# Radiation-Induced Graft Copolymerization of 2-Vinylpyridine and Styrene onto Isotactic Polypropylene Fiber

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ABSTRACT: Isotactic polypropylene fiber (IPP) was graft-copolymerized using 2-vinyl pyridine (2-VP) and styrene (sty) as the monomers by the mutual irradiation method in air. The percentage of grafting was determined as a function of various reaction parameters and it was found that the maximum grafting of 2-VP (114%) and sty (76%) was obtained at an optimum dose of  $1.08 \times 10^4$  and  $0.64 \times 10^4$  Gy using  $1.8 \times 10^{-2}$  mol of 2-VP and  $4.3 \times 10^{-2}$  mol of sty, respectively. The graft copolymers were characterized by differential scanning calorimetric analysis and isolation of the grafted chains from the grafted iPP samples. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2959–2969, 1999

**Key words:** graft copolymerization; mutual irradiation; isotactic polypropylene; 2-vinyl pyridine; styrene

## INTRODUCTION

Polypropylene (PP), being a hydrocarbon, is inert to most chemicals at or near ambient temperature; it possesses useful resistance to alteration by the environment. However, this inertness excludes its industrial applications in those areas where chemical affinity or the penetration of components is required. Therefore, modification of PP by incorporating various functionalities through graft-copolymerization methods has been successfully achieved. Dyeing and heat-resistant properties of preirradiated PP grafted with styrene (sty)– maleic anhydride showed improvement over unmodified isotactic polypropylene (IPP).<sup>1</sup> Torikai et al.<sup>2</sup> grafted different vinyl monomers onto preirradiated PP and studied the mechanical, thermal,

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Journal of Applied Polymer Science, Vol. 73, 2959–2969 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/142959-11 and dyeing behavior of the graft. Gamma radiation-induced grafting of PP in an acrylic acid solution was studied by Jozef et al.<sup>3</sup> and grafting resulted in increased moisture sorption and improved the dyeability of the grafted sample. Garnett and Yen<sup>4</sup> reported the effect of acids during grafting of sty onto PP using gamma and UV radiation. Lee et al.<sup>5</sup> grafted hydroxyethyl methacrylate onto PP and observed a linear relationship between the grafting percentage and the dose rate. The effect of grafting temperature, crystallinity of the polymers, and preirradiation dose was investigated by different groups of workers.<sup>6,7</sup> Misra et al. radiochemically grafted various vinyl monomers such as acrylonitrile,<sup>8,9</sup> acrylic acid,<sup>10</sup> acrylamide,<sup>10</sup> 4-vinylpyridine,<sup>11</sup> 2-vinylpyridine, and sty<sup>12</sup> onto IPP by a preirradiation method. In the present article, we report here the graft copolymerization of 2-VP and sty onto IPP fiber by the mutual irradiation method.

Sample	Endothermic Peak (°C)	H (J/g)	Exothermic Peak (°C)	H (J/g)	Exothermic Peak (°C)	H (J/g)	Exothermic Peak (°C)	H (J/g)
IPP-g-poly(2-VP) IPP-g-poly(sty)	160.5 159.8	53,472 450,52	$198.3 \\ 252.8$	200,7 79,901	$438.9 \\ 427.4$	2248,9 1824,7	545.9 —	267,52

Table I Differential Scanning Colorimetric Data of IPP-g-poly(2-VP) and IPP-g-poly(sty)

## **EXPERIMENTAL**

## **Materials and Methods**

IPP fiber was obtained from the National Rayon Corp. (Bombay, India). The monomers, 2-vinylpyridine (2-VP) (Fluka, Switzerland) and sty (Merck, Switzerland), were distilled before use. The grafting reactions of 2-VP and sty were studied in water and a water-methanol solvent system, respectively.



**Figure 1** (a) Effect of total dose on percentage of grafting of 2-VP onto IPP fiber. IPP = 100 mg; [2-VP] =  $1.8 \times 10^{-2}$  mol; H<sub>2</sub>O = 10 mL; dose rate =  $0.128 \times 10^4$  Gy/h. (b) Effect of total dose on percentage of grafting of sty onto IPP fiber. IPP = 100 mg; [sty] =  $4.3 \times 10^{-2}$  mol; H<sub>2</sub>O : MeOH = 5.5 mL; dose rate =  $0.128 \times 10^4$  Gy/h.



