Grafting onto Polypropylene. V. Graft Copolymerization of 4-Vinyl Pyridine and Binary Mixture of 4-Vinyl Pyridine with Acrylonitrile by Preirradiation Method

INDERJEET KAUR and RAGHUVIR BARSOLA, *Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171005, India*

Synopsis

Radiation-induced graft copolymerization of 4-vinyl pyridine (4-VP) and its binary mixture with acrylonitrile (AN) onto isotactic polypropylene has been studied in aqueous medium. Percentage of grafting has been studied as a function of different reaction parameters and the optimum conditions for affording maximum percentage of grafting have been evaluated. It was observed that there exists an optimum composition of the binary mixture at which percentage of grafting is maximum. The maximum percentage of grafting is obtained at the total monomer concentration of [AN + 4VP] = 0.009 moles. The graft copolymers were characterized by IR spectroscopic methods. An attempt has been made to discuss the effect of acceptor monomer (AN) on percentage of grafting of donor monomer (4-VP).

INTRODUCTION

Polypropylene fiber is hydrophobic, resistant to chemicals at or near ambient temperature and is stable to air and sunlight. This inertness excludes its application where chemical affinities or penetration of components is necessary, for example, dyeing of fibers, printing of films, paintability, adhesion, etc. Due to its low heat resistance it cannot be used under high-temperature conditions. However, these drawbacks can be overcome by suitably modifying polypropylene by incorporating appropriate functional groups.

Canterino[1] grafted a mixture of acrylate monomers onto polypropylene using benzoyl peroxide as radical initiator. 4-Vinyl pyridine was grafted onto isotactic polypropylene using trihexylboron in benzene by Kirshenbaum and Stanley,[2] the product containing 13.8% grafted poly(4-VP). Photografting of methacrylic acid and acrylamide using benzophenone as photosensitizer has been attempted by Gao et al.[3] High yields of polypropylene graft copolymer during photografting with 4-vinyl pyridine were reported using biacetyl and benzoin ethyl ether as photosensitizers.[4] Nabieva et al.[5] grafted 4-vinyl pyridine radio-chemically onto polypropylene material to yield graft copolymer with total ion-exchange capacity of 4.0–6.6 meq/g. Misra et al.[6] have successfully grafted acrylonitrile onto preirradiated isotactic polypropylene. Effect of other solvents on percentage of grafting of acrylonitrile has also been studied. In the present study, we report on the grafting of 4-vinyl pyridine and its mixture with acrylonitrile onto preirradiated polypropylene fiber.

Journal of Applied Polymer Science, Vol. 41, 2067–2076 (1990)
© 1990 John Wiley & Sons, Inc. CCC 0021-8995/90/9-102067-10$04.00

EXPERIMENTAL

Materials and Methods

Isotactic polypropylene (IPP) was received from National Rayon Corporation, Bombay, in the fiber form. 4-Vinyl pyridine (4-VP) (Fluka) was used as received. Acrylonitrile (AN) was distilled before use. In all experiments distilled water was used.

Isotactic polypropylene fiber was irradiated in air from a 2100 $CiCo^{60}$ source at a constant dose rate of 0.20 MR/h for different time periods.

Graft Copolymerization Method

Irradiated IPP (100 mg) was taken in a flask and to it was added definite amount of water followed by a known volume of monomer [4-VP/(4VP + AN)]. The flask was placed in an oil bath maintained at 100°C. A long water cooled condenser was attached to the flask. The reaction was allowed to continue for different time periods. After the completion of reaction, the mixture was filtered and the residue thoroughly washed with water and finally extracted with methanol to ensure complete removal of homopolymer [poly(4-VP)/poly(4VP-Co-AN)]. The grafted fiber was dried at 50°C until constant weight was obtained. Percentage of grafting was calculated from the initial increase in weight of the original fiber as

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

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

Evidence of Grafting

IR spectra of IPP-*g*-poly(4-VP) and IPP-*g*-poly(4-VP-Co-AN) showed peaks at 1580 cm^{-1} and 2940 cm^{-1} assigned to $-C=N$ and $-CH$ stretching of vinyl pyridine and 2260 cm^{-1} assigned to $-C\equiv N$ of acrylonitrile. These peaks were absent in the IR spectrum of IPP.

