of grafting with IPP powder (1500% at 4.75 Mrad) than when grafted onto IPP fiber (814% at 5.15 Mrad). The percentage of

grafting of (4-VP + AN) onto IPP powder is less (295% at 4.08 Mrad) than in case of grafting onto IPP fiber (803% at 5.26 Mrad). Maximum percentage of grafting at a much lower total dose in the case of IPP powder can be explained by assuming that the powdered form of recrystallized IPP beads provides a larger surface area as compared to IPP fiber, which in turn helps in effecting maximum hydroperoxidation in the former case at a much lower total dose. Also the accessibility of the monomer to the active sites on the powdered form of IPP-OOH is greatly enhanced resulting in a higher percentage of grafting.

Effect of Monomer Concentration

Effect of concentration of AN on percentage of grafting at optimum total dose is presented in Figure 3 (curve a). It is observed that with a small increase

in concentration of AN, percentage of grafting increases suddenly from 10 to 1500% where a probable Tromdorff's effect is operating. Maximum percentage of grafting is obtained at $[AN] = 4.5 \times 10^{-2}$ mol beyond which it decreases. Monomer transfer constant⁸ (C_M at $60^\circ\text{C} = 0.26 \times 10^{-4}$) for AN and polymer transfer constant⁹ (C_p at $60^\circ\text{C} = 3.5 \times 10^{-4}$) for PAN being quite high, termination of the growing polymeric chains are accelerated resulting in decreased percentage of grafting at higher monomer concentrations. Figure 3 (curve b) represents the effect of total monomer concentration of the binary mixture (4-VP + AN) on percentage of grafting. Total monomer concentration is taken as the sum total of the individual monomer concentrations in moles in the binary mixture. Maximum percentage of grafting (290%) of the binary mixture is obtained at $[4\text{-VP} + \text{AN}] = 2.4 \times 10^{-2}$ mol beyond which it decreases.

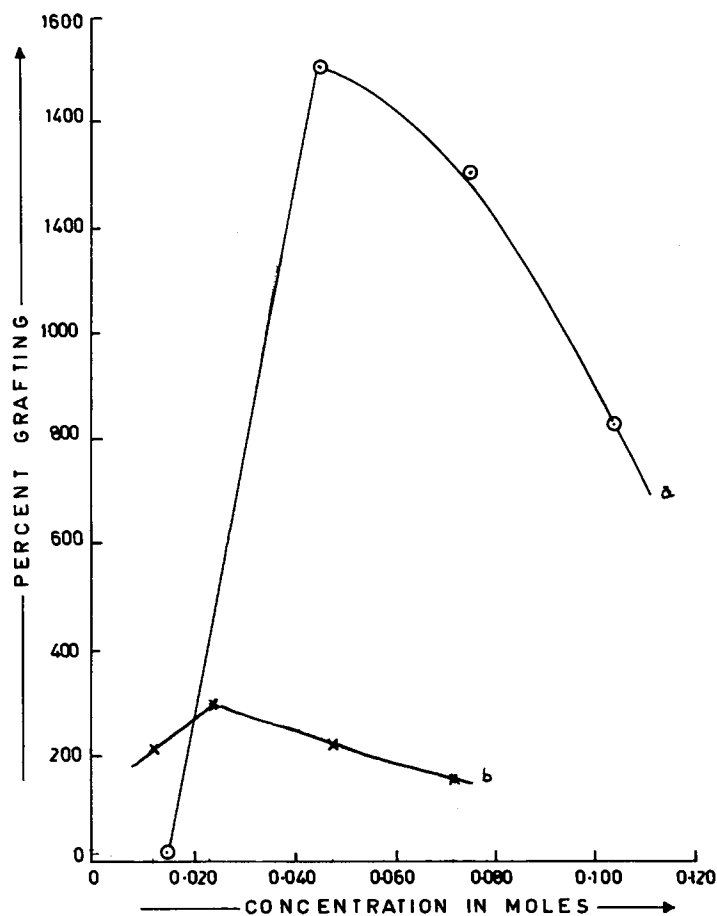


Figure 3 Curve a: IPP = 50 mg; total dose = 4.75 Mrad; water = 10 mL; reaction temperature = 100°C ; reaction time = 180 min. Curve b: IPP = 50 mg; total dose = 4.08 Mrad; water = 10 mL; reaction temperature = 100°C ; reaction time = 180 min.