## **Graft Copolymerization**

IPP fiber (100 mg) was suspended in a known volume of the reaction medium [water/water-methanol (1 : 1)] in a conical flask. To it was added a known amount of the monomer (2-VP/sty) and the contents were thoroughly mixed. The reaction flask was then placed in the gamma chamber for irradiation for different time periods at a constant dose rate of  $0.128 \times 10^4$  Gy/h. At the end of the required time period, the reaction flask was removed from the chamber and the contents of the flask were filtered. The homopolymers, poly(2-VP) and poly(sty), formed during the reaction were removed by washing with the appropriate solvent [methanol for

poly(2-VP) and ethyl acetate for poly(sty)] and finally extracted with the respective solvents to ensure complete removal of the homopolymer. The extraction was carried out until a constant weight of the graft copolymer was obtained. The percentage of grafting was calculated from the initial increase in the weight of the original fiber upon grafting after complete removal of the homopolymer.

### **Evidence of Grafting**

#### Solvent Extraction

Physical mixtures of IPP fiber and poly(2-VP) and poly(sty) prepared separately in methanol and



**Figure 3** (a) Rate of grafting of 2-VP as a function of total initial monomer concentration onto IPP fiber:  $(\bigcirc - \bigcirc) 0.9 \times 10^{-2} \text{ mol}; (\Box - \Box) 1.8 \times 10^{-2} \text{ mol}; (\triangle - \triangle) 2.8 \times 10^{-2} \text{ mol};$  IPP = 100 mg; total dose =  $1.08 \times 10^4$  Gy; H<sub>2</sub>O = 10 mL; dose rate =  $0.128 \times 10^4$  Gy/h. (b) Rate of grafting of sty as a function of total initial monomer concentration onto IPP fiber:  $(\bigcirc - \bigcirc) 0.8 \times 10^{-2}$  mol;  $(\Box - \Box) 2.5 \times 10^{-2}$  mol;  $(\bullet - \bullet) 43 \times 10^{-2}$  mol. IPP = 100 mg; total dose =  $0.64 \times 10^4$  Gy; H<sub>2</sub>O : MeOH = 5.5 mL; dose rate =  $0.128 \times 10^4$  Gy/h; H<sub>2</sub>O : MeOH = 5.5 mL.

ethyl acetate, respectively, were stirred for 48 h and filtered. The residue was extracted with the respective solvents for 24 h and filtered and dried. No increase in the weight of the IPP fiber was noticed, which ensured that extraction with the appropriate solvent completely removes the homopolymer.



Figure 3 (Continued from the previous page)

## Isolation of the Grafted Polymer from IPP-gpoly(2-VP) and IPP-g-poly(sty)

The grafted polymeric chains of poly(2-VP) and poly(sty) were isolated by the method of McGary<sup>13</sup> and identified by IR spectroscopy. The isolation of these polymers confirms that grafting occurred during mutual irradiation of these monomers in the presence of the IPP fiber.

## **Differential Scanning Colorimetric Analysis**

The differential scanning colorimetric (DSC) analysis of IPP-g-poly(2-VP) and IPP-g-poly(sty) was carried out and the results are presented in Table I. It is observed from the table that both IPP-g-poly(2-VP) and IPP-g-poly(sty) show endothermic peaks at 160.5 and 159.8°C, respectively. Exothermic peaks are observed at 198.3, 438.9, and 545.9°C for IPP-

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Irradiation of iPP:

*g*-poly(2-VP) and at 252.8 and 427.4°C for IPP-*g*-poly(sty). The endothermic peaks correspond to the melting of the grafted chains, while the exothermic peaks indicate that the degradation may take place at higher temperatures.

## **RESULTS AND DISCUSSION**

The irradiation of IPP in air leads to the formation of hydroperoxide groups on the polymeric backbone because of the presence of a number of labile tertiary hydrogen atoms which provide active sites for grafting. The following reactions seem to take place during grafting of 2-VP and sty onto the IPP fiber by the mutual method:

$$\begin{array}{ccc} CH_{3} & CH_{3} \\ | & & | \\ \uparrow CH_{2} & -C & -CH_{2} \\ | & & \rightarrow \\ H \end{array} \xrightarrow{\gamma \text{-rays}} & \mathcal{M} CH_{2} - C & -CH_{2} \\ \mathcal{M} & +H^{\bullet} \end{array}$$
(i)

$$CH_{3} \qquad CH_{3} \\ | \\ mCH_{2} - C - CH_{2} - + O_{2} \rightarrow mCH_{2} - C - CH_{2} m \\ | \\ OO^{\bullet}$$
(ii)

Intermolecular H abstraction:



Intramolecular H abstraction:



Unimolecular decomposition:

 $\begin{array}{ccc} CH_{3} & CH_{3} \\ | & | \\ mCH_{2} & -C & -CH_{2} & m \\ & | \\ CH_{2} & -C & -CH_{2} & m \\ | & | \\ OOH & O^{\bullet} \end{array}$  (v)

