

Graft Copolymerization of 4-Vinyl Pyridine onto Isotactic Polypropylene Hydroperoxide by Mutual Irradiation Method

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SYNOPSIS

An attempt has been made to graft copolymerize 4-vinyl pyridine onto isotactic polypropylene hydroperoxide by mutual irradiation method in an aqueous medium. Polypropylene hydroperoxide has been prepared by irradiating recrystallized polypropylene beads from a Co^{60} source in the presence of air. The resulting polypropylene hydroperoxide beads have been used as the backbone polymer and grafting of 4-vinyl pyridine has been studied as a function of various reaction parameters. Optimum conditions for maximum percentage of grafting have been evaluated. Rate of grafting (R_g) has been determined as a function of preirradiation dose and initial monomer concentration. Water has been found to affect percentage of grafting. The graft copolymers have been characterized by spectroscopic method and isolation of the grafted poly(4-VP) from the graft copolymer. A plausible mechanism is proposed to explain the mutual grafting of 4-vinyl pyridine onto polypropylene hydroperoxide. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Radiation-induced grafting of various vinyl monomers onto different backbone polymers has been successfully attempted and fairly good results have been obtained. In nonfunctional polymers such as polypropylene and polyethylene, preirradiation leads to the functionalization of the polymer backbone by introducing either hydroperoxide or peroxide groups that serve as the sites for grafting. Extensive work has been reported on modification of these polymers using preirradiation method. Lee et al.¹ grafted hydroxyethyl methacrylate (HEMA) onto polypropylene and observed a linear relationship between grafting percentage and dose rate. Torikai et al.² grafted, at different temperatures, vinyl monomers onto preirradiated polypropylene and studied the thermal and mechanical properties and dyeability of the graft copolymers. The effect of synthesis conditions³ and effect of solvent⁴ on the graft copolymerization of methacrylic acid onto polypropylene fiber by simultaneous irradiation technique has been studied by Mukherjee and Gupta.^{3,4} *N*-vinyl-2-pyrrolidinone and acrylic acid were grafted

onto polypropylene by Hsieti.⁵ Taher et al.⁶ studied the effect of different solvents such as benzene, distilled water, dimethylformamide, isopropanol, and isopropanol-water mixture on the swelling and grafting of methacrylic acid onto polypropylene films. Solvent effects on radiation-induced graft copolymerization of acrylonitrile onto polypropylene fiber has been studied by Misra et al.^{7,8} Water was found to be an excellent solvent. However no studies are reported on grafting of vinyl monomers onto preirradiated polypropylene by mutual irradiation method. In the present manuscript, we report on grafting of 4-vinyl pyridine onto preirradiated polypropylene beads by mutual irradiation method.

EXPERIMENTAL

Materials and Method

Isotactic polypropylene (IPP) in the form of beads was received from Indian Petrochemical Company Ltd., Baroda (India). The beads were recrystallized from *p*-xylene and the powdered IPP thus obtained was used in all grafting reactions. 4-Vinyl pyridine (4-VP) (Fluka) was used as received. Distilled water was used as the reaction medium.

IPP powder was irradiated in air from a 2100 Ci Co⁶⁰ source at a constant dose rate of 0.16 mrad/h for different time periods.

Graft Copolymerization

Irradiated IPP powder (50 g) was suspended in a known amount of water in an Erlenmeyer flask. To it was added a definite amount of the monomer and the reaction mixture was irradiated for different time periods. After the completion of the reaction, the contents were filtered, washed thoroughly with methanol, and finally extracted with methanol to ensure complete removal of the homopolymer, poly(4-VP). The homopolymer free residue was filtered and dried in an oven at 50°C until constant weight was obtained. Percentage of grafting was calculated from the initial increase in weight of the original IPP 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 spectrum of IPP-*g*-poly(4-VP) showed peaks at 1580 cm⁻¹ due to —C=N of pyridine ring and at 2940 cm⁻¹ caused by —CH stretching of vinyl pyridine indicating that 4-VP has been grafted onto the macro-hydroperoxidized IPP beads.