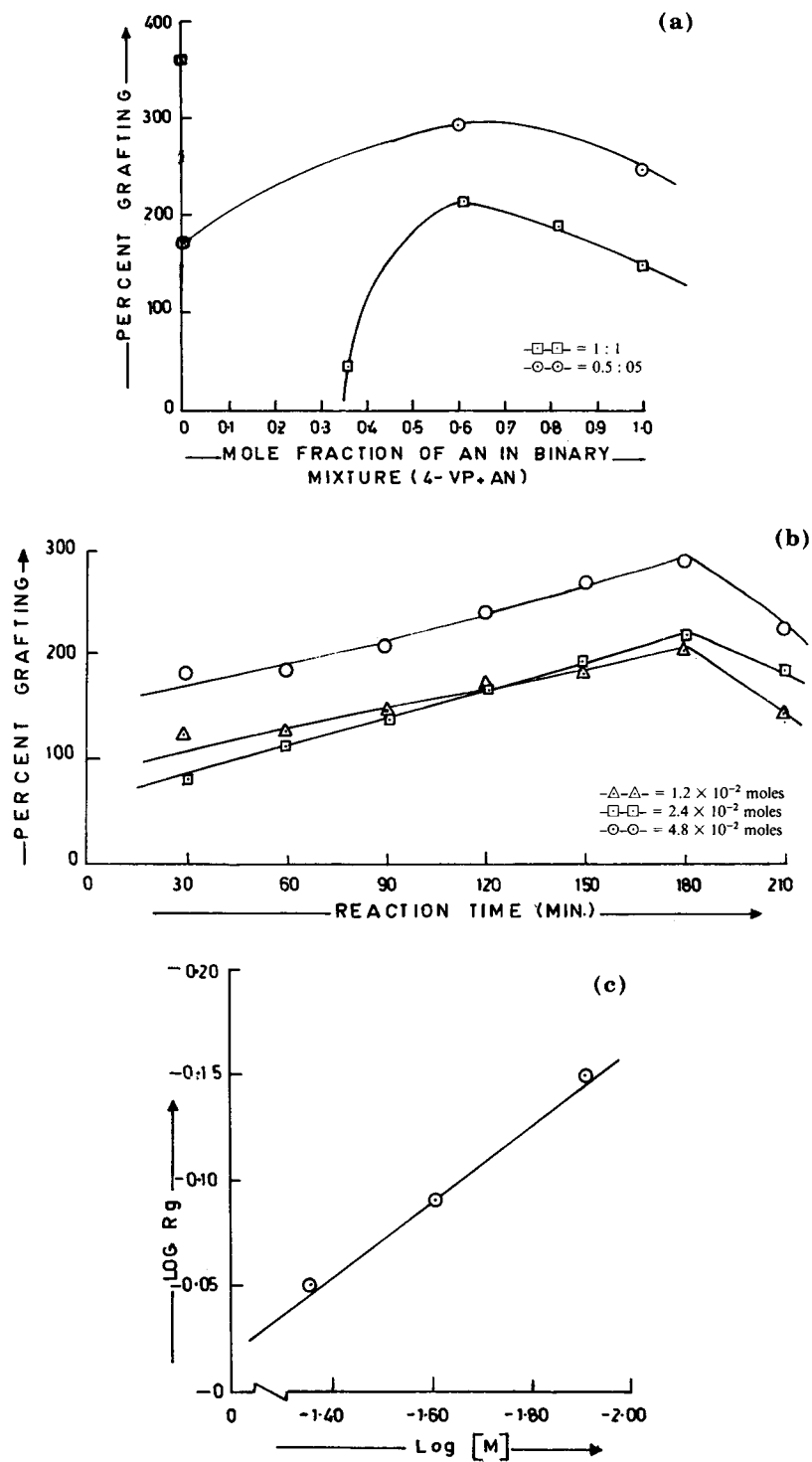


Figure 4 (a) IPP = 50 mg; total dose = 4.08 Mrad; water = 10 mL; reaction temperature = 100°C; reaction time = 180 min. (b) IPP = 50 mg; total dose = 4.08 Mrad; water = 10 mL; reaction temperature = 100°C. (c) IPP = 50 mg; total dose = 3.94 Mrad; water = 10 mL; reaction temperature = 100°C.

Table II Rate of Grafting (Rg) of (4-VP + AN) and AN as a Function of Total Initial Monomer Concentration

Monomer	Total Dose (Mrad)	[M] (mol)	Rg (%/min)
(4-VP + AN)	4.08	1.2×10^{-2}	0.70
(4-VP + AN)	4.08	2.4×10^{-2}	0.80
(4-VP + AN)	4.08	4.8×10^{-2}	0.885
AN	4.75	4.5×10^{-2}	3.5

Reaction conditions: IPP = 50 mg; water = 10 mL; reaction temperature = 100°C; reaction time = 180 min.

A plot of percentage of grafting of the binary mixture against mole fraction of AN [Fig. 4(a)] reveals that the percentage of grafting of 4-VP increases with an increase in mole fraction of AN and then decreases. Maximum grafting of binary mixture

(290%) has been found to be less than those of the individual monomers, AN (1500%) (Fig. 3, curve a) and 4-VP (360%) thus indicating that the addition of AN, an acceptor monomer, decreases the percentage of grafting of donor monomer 4-VP. However, the opposite has been observed during the grafting of these monomers onto IPP fiber,⁷ where percentage of grafting of 4-VP increased from 365 to 803% in the binary mixture of (4-VP + AN). This anomalous behavior may be explained by the fact that some poly(4-VP) produced during grafting, being soluble in water, raises the viscosity of the medium. This effect combined with the pronounced gelling effect of AN during grafting onto IPP powder would decrease the percentage of grafting of the binary mixture significantly.

Rate of grafting (Rg) of the binary mixture (4-VP + AN) [Fig. 4(b)] as a function of total initiator monomer concentration has been determined and