Separation of Graft From the IPP-g-Poly(4VP) and IPP-g-Poly(4VP-Co-PAN)

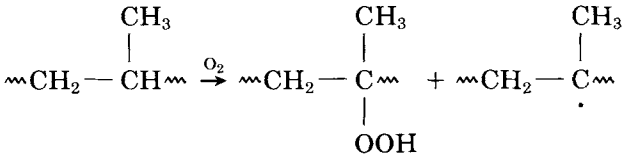
The grafted poly(4-vinyl pyridine) and poly[4VP-co-AN] chains were separated from the graft copolymer by the method reported for separating grafted poly(styrene) chains from polyethylene oxide-g-poly(sty).[7]

The grafted sample (500 mg) was suspended in a solution of 0.02 g $CuCl_2$ in 50 mL of 30% hydrogen peroxide and kept at room temperature for 2 days and filtered. The residue was dried and weighed. Quantitative amount of IPP fiber was isolated and identified by IR spectroscopy. The filtrate was neutralized with sodium hydroxide solution and the polymer was precipitated by the addition of dimethylsulphoxide, filtered, and dried. IR spectra of isolated polymers [poly(4-VP and poly(4-VP-Co-AN)] showed peaks at 1570 cm^{-1}, and 2940

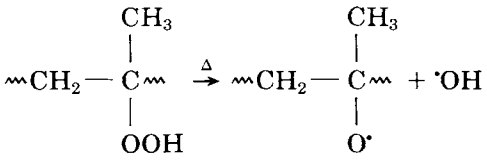
cm^{-1} due to $-C=N$ and $-CH$ of 4-vinyl pyridine and a peak at 2480 cm^{-1} due to nitrile group of acrylonitrile. Isolation of the grafted polymer upon hydrolysis provides additional evidence for the formation of the graft.

RESULTS AND DISCUSSION

Irradiation of polypropylene in air leads to the fomation of hydroperoxide groups on the polymeric backbone because of the presence of a large number of tertiary hydrogen atoms. These hydroperoxide groups decompose upon heating to generate macro radical (IPP—$\dot{O}$) and hydroxy radical ($\dot{O}H$) which are responsible for producing graft copolymer or homopolymer in the following manner



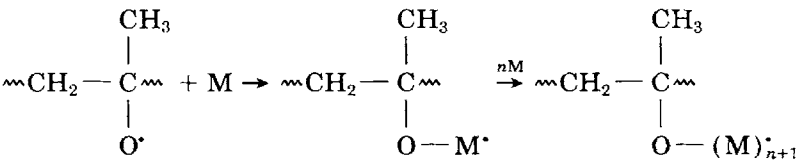
(1)



(2)

(3)

(4)



(5)

The extent of formation of graft copolymer is much dependent on the reaction conditions. It was therefore desirable to evaluate the optimum conditions leading to maximum graft formation. The percentage of grafting was studied as a function of total dose, monomer concentration, time, and temperature of grafting reaction.

Effect of Total Dose

Grafting of 4-VP and binary mixture of (4-VP + AN) onto preirradiated IPP was 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 of 4-VP increases with increasing total dose and becomes constant after attaining a maximum value (365%) at a total dose of 12.54 MR. When a binary mixture of (4-VP + AN) is grafted, percentage of grafting increases and then decreases. Maximum percentage of grafting (803%) is obtained at a total dose of 5.264 MR indicating that AN enhanced grafting of 4-VP.