Isolation of the Grafted Poly(4-VP) from Graft Copolymer

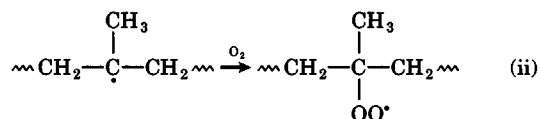
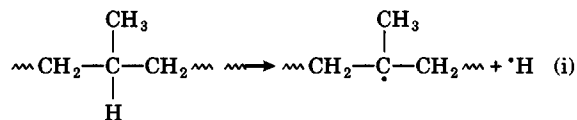
IPP-*g*-poly(4-VP) sample (500 mg) was suspended in a solution of 0.02 g CuCl₂ in 50 mL of 30% hydrogen peroxide and left at room temperature for 2 days. The contents were filtered and the residue was identified as IPP by IR spectroscopy. The filtrate was neutralized with aqueous sodium hydroxide solution and the polymer was precipitated by the addition of dimethyl sulphoxide. The polymer was filtered, dried, and characterized by IR spectroscopy as poly(4-VP), thus providing an additional evidence for the formation of the graft copolymer.

RESULTS AND DISCUSSION

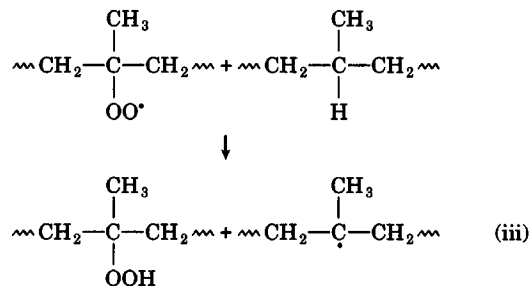
Irradiation of IPP in air leads to the formation of hydroperoxide groups on the polymer backbone be-

cause of the presence of a number of labile tertiary hydrogen atoms. These hydroperoxide groups provide active sites for grafting of vinyl monomers. The following reactions take place during irradiation of isotactic polypropylene in air and the grafting of 4-VP onto preirradiated IPP by mutual irradiation method. Based on these reactions we propose the following tentative mechanism.