Bimolecular decomposition:



Induced hydroperoxide decomposition:

$$H_2Om \xrightarrow{\gamma \text{-}rays} H^{\bullet} + OH$$
 (viii)

$$\mathbf{M} \xrightarrow{\gamma \text{-}rays} \mathbf{M}^{\bullet} \xrightarrow{nM} \overset{\mathbf{M}}{\longrightarrow} \mathbf{M}^{\bullet} (\mathbf{M})_{\mathbf{n}}$$
(ix)

$$M + \stackrel{\bullet}{O}H \rightarrow M^{\bullet} - OH \xrightarrow{nM} \stackrel{\bullet}{\longrightarrow} M^{\bullet} - (M)_{n} - OH$$
 (x)

Termination:

$$\begin{array}{cccc} CH_{3} & CH_{3} & & \\ & | & & | \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

Termination by  $\beta$ -scission:

$$\sim CH_{2} - (C \xrightarrow{a} CH_{3} \xrightarrow{b} CH_{2} \sim \xrightarrow{a} \sim CH_{2} - C - CH_{2} \sim + \dot{C}H_{3} \qquad (xiii)$$

$$\downarrow O \xrightarrow{b} O CH_{2} - C \xrightarrow{CH_{3}} + \dot{C}H_{2} \sim (xiii)$$

Chien et al.<sup>14</sup> observed that an intramolecular peroxy radical attack on the PP chain could lead to a sequence of neighboring hydroperoxy groups. In the intramolecular propagation [step (iv)], the peroxy radical attacks the C—H bond at the  $\beta$ position and migrates along the macromolecule, leaving behind a fence of hydroperoxy groups. In the intermolecular reaction [step (iii)], a peroxy radical attacks the tertiary hydrogen atom of the other molecule, resulting in the formation of hy-droperoxy groups.<sup>15,16</sup> Zolotova and Denisov<sup>15</sup> also proposed unimolecular and bimolecular reactions for the decomposition of the hydroperoxide [steps (v) and (vi)]. Induced hydroperoxide decomposition (step vii) was observed by Chien et al.<sup>14</sup> during oxidative photodegradation of IPP, which results in the hydroxyl group formation. It was

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Table II Rate of Grafting (Rg) of 2-VP and Sty as a Function of Total Initial Monomer Concentration

Sample No.	Monomer	$[M] imes 10^2 \ \mathrm{mol}$	<i>Rg</i> (%/min)
1	2-VP <sup>a</sup>	0.9	0.266
2	$2\text{-VP}^{\mathrm{a}}$	1.8	0.386
3	$2\text{-VP}^{\mathrm{a}}$	2.8	0.215
4	$\mathrm{Sty}^{\mathrm{b}}$	0.8	0.077
5	$Sty^{b}$	2.5	0.182
6	$\mathrm{Sty}^\mathrm{b}$	4.3	0.204

 $^{\rm a}$  IPP = 100 mg; H\_2O = 10 mL; total dose =  $1.08 \times 10^4$  Gy. <sup>b</sup> IPP = 100 mg;  $H_2O$  + MeOH = (5 + 5) mL; total dose  $= 0.64 \times 10^4$  Gy.



**Figure 4** (a) Effect of amount of water on percentage of grafting of 2-VP onto IPP fiber. IPP = 100 mg; total dose =  $1.08 \times 10^4$  Gy;  $[2\text{-VP}] = 1.8 \times 10^{-2}$  mol; dose rate =  $0.128 \times 10^4$  Gy/h. (b) Effect of solvent system on percentage of grafting of  $2\text{-VP}^1$  and sty<sup>2</sup> onto IPP fiber. IPP = 100 mg; total dose =  $2\text{-VP} = 1.08 \times 10^4$  Gy; sty =  $0.64 \times 10^4$  Gy;  $[2\text{-VP}] = 1.8 \times 10^{-2}$  mol; [sty] =  $4.3 \times 10^{-2}$  mol; dose rate =  $0.128 \times 10^4$  Gy/h. (c) Effect of amount of H<sub>2</sub>O/CH<sub>3</sub>OH on percentage of grafting of styrene onto IPP fiber:  $(\bigcirc - \odot)$  MeOH;  $(\bigcirc - \odot)$  H<sub>2</sub>O. IPP = 100 mg; total dose =  $0.04 \times 10^4$  Gy; [sty] =  $4.3 \times 10^{-2}$  mol; dose rate =  $0.128 \times 10^4$  Gy; [sty] =  $4.3 \times 10^{-2}$  mol; dose rate =  $0.04 \times 10^4$  Gy; [sty] =  $4.3 \times 10^{-2}$  mol; dose rate =  $0.128 \times 10^4$  Gy/h.

suggested by Carlsson et al.<sup>17,18</sup> that  $\beta$ -scission of tertiary alkoxy radicals [step (xiii)] is the major source of chain scission during the photodegradation of IPP.