Effect of Monomer Concentration

Percentage of grafting of 4-VP as a function of monomer concentration is presented in Figure 2. It is observed from the figure that percentage grafting of 4-VP increases with increasing monomer concentration and shows Tromsdorff's effect at maximum percentage of grafting. When a mixture of (4-VP + AN) is grafted, presence of acceptor monomer (AN) greatly affects the reactivity of the donor monomer (4-VP). In Figure 3 is presented the percentage of grafting of (4-VP + AN) as a function of mole fraction of acrylonitrile in the binary mixture. It is observed from the figure that percentage of grafting increases with increase in mole fraction of AN in the binary mixture and reaches

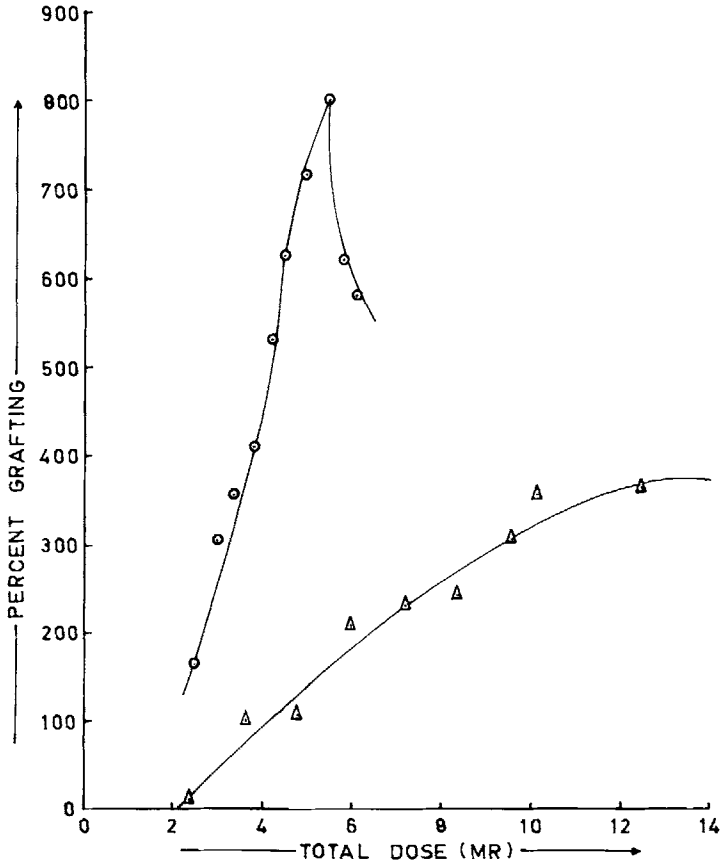


Fig. 1. Effect of total dose on percentage of grafting of 4VP(△—△) and 4VP + AN (⊙—⊙).

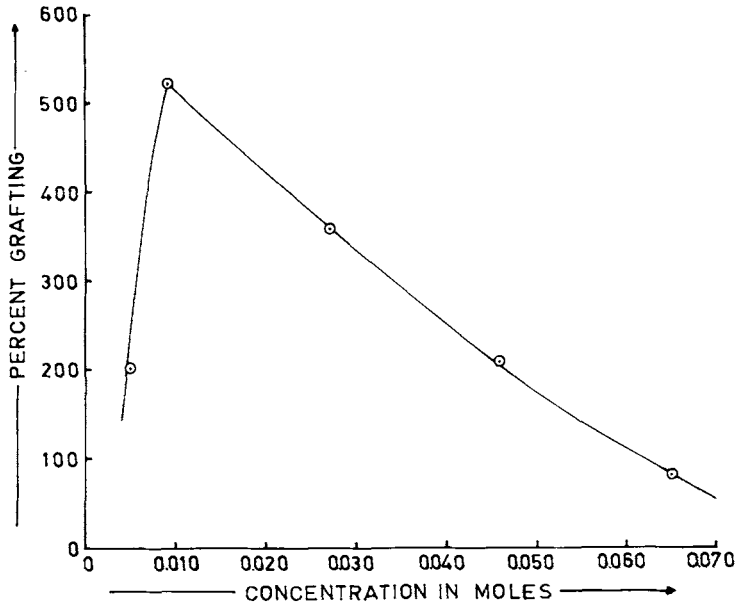


Fig. 2. Effect of [4VP] percentage of grafting.

maximum. Further increase in the mole fraction of acrylonitrile decreases percentage of grafting.