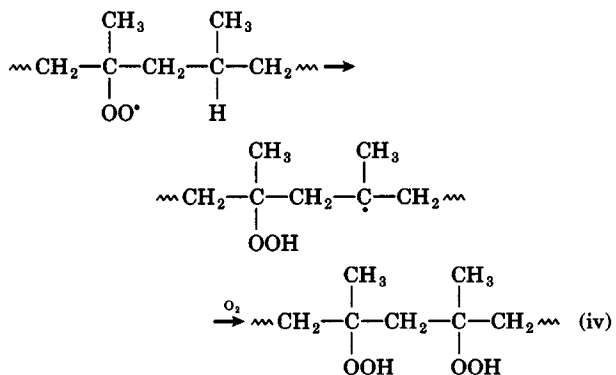
Preirradiation of IPP



Intermolecular H-abstraction

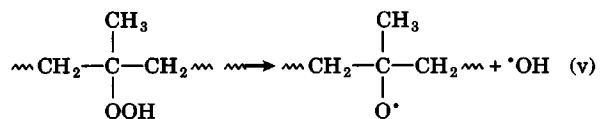


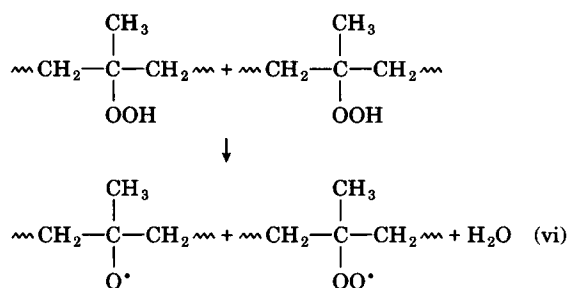
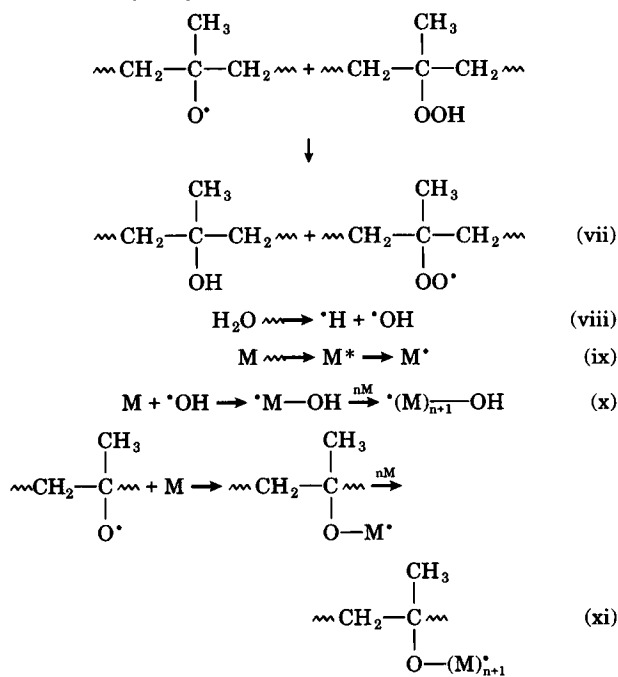
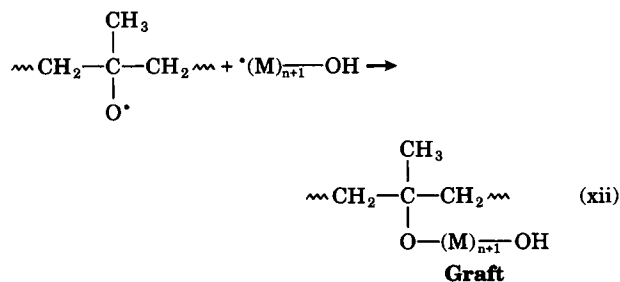
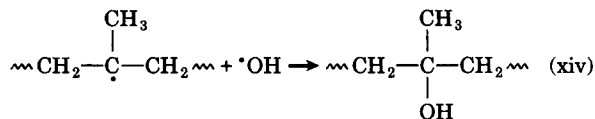
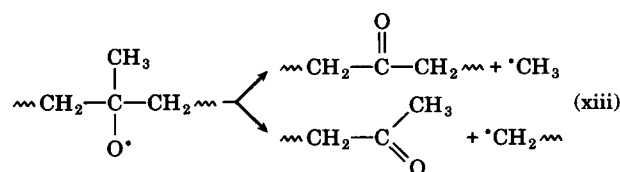
Intramolecular H-abstraction



Reactions during Mutual Grafting

Unimolecular Decomposition



Bimolecular Decomposition**Induced Hydroperoxide Decomposition****Termination****Termination by β -Scission**

The various steps discussed in the above mechanism have been reported by many workers.⁹⁻¹⁴

It is observed from the above proposed mechanism that the reactive sites on the backbone polymer can be generated by steps (v) and (vi) leading to the formation of polypropylene oxide macroradical (IPP—O[•]). The formation of polypropylene dioxide radical (IPP—O—O[•]) in steps (vi) and (vii) can either abstract a hydrogen atom from the polymer, monomer, or solvent molecule to give hydroperoxide that can then generate more active sites where grafting can occur. The formation of hydroxyl radical (OH[•]) occurs either by the decomposition of hydroperoxide groups, step (v) or it is formed as a radiolytic product of water, step (viii). The hydroxyl radical initiates the polymerization reaction to produce growing polymeric chains, step (x) that can attack the active sites of the backbone polymer to give the graft copolymer, step (xii). Gamma rays are known to initiate vinyl polymerization and the resulting growing polymeric chain can lead to the formation of either homopolymer, step (x) or the graft copolymer, step (xii).

