

# Grafting of Polypropylene Fibers. I. Radiation Grafting of Vinyl Monomers, Dyeing, and Hydrophilic Characteristics of the Grafted Polymer

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## Synopsis

Radiation-initiated grafting of methacrylic acid, acrylonitrile, and vinyl acetate on polypropylene fibers and the moisture content and dyeing characteristics of the grafted fibers have been reported. The extent of grafting with methacrylic acid is quite large when compared to acrylonitrile and vinyl acetate. The grafted fibers show an increase in moisture content with increase in the amount of graft. In general, the dyeability with disperse dyes increases due to grafting. In the case of cationic dyes, the polypropylene fibers grafted with methacrylic acid and acrylonitrile alone could be dyed.

## INTRODUCTION

Polypropylene is a hydrophobic material lacking in either hydrophilic or reactive groups. In order to improve its properties in the desirable direction many attempts have been made to graft vinyl monomers by various techniques. Peroxidation method was adopted for grafting of acrylonitrile onto polypropylene.<sup>1</sup> Polypropylene articles were made more receptive for dyeing by grafting on them a mixture of isopropenyl pyridine and methyl methacrylate.<sup>2</sup> Postirradiation grafting method was employed for grafting acrylic acid onto polypropylene using Van de Graaff accelerator and the dyeing properties with rhodamine were studied.<sup>3</sup> Sakurada et al.<sup>4</sup> have studied the grafting of polypropylene with styrene-SO<sub>2</sub> mixture by postirradiation method and investigated the dyeing characteristics of the product. Sharnberg and Hoigne<sup>5</sup> have studied the grafting of various vinyl monomers onto polyester, polyamide, polypropylene, and polyacrylonitrile and found that maximum grafting was attained at the glass transition temperature of the base polymer. We have earlier reported on grafting of acrylic acid onto polyester,<sup>6,7</sup> polyamide,<sup>8</sup> polyformaldehyde,<sup>9</sup> and polypropylene<sup>10</sup> by both radiation and chemical methods. In this paper we are reporting on the radiation-initiated grafting of methacrylic acid, acrylonitrile, and vinyl acetate onto polypropylene in the presence of scavengers, their dyeing characteristics, and hydrophilicity. The results obtained are discussed.

## EXPERIMENTAL

**Fiber.** The fiber used is melt-spun, isotactic polypropylene fiber, Tubes' obtained from Monte Catini Edison Group, Italy, having an m.p. of 170–175° and capacity of 4-5 g/d Tex.

**Monomers.** All monomers used were of commercial quality and they were distilled before use.

**Dyes.** The following dyes were used:

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Disperse dyes

Dispersol Red A 2 B pdr (CI) Disperse Red 82)  
Dispersol Red C 3 B gran (CI) Disperse Red 15)

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Cationic dyes

Sandocryl Red B6B (C.I) Basic Violet 16)  
Sandocryl Blue B3G (C.I.) Basic Blue 3)  
Sandocryl Orange B G (C.I) Basic Orange 21)

**Radiation source.** A cobalt-60 gamma source of 300 Krad/h strength was used for these studies. For varying dose rates, different  $\gamma$ -cells were employed.

**Process of grafting.** The grafting was carried out in contact with monomer solutions in the presence of reagents for homopolymer suppression. The system was purged with oxygen-free nitrogen before irradiation.

Acrylonitrile was irradiated in dimethyl formamide solution containing M/50 CuSO<sub>4</sub>. Vinyl acetate and methacrylic acid were grafted in methanol solution and in aqueous solution containing M/50, CuSO<sub>4</sub>.

**Hydrolysis of acetyl group.** The hydrolysis of the grafted vinyl acetate was carried out with 0.01% alcoholic KOH at 60° for 2 h keeping liquor ratio of 50.

**Removal of homopolymer.** The homopolymer was removed by treatment with appropriate solvents, namely DMF for polyacrylonitrile, methanol for polyvinyl acetate, and boiling water for polymethacrylic acid.

## RESULTS AND DISCUSSION

The amount of grafting on the polypropylene fiber with vinyl acetate acrylonitrile and methacrylic acid are shown in Table I. It is observed that with all the monomers, the yields increase with increased radiation dose. Since the amount of graft formation for methacrylic acid is very high at higher concentrations of the monomer, the results obtained only at lower concentrations of 5 and 10% are shown in Figure 1. Graft yields for 20% concentration for various dose rates are shown in Figure 2.