Rate of grafting as a function of initial monomer concentration of 4-VP and binary mixture of 4-VP and AN has been evaluated. The total monomer concentration in the binary mixture is taken as the sum total of individual concentrations of 4-VP and AN in moles. The ratio of concentration of the 2 monomers in the binary mixture is kept constant at 1 : 1 v/v. The results are presented in Figure 4(a and b). It is observed from Figure 4(a) that the rate

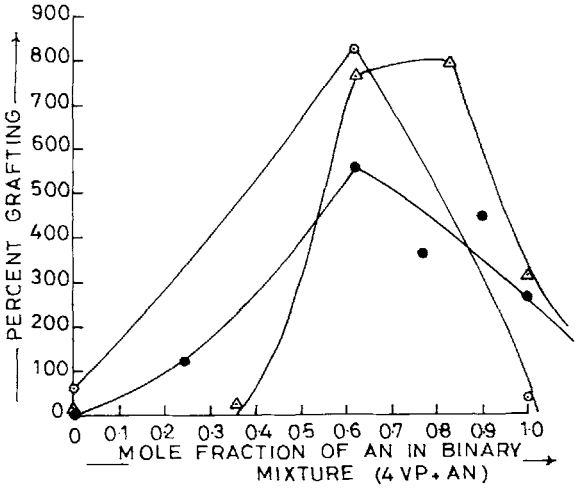


Fig. 3. Effect of AN on percentage of grafting of 4VP in binary mixture.

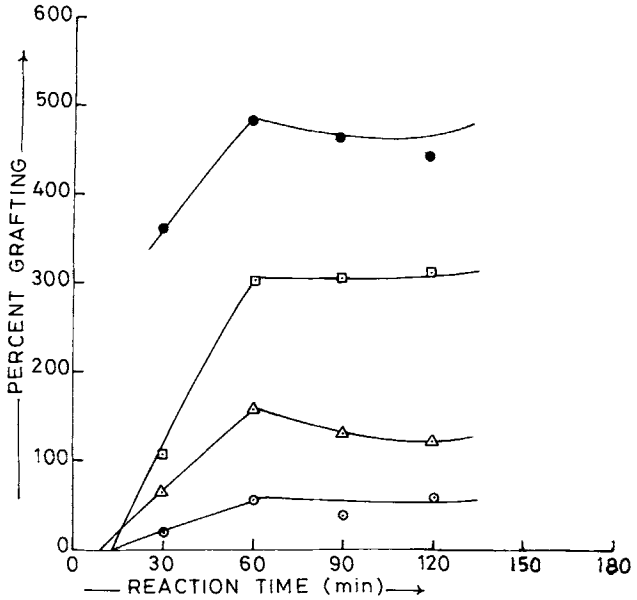


Fig. 4a. Rate of grafting (Rp) as a function of initial monomer concentration of 4VP.