Termination of various active species in the reaction mixture may take place by β -scission of the growing polymeric chains,¹²⁻¹⁴ step (xiii). Also the hydroxyl radical formed during the decomposition of hydroperoxide is quite reactive and can terminate the reaction via process xiv.

Effect of Total Dose during Preirradiation

The effect of total dose during preirradiation on percentage of grafting of 4-VP has been studied and the results are presented in Figure 1. It is observed from the figure that percentage of grafting increases linearly with increase in preirradiation dose, reaches maximum (408%) at a total dose of 4.13 mrad beyond which it decreases. The increase in percentage of grafting is attributed to the fact that the number of hydroperoxide groups, the active site for grafting, increases with increasing dose. Decrease in percentage of grafting beyond optimum total dose is caused by induced hydroperoxide decomposition, step (vii) producing macropoxy radicals that are not reactive enough to produce grafting and consequently percentage of grafting decreases.

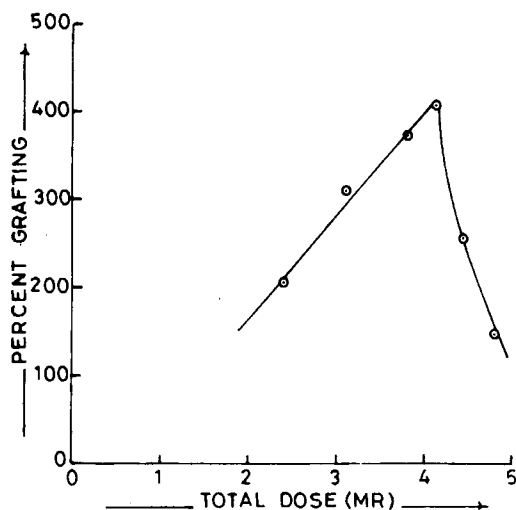


Figure 1 Effect of total dose during preirradiation on percentage of grafting of 4-VP.

Effect of Total Dose in Mutual Grafting

Figure 2 represents the effect of total dose on percentage of grafting of 4-VP onto polypropylene hydroperoxide. Increase in percentage of grafting with increasing total dose is observed with maximum (576%) at an optimum total dose of 0.86 mrad beyond which it decreases. Initial increase in percentage of grafting is caused by the fact that with increasing total dose, various initiation steps leading to generation of hydroxyl radicals ($\cdot\text{OH}$) via process vii and viii are facilitated that are responsible for the polymerization process, step (x). Termination of growing polymeric chains can take place via process xii to produce the graft copolymer. Decrease in percentage of grafting with further increase in total dose may be explained by the fact that at higher doses termination of grafting by β -scission is accelerated, step (xiii). The hydroxyl radicals formed during the decomposition of hydroperoxides can also terminate grafting by step (xiv). Higher doses may also kill the tertiary carbon-free radical sites¹⁵ present in the backbone polymeric chain, leading to decrease in number of active sites and hence percentage of grafting in the following manner:

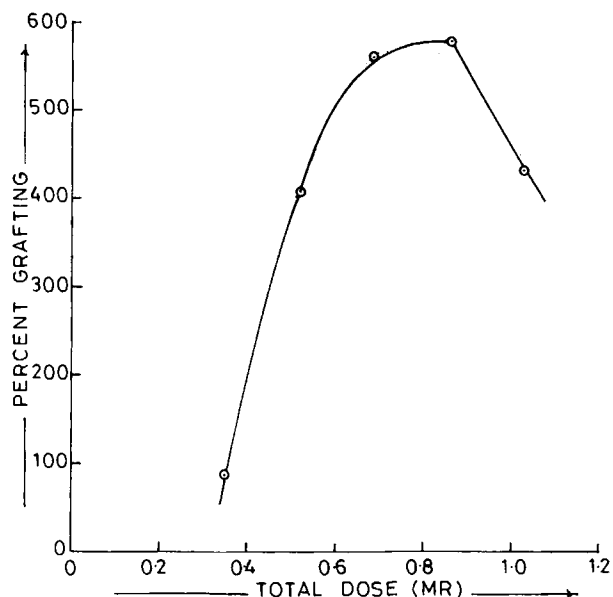
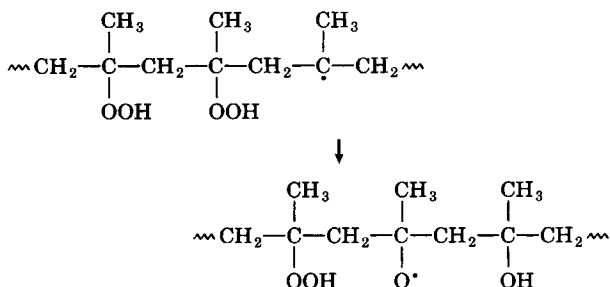


Figure 2 Effect of total dose on percentage of grafting of 4-VP onto polypropylene hydroperoxide.

Effect of Monomer Concentration

Percentage of grafting has been studied as a function of monomer concentration and the results are presented in Figure 3. It is observed from the figure that the maximum percentage of grafting (576%) is obtained at $[4\text{-VP}] = 0.9 \times 10^{-2} M$ beyond which it decreases. Decrease in percentage of grafting at higher monomer concentration is due to the fact that the homopolymer formation becomes the pre-

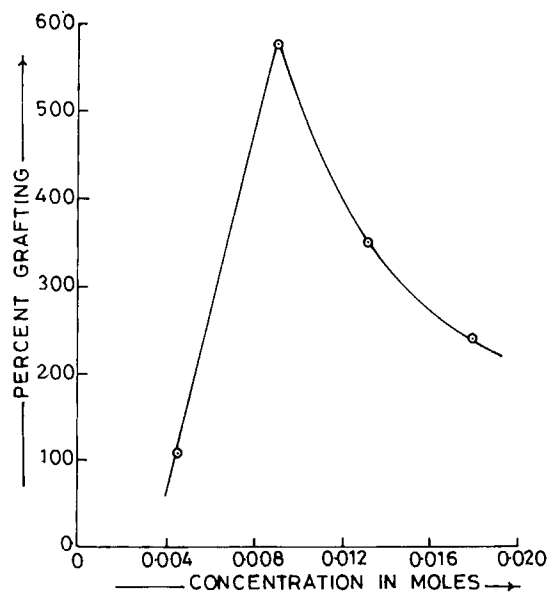


Figure 3 Effect of $[4\text{-VP}]$ on percentage of grafting.

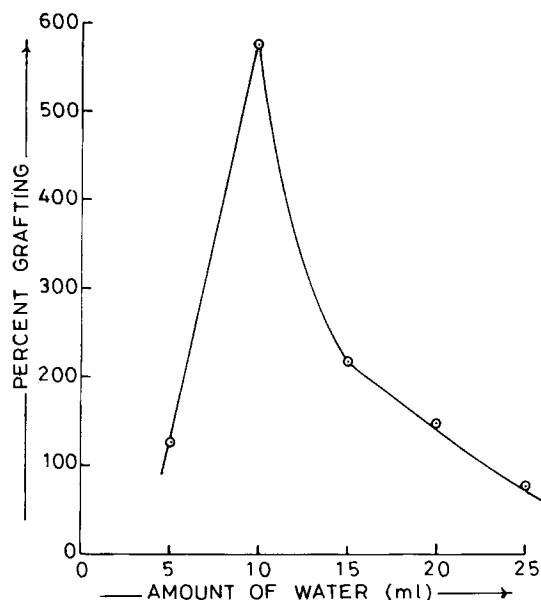


Figure 4 Effect of amount of water on percentage of grafting of 4-VP.

ferred process. Moreover, 4-VP, having high monomer transfer constant¹⁶ (C_M at 25°C = 6.7×10^{-4}) gets involved in side reactions leading to wastage of monomer and hence decrease in percentage of grafting is observed.