Thus, from the above-proposed mechanism, the active sites on the backbone polymer can be gen-

erated by steps (v) and (vi), leading to the formation of the poly(propylene oxide) macroradical (IPP-O<sup>•</sup>). The poly(propylene dioxide) radical (IPP-O—O<sup>•</sup>) formed in steps (vi) and (vii) can abstract a hydrogen atom from the polymer, monomer, or solvent molecule to give hydroperox-



Figure 4 (Continued from the previous page)

ide, which can then generate more active sites where grafting can occur. The formation of the hydroxyl radical (OH) can occur either by the decomposition of hydroperoxide groups or it is formed as the radiolytic product of water [step (viii)]. The hydroxyl radical initiates the polymerization reaction to produce growing polymeric chains [step (x)] which can attack the active sites of the backbone polymer to give the graft copolymer (step xii). Gamma rays are known to initiate vinyl polymerization directly and the resulting polymeric chain can lead to the formation of either a homopolymer (step ix) or the graft copolymer (step xii). Termination of various active species in the reaction mixture may take place by  $\beta$ -scission of the polymeric chains [step (xiii)].

The effects of the reaction conditions, such as total dose, concentration of the monomers, and the amount and nature of the solvent used as the reaction medium, on the percentage of grafting of 2-VP and sty were studied and the results are discussed in the light of the proposed mechanism.

## Effect of Total Dose

The percentage of grafting of 2-VP and sty onto IPP was studied as a function of the total dose and the results are presented in Figure 1(a,b). It can be observed from the figure that maximum grafting (114%) of 2-VP is obtained at a total dose of  $1.08 \times 10^4$  Gy, beyond which it decreases. The initial increase in the percentage of grafting is due to the fact that, with increasing total dose, various initiation steps leading to the generation of hydroxyl radicals (OH) via processes (v) and (viii) are facilitated which are responsible for the polymerization process [step (x)]. Termination of a growing polymeric chain can take place via process (xi) to produce the graft copolymer. A decrease in the percentage of grafting, with further

increase in the total dose, may be explained by the fact that at higher doses the termination of grafting by  $\beta$ -scission is accelerated (step xiii). Increase in the total dose may also lead to a decrease in the number of hydroperoxide groups and, hence, the percentage of grafting, by intramolecular abstraction of the hydroxyl radical by the tertiary alkyl radical on the polymeric backbone as shown below:



The percentage of grafting of sty increases to 76% at a total dose of  $0.64 \times 10^4$  Gy, beyond which it levels off. The initial increase in the percentage of grafting is due to the formation of a number of hydroperoxide groups on the polymeric backbone. The initiation of grafting reactions by hydroxyl radicals (OH) as discussed above decreased in the present case because the radiolytic products of methanol (CH<sub>3</sub>OH<sup>\$\lambda\$</sup>)  $\rightarrow$  CH<sub>2</sub>OH + H<sup>•</sup>) may kill some of the hydroxyl radicals because the presence of excess hydrogen atoms. This may lead to a decrease in the percentage of grafting.

## **Effect of Monomer Concentration**

Figure 2(a,b) represents the effect of monomer concentration on the percentage of grafting of 2-VP and sty. The percentage of grafting of both monomers increases with increasing monomer concentration and then decreases. The maximum percentage of grafting of 2-VP and sty (114 and 76%) is obtained at [2-VP] =  $1.8 \times 10^{-2}$  mol and [sty] =  $4.3 \times 10^{-2}$  mol, respectively. The decrease in grafting with further increase in monomer concentration may be due to that the homopolymerization becomes the preferred process. The monomer chain-transfer constant of 2-VP ( $C_M = 2.9 \pm 3.4 \times 10^{-5}$  at 55°C)<sup>19</sup> and sty ( $C_M = 0.279 \times 10^{-4}$  at 25°C)<sup>20</sup> also leads to wastage of the monomer in the side reactions, leading to decrease in the percentage of grafting.