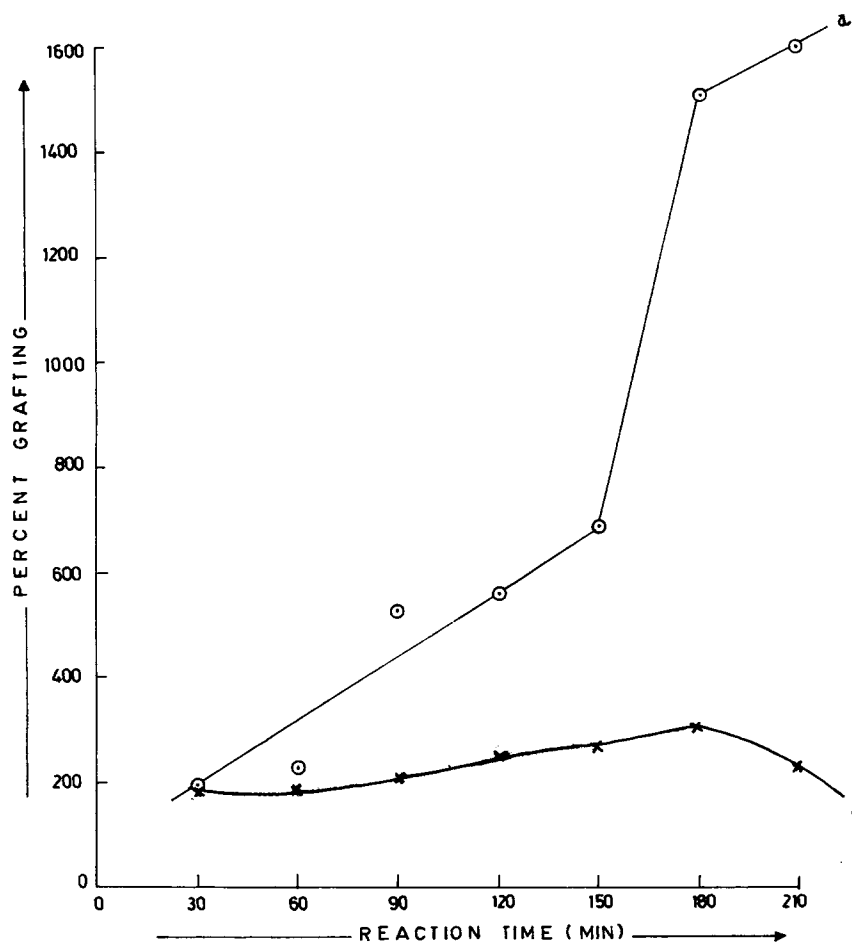


Figure 5 Curve a: IPP = 50 mg; total dose = 4.75 Mrad; water = 10 mL; [AN] = 4.5×10^{-2} mol; reaction temperature = 100°C. Curve b: IPP = 50 mg; total dose = 4.08 Mrad; water = 10 mL; [4-VP + AN] = 2.4×10^{-2} mol; reaction temperature = 100°C.

the results are presented in Table II. A plot of $\log R_g$ vs. \log total initial monomer concentration [Fig. 4(c)] shows that the rate of grafting is dependent on the 0.7 power of (4-VP + AN). Maximum rate of grafting of the binary mixture (4-VP + AN) (0.885%/min) is obtained at $[4\text{-VP} + \text{AN}] = 4.8 \times 10^{-2}$ mol. Rate of grafting of AN (3.5%/min) evaluated from the single monomer concentration (Fig. 5, curve a) is not correct because AN shows a pronounced gel effect with a small change in the concentration.

Effect of Reaction Time

Figure 5 (curves a and b) show the plots of percentage of grafting of AN and (4-VP + AN), respectively, as a function of reaction time. Percentage of grafting of AN (Fig. 5, curve a) increases steadily with increasing reaction time up to 150 min and

then shows a sudden jump with a further increase in reaction time that may be due to autoacceleration. However, percentage of grafting of the binary mixture (Fig. 5, curve b) increases steadily with increasing reaction time giving the maximum (290%) within 180 min and then decreases. This may indicate that within 180 min all the active sites are exhausted and a further increase in reaction time would preferentially lead to homopolymer formation.

Effect of Temperature

Effect of temperature on percentage of grafting of AN and (4-VP + AN) is presented in Figure 6 (curves a and b), respectively. Percentage of grafting of AN (Fig. 6, curve a) increases sharply with an increase in temperature giving a maximum of 1500% at 100°C. A further increase in temperature leads to a decrease in grafting percentage that may be due