Effect of Amount of Water

Figure 4 represents the effect of amount of water on percentage of grafting of 4-VP. It is observed from

Table I Rate of Grafting of 4-VP as a Function of Total Dose and Initial Monomer Concentration

S. No.	Total Dose during Preirradiation (MR)	[4-VP] (M)	R_g (%/min)
1	3.10	9.0×10^{-3}	5.06
2	3.78	9.0×10^{-3}	5.16
3	4.13	9.0×10^{-3}	5.29
4	4.13	4.5×10^{-3}	0.34
5	4.13	9.0×10^{-3}	5.29
6	4.13	13.0×10^{-3}	1.67

Reaction conditions: IPP = 50 mg; water = 10 mL.

the figure that there is a sudden increase in percentage of grafting when the amount of water is varied between 5 mL and 10 mL producing maximum percentage of grafting (576%) with 10 mL of water under optimum conditions beyond which it decreases. Decrease in percentage of grafting with increasing amount of water beyond optimum may be attributed to the fact that as the amount of water is increased, number of hydroxyl radicals ($\cdot\text{OH}$) increases simultaneously by radiolysis of water, step (ix). The excess of hydroxyl radicals can enter into various side reactions, step (xiv) that can lead to decrease in number of active sites and also percentage of grafting. Further in the presence of excess of water significant amount of $\text{HO}_2\cdot$ may be formed that may interact with the macroperoxide radical in

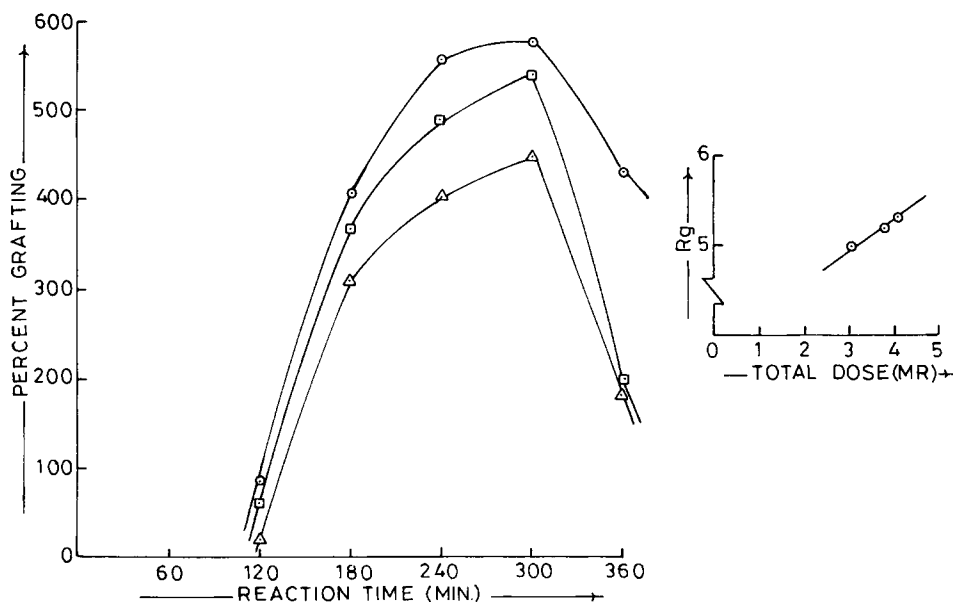


Figure 5 Rate of grafting (R_g) of 4-VP as a function of total dose during preirradiation. Δ — Δ 3.096 MR, \square — \square 3.784, and \circ — \circ 4.128 MR.