The rate of grafting (Rg) of 2-VP and sty was evaluated as a function of the total initial monomer concentration from Figure 3(a,b) and the results are presented in Table II. It can be observed from the table that the rate of grafting of 2-VP increases with increase in the monomer concentration and then decreases. The maximum rate (0.386%/min) is obtained with  $[2\text{-VP}] = 1.8 \times 10^{-2}$  mol. Sty, on the other hand, shows a regular increase in the rate of grafting with increasing monomer concentration. The plot of log Rg versus log [M] for sty shows that the rate of grafting bears a linear relationship with the monomer concentration [Fig. 3(c)] and the monomer exponent was found to be 0.8.

#### Effect of Solvent System

The effect of water, methanol, and water-methanol on the percentage of grafting of 2-VP and sty was studied and the results are presented in Figure 4(a-c). It can be observed from Figure 4(a)that the maximum percentage of grafting (114%) of 2-VP is obtained using 10 mL of water, beyond which the grafting percentage decreases. When the grafting of 2-VP was attempted in a watermethanol system, it was observed that the percentage of grafting decreased with increase in the amount of methanol in the binary solvent system [Fig. 4(b)]. The volume of the binary system was kept constant at 10 mL. The decrease in grafting with an increasing amount of methanol may be due to the various chain-transfer reactions leading to wastage of the monomer. However, in the case of sty, the percentage of grafting increased with an increasing amount of methanol and then decreased. Maximum grafting (75%) was obtained using  $N_{CH_{3}OH} = 0.38$  (1 : 1, v/v  $H_{2}O$  :  $CH_{3}OH$ ). When grafting of sty was attempted in the water medium and in the methanol medium separately, it was observed [Fig. 4(c)] that the percentage of grafting of sty increases with an increasing amount of water, giving a maximum (40%) in 15 mL of water, remained constant in 20 mL H<sub>2</sub>O, and then decreased. However, in methanol, the maximum grafting of sty (80%) was obtained using 5 mL of methanol, beyond which it decreased.

Thus, from the results, it is observed that the percentage of grafting of sty decreases from 80% obtained in pure methanol to 75% obtained in the water-methanol system. Thus, a methanol or methanol-water solvent system (1 : 1, v/v) affords a better grafting medium for sty than does a solely aqueous medium, which is found to be a better medium for 2-VP grafting.

## REFERENCES

- 1. Umezawa, M.; Hirota, K. Nippon Hoshasen Kobunshi Kenkyu Kyokai Nempo 1962, 4, 241.
- Torikai, S.; Kubo, M.; Mukoyama, E. Kobunshi Kagaku 1964, 21(226), 132.
- Pruzinec, J.; Jambrich, M.; Kadlecik, J. Chem Vlakna 1983, 33(4), 158.
- Garnett, J. L.; Yen, N. T. Aust J Chem 1979, 32, 585.
- Lee, H. B.; Shim, H. S.; Andrade, J. D. Report 1972, COO-2147-1, 11 pp. Avail. Dep. NTIS from Nucl Sci Abstr 1972, 26(20), 47774.
- Miura, M.; Kawamatsu, S. Kobunshi Kagaku 1962, 19, 175.

- Kadonaga, M.; Abe, K.; Iida, K.; Ueda, N.; Furushashi, A.; Matsuo, H.; Matsuyama, K. Nippon Isotope Kaigi Hobunshu 1961, 4, 340.
- Misra, B. N.; Sood, D. S.; Kaur, I. J Polym Sci Polym Chem Ed 1985, 23, 1749.
- Kaur, I.; Sood, D. S.; Misra, B. N. J Polym Sci Polym Chem Ed 1989, 27, 53.
- Kaur, I.; Kumar, S.; Chauhan, G. S.; Misra, B. N. J Appl Polym Sci 1990, 41, 1171.
- Kaur, I.; Misra, B. N.; Barsola, R. Polym Prepr 1990, 32, 192.
- Kaur, I.; Kumar, S.; Misra, B. N. Polym Polym Compos 1995, 3, 375.
- McGary, C. W., Jr. J Polym Sci Polym Chem Ed 1960, 46, 51.
- Chien, J. C. W.; Vandenberg, E. J.; Jobloner, H. J Polym Sci A-I 1968, 6, 381.
- Zolotova, N. V.; Denisov, E. T. J Polym Sci A-I 1971, 9, 3311.
- Carlsson, D. J.; Wiles, D. M. J Macromol Sci Rev Macromol Chem C 1976, 14, 65.
- Carlsson, D. J.; Wiles, D. M. Macromolecules 1969, 2, 597.
- Carlsson, D. J.; Clark, F. R. S.; Wiles, D. M. Text Res J 1976, 46, 590.
- Howard, G. J.; Lai, S.-H. J Polym Sci Polym Chem Ed 1979, 17, 3273.
- 20. Burnett, G. M. Q Rev (Lond) 1950, 4, 292.