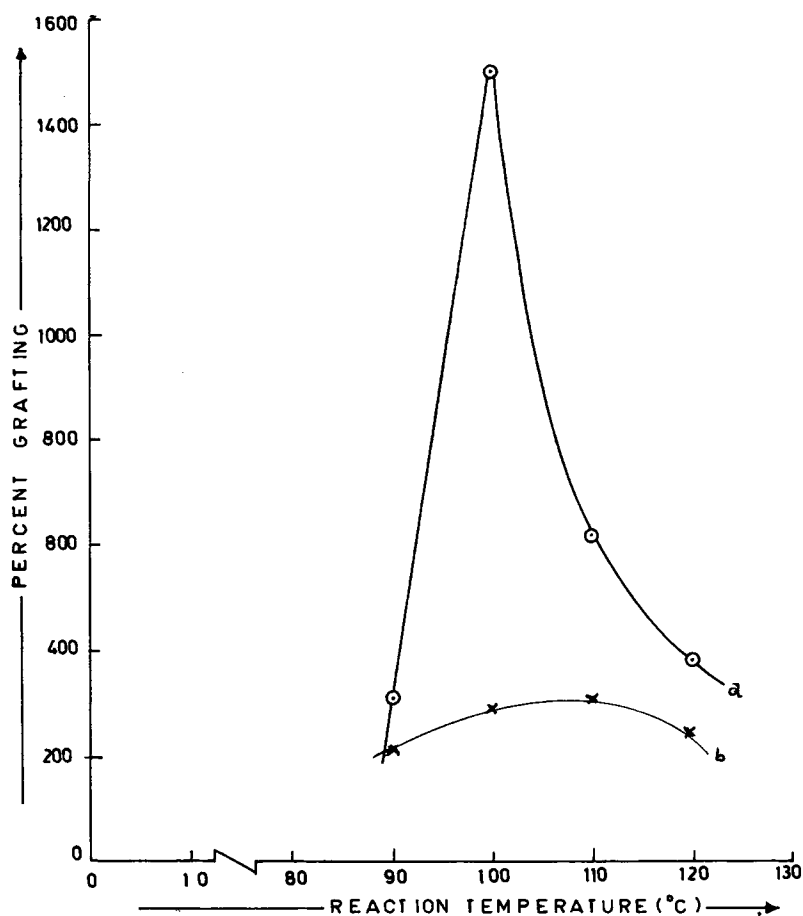


Figure 6 Curve a: IPP = 50 mg; total dose = 3.94 Mrad; water = 10 mL; $[\text{AN}] = 4.5 \times 10^{-2}$ mol; reaction time = 180 min. Curve b: IPP = 50 mg; total dose = 4.08 Mrad; water = 10 mL; $[4\text{-VP} + \text{AN}] = 2.4 \times 10^{-2}$ mol; reaction time = 180 min.

to the increase in chain transfer as well as various other wastage reactions. The effect of temperature on percentage of grafting of the binary mixture (Fig. 6, curve b) follows the same trend with the difference that there is no sharp increase in grafting percentage with an increase in temperature.

Effect of Amount of Water

Percentage of grafting of AN and (4-VP + AN) as a function of the amount of water has been determined. Maximum percentage of grafting of AN (1630%) along with the occurrence of gelling is obtained using 5 mL of water, beyond which there is a sharp decrease in grafting percentage with the increasing amount of water. In the case of grafting of AN onto IPP fiber,⁴ maximum percentage of grafting (814%) is obtained using 3 mL of water. These results suggest that a small amount of water is required for producing maximum percentage of grafting. In the case of the binary mixture however, there is an increase in percentage of grafting with the increasing amount of water giving maximum (290%) with 10 mL of water. A further increase in the amount of water leads to a decrease in grafting.

R. B. is grateful to CSIR, New Delhi, for providing financial assistance.

REFERENCES

1. C. H. Ang, J. L. Garnett, R. Levot, M. A. Long, and N. T. Yen, *J. Polym. Sci. Lett. Ed.*, **18**, 471 (1980).
2. A. M. Nabieva, U. N. Musaev, Sh. A. Kurbanov, A. V. Veasov, and B. L. Tsetlin, *Izve Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, **27**, 235 (1984).
3. I. Noh, C. H. Yoon, and I. I. J. Hwang, *Nonmunjip-Sanop Kwahak Kisul Yonguso*, **7**, 99 (1980).
4. B. N. Misra, D. S. Sood, and I. K. Mehta, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1749 (1985).
5. I. K. Mehta, D. S. Sood, and B. N. Misra, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 53 (1989).
6. I. K. Mehta, S. Kumar, G. S. Chauhan, and B. N. Misra, *J. Appl. Polym. Sci.*, **41**, 1171 (1990).
7. I. Kaur and R. Barsola, *J. Appl. Polym. Sci.*, **41**, 2067 (1990).
8. S. K. Das, S. R. Chatterjee, and S. R. Palit, *Proc. Roy. Soc., Ser. A227*, 252 (1955).
9. G. E. Ham, *J. Polym. Sci.*, **21**, 337 (1956).

Received October 25, 1993

Accepted September 6, 1994