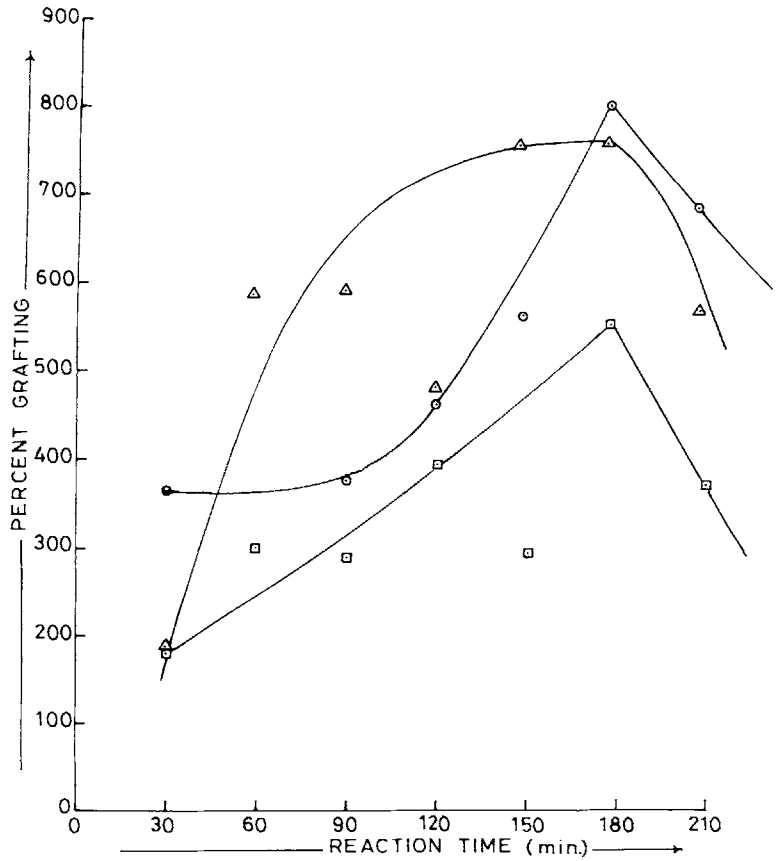


Fig. 4b. Rate of grafting (Rp) as a function of total initial monomer concentration of 4VP + AN 1 : 1 (⊙—⊙), 2 : 2 (△—△), 313 (⊡—⊡).

of grafting is maximum (6.37%/min) at [4-VP] = 0.018 moles. Further increase in monomer concentration decreases the rate of grafting. Maximum rate of grafting (3.11%/min) of binary mixture (4VP + AN) is obtained at 0.048 total monomer concentration of binary mixture. Further increase in concentration of binary mixture decreases the rate of grafting [Fig. 4(b)]. Rate of grafting as determined from the figures is presented in Table I.

Effect of Time of Reaction

Percentage of grafting of 4-VP and (4VP + AN) has been evaluated as a function of time of reaction and the results are presented in Figure 5. It is observed from the figure that grafting percentage of 4-VP increases with increase in time of reaction and then levels off. Maximum amount of graft is formed in 180 min under optimum conditions. Grafting of binary mixture of (4VP + AN) increases sharply with increasing time and reaches maximum (803%) within 180 min indicating that binary mixture (4VP + AN) shows Tromsdorff's effect.

Effect of Temperature of Reaction

In Figure 6 is plotted percentage of grafting of 4-VP and (4VP + AN) mixture as a function of temperature of reaction. Percentage of grafting of 4-VP and (4VP + AN) is found to increase with increasing temperature and then decreases. Maximum percentage of grafting is obtained at 115°C with both 4-VP and the binary mixture of (4VP + AN).

Effect of Amount of Water

Misra et al.[6] observed that grafting of AN onto preirradiated IPP was maximum when water was used as reaction medium. In the present work, grafting was studied in water and it was observed that maximum amount of grafting of 4-VP and binary mixture (4-VP + AN) was obtained when 5 mL and 20 mL of water was used respectively (Fig. 7).

TABLE I
Rate of Grafting (R_p) of 4-VP and (4-VP + AN) Determined as a Function of Initial Monomer Concentration

S. no.	Monomer	[M] (moles)	R_p (%/min)
1	4-VP[a]	0.009	4.20
2	4-VP[a]	0.018	6.37
3	4-VP[a]	0.027	3.0
4	4-VP[a]	0.037	1.32
5	(4-VP + AN)[b]	0.024	2.95
6	(4-VP + AN)[b]	0.048	3.11
7	(4-VP + AN)[b]	0.072	2.49

[a] PP = 100 mg; H_2O = 20 mL; temperature = 100°C; total dose = 10.20 MR.
[b] PP = 100 mg; H_2O = 20 mL; temperature = 100°C; total dose = 5.26 MR.