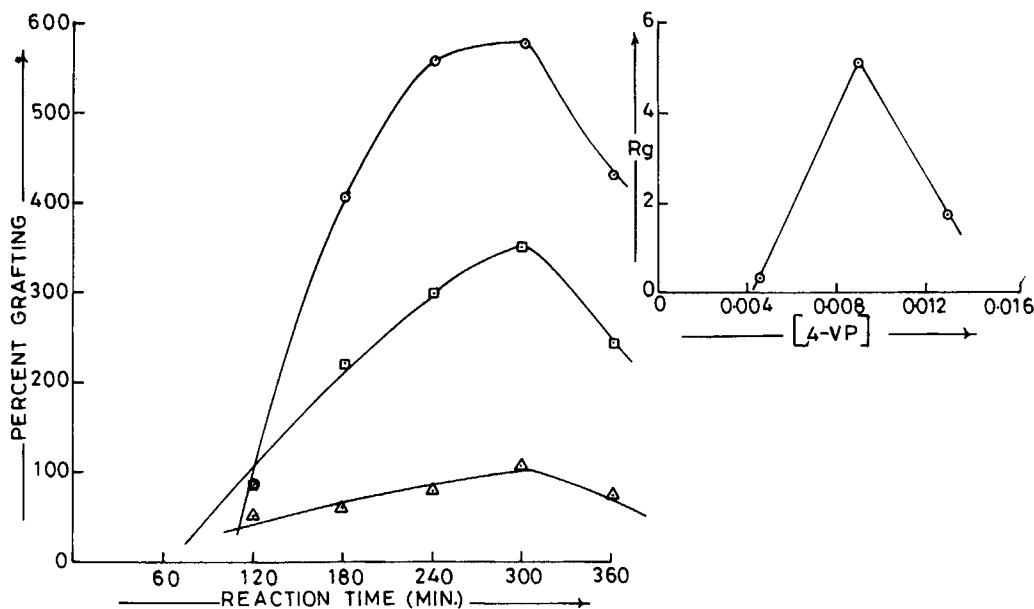
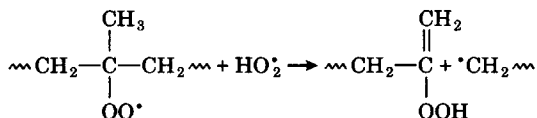


Figure 6 Rate of grafting (R_g) as a function of initial monomer concentration of 4-VP. \triangle — \triangle 0.0045, \circ — \circ 0.009, \square — \square 0.013.

the following manner, leading to a decrease in percentage of grafting.



Baxendale and Thomas¹⁷ and Alexander and Charlesby¹⁸ also observed such β -scission involving the reaction between HO_2^\cdot and PO_2^\cdot .

Rate of Grafting (R_g) of 4-VP onto Polypropylene-Hydroperoxide Beads

R_g as a Function of Total Dose during Preirradiation

Rate of grafting as a function of total dose during preirradiation has been evaluated from Figure 5 and the results are presented in Table I. It is observed from the table that the rate of grafting of 4-VP increases with increasing preirradiation total dose. Maximum rate (5.295%/min) is obtained at a total dose of 4.13 mrad. Increase in rate with increasing total dose suggests that rate of grafting depends upon the number of hydroperoxide groups formed during irradiation. However, in the present study no attempt has been made to determine the number of hydroperoxide groups formed during preirradiation.

R_g as a Function of Total Initial Monomer Concentration

Rate of grafting as a function of total initial monomer concentration has been calculated from the slopes of the Figure 6 and the results are presented in Table I. It is observed from the table that the rate of grafting increases with increasing monomer concentration and then decreases. This indicates that there exists a critical monomer concentration at which percentage of grafting is maximum. A plot of R_g versus monomer concentration shows that rate of grafting follows a linear relationship up to $[M] = 9 \times 10^{-3} M$ beyond which it decreases. Decrease in rate at higher monomer concentration may be explained by the fact that because of the significant amount of homopolymer formation the viscosity of the medium increases that inhibits the diffusion of growing polymeric chains to the active sites leading to decrease in grafting.

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