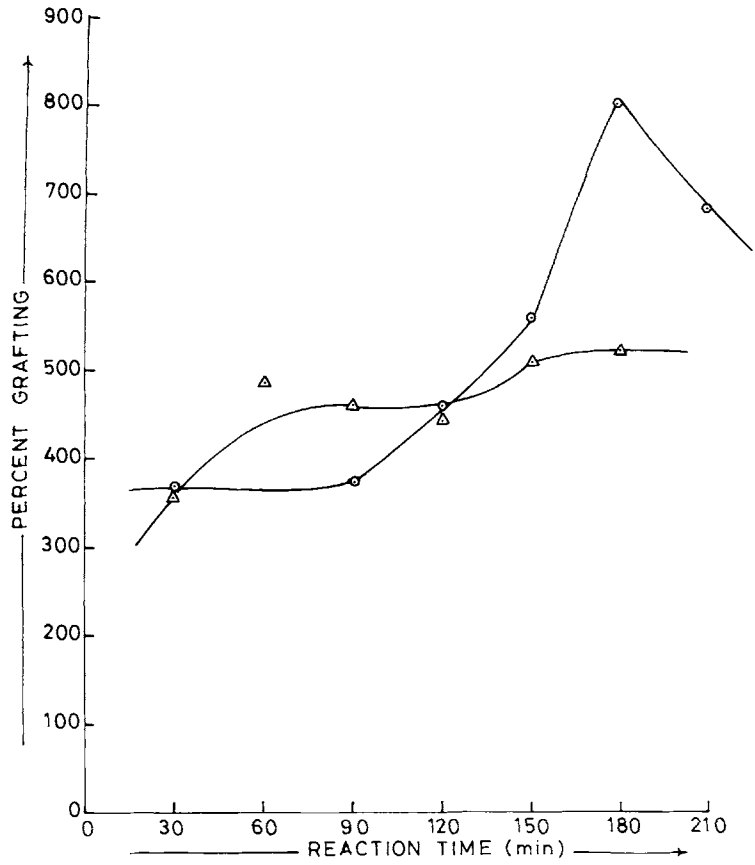


Fig. 5. Effect of time of reaction on percentage of grafting of 4VP (△—△) and 4VP + AN (⊙—⊙).

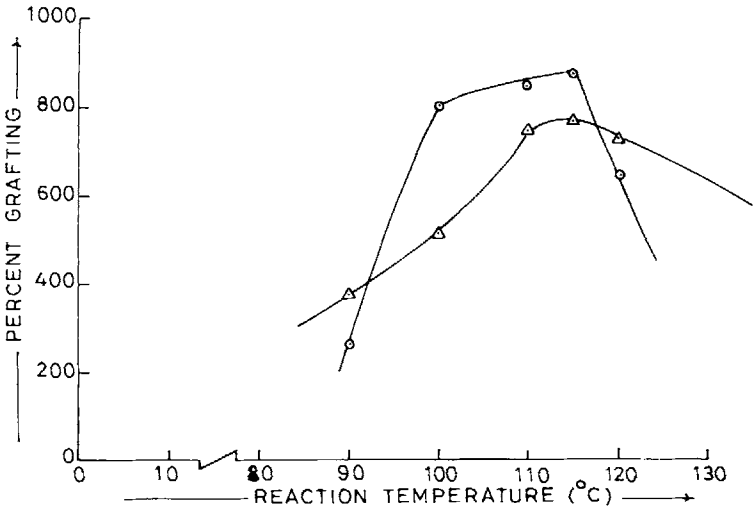


Fig. 6. Effect of temperature on percentage of grafting of 4VP (△—△) and 4VP + AN (⊙—⊙).

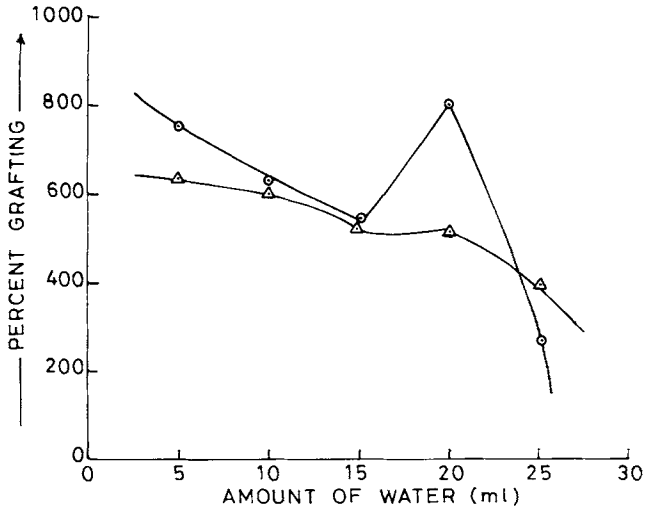
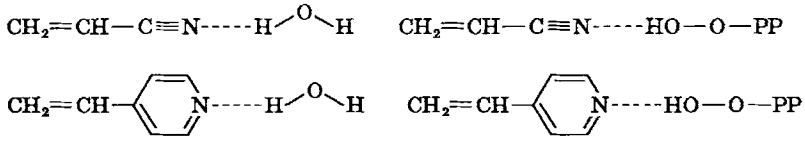


Fig. 7. Effect of amount of water on percentage of grafting of 4VP (△—△) and 4VP + AN (⊙—⊙).

Reactivity of 4-Vinyl Pyridine and Acrylonitrile

Misra et al.[6] in their study of grafting of AN onto preirradiated IPP found that AN, an acceptor monomer, produced maximum percentage of grafting (814%) at a total dose of 5.5 MR in an aqueous medium. The formation of graft copolymer was explained on the basis of its solubility in water which facilitates the monomer to reach the active sites and produce the graft. However, in the present work, 4-VP and its mixture with AN has been used as monomers to graft preirradiated IPP. 4-VP is an electron donor monomer and is also soluble in water. But when 4-VP is used, maximum percentage of grafting under optimum conditions is 638% and the mixture of 4-VP with AN gives higher percentage of grafting (803%). These results suggest that AN is more reactive towards grafting than 4-VP. The reactivity can be rationalized by the fact that 4-VP has a very high chain transfer constant (C_M at 25°C = 6.7×10^{-4}) whereas AN has a much lower chain transfer constant (C_M at 25°C = 0.105×10^{-4}). High chain transfer constant value for 4-VP leads to wastage of monomer in the side reactions leading to homopolymer formation thereby giving a low grafting percentage.

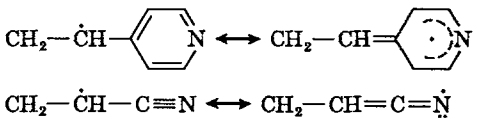
In addition to this, both 4-VP and AN enter, into hydrogen bond formation with water, the reaction medium, and hydroperoxide groups on the polymeric backbone.



Long-range conjugation present in hydrogen bonded 4-VP as compared to AN permits a stronger hydrogen bond formation with either water or hydro-

peroxide functions of polypropylene. This decreases the reactivity of 4-VP. When the monomer reactivity ratios of AN and 4-VP in the copolymerization mixture are compared, it is found that AN prefers to react with 4-VP rather than with its own polymeric chains to produce homopolymer (r_1 = 0.113), whereas 4-VP tends to produce more of homopolymer than the copolymer (r_2 = 0.41). This fact is further substantiated by the higher chain transfer constant to its monomer (4-VP) than AN.

Another factor which is responsible for the low reactivity of 4-VP is that 4-VP forms a more stable and therefore, less reactive free radical than AN.



In Figure 3, the effect of mole fraction of acrylonitrile in binary mixture (4VP + AN) on percentage of grafting is described. It is observed that percentage grafting increases with increasing mole fraction of AN in the binary mixture up to a certain point and then decreases indicating that there exists a critical composition of the binary mixture for affording maximum grafting.

References

1. P. J. Canterino, U.S. Patent, 3,162,697 (1964), *Chem. Abstr.*, **62,** 7953 (1965).
2. I. Kirshenbaum, B. M. Stanley, and G. Karoly, *Chem. Abstr.* **61,** 9636 (1964).
3. Zhimin Gao, Yongyuan Yang, Shujing Feng, and Shikang Wu, *Ganguang Kixue Yu Kyang Huaxne,* **4,** 54 (1984).
4. C. H. Ang, J. L. Garnett, R. Levot, M. A. Long, and N. T. Yen, *J. Polym. Sci. Lett. Ed.,* **18,** 471 (1980).
5. A. M. Nabieva, U. N. Musaev, Sh. A. Kurbanov, A. V. Veasov, B. L. Tsetlin, *Izve Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **27,** 235 (1984).
6. B. N. Misra, I. K. Mehta, and D. S. Sood, *J. Polym. Sci. Polym. Chem. Ed.,* **23,**1749 (1985).
7. C. W. McGary, Jr., *J. Polym. Sci. Polym. Chem. Ed.,* **46,** 51 (1960).

Received October 2, 1989
Accepted December 13, 1989