**Methacrylic acid.** Unlike acrylic acid with polypropylene, wherein a saturation grafting of ~ 29% was observed,<sup>10</sup> at 50% concentration of the monomer, with methacrylic acid for the same dose a graft yield of ~ 270% is observed which is a ninefold increase. This can be explained by assuming that a three-dimensional network structure formation takes place with acrylic acid, which is not so with methacrylic acid. Figures 1 and 2 show an acceleration at

TABLE I  
Percentage Grafting of Various Monomers onto Polypropylene for Different Concentrations  
at 27°C

Total dose (M rad)	Monomer concentration 20% % Graft		Monomer concentration % Graft		
	VA	AN	VA (40%)	AN (40%)	MAA (50%)
0.3	1.33	1.54	5.82	2.36	9.2
0.45	—	—	15.53	—	—
0.60	8.87	3.23	23.17	—	89.8
0.90	11.85	5.41	29.78	7.78	186.3
1.20	18.80	—	—	17.30	276.3
1.50	—	8.32	—	28.20	—
1.80	—	9.95	—	40.00	—

all concentrations of the monomer except at the 5% concentration and the three dose rates studied. At low concentrations the acceleration is not observed due to low grafting yield. In all cases, the stage (i.e., the concentration at which the acceleration begins) decreases with both the decrease in the dose rates as well as the monomer concentration. This leads one to believe that the "viscosity effect" does not play an important role, but chain transfer from the growing grafted chain occurs to the backbone polymer, thus starting a new graft chain, as is observed in grafting reactions. From Figure 1, it could be seen that the initial rate of grafting depends upon the monomer concentration and increases with the increase in concentration of the monomer. As shown in Figure 2, 20% concentration indicates that the initial rate of grafting increases

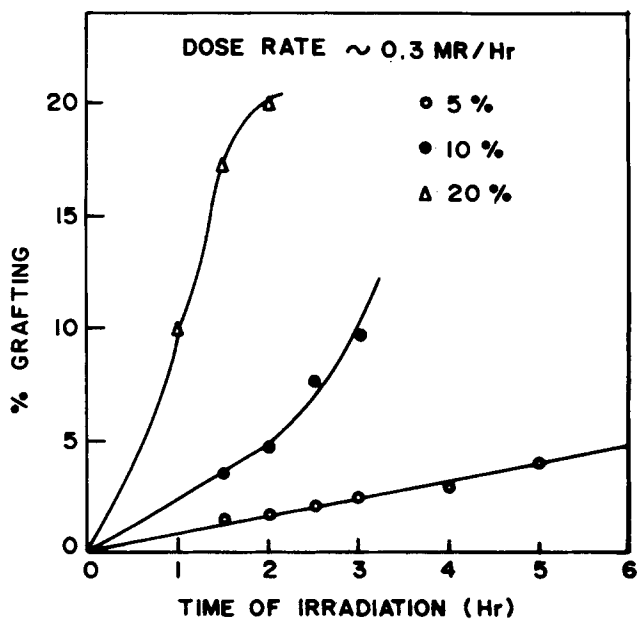


Fig. 1. Grafting of methacrylic acid-poly propylene at various concentrations. Dose rate 0.3 MR/hr. (○) 5%, (●) 10%, (△) 20%.

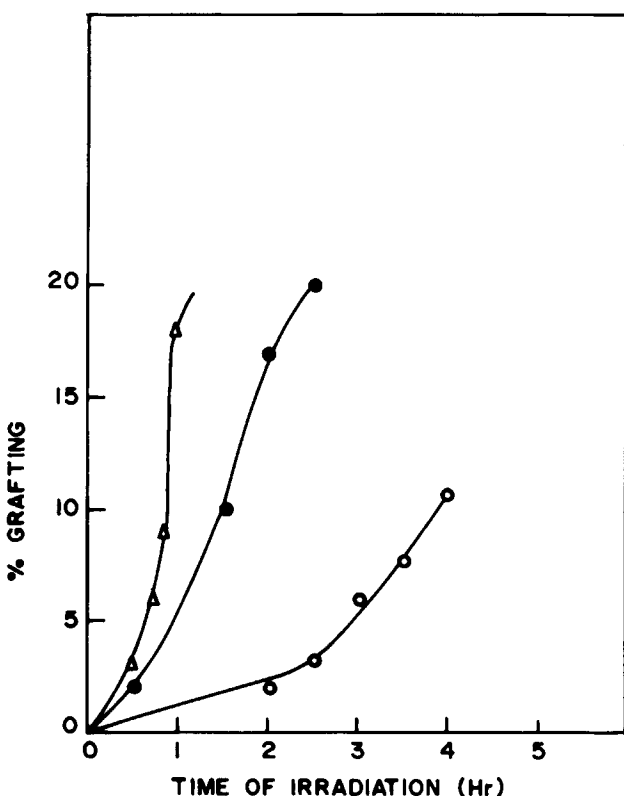


Fig. 2. Grafting a methacrylic acid with polypropylene as a function of dose rate, (○) 0.1 MR/hr, (●) 0.3 MR/hr, (△) 0.6 MR/h.

with the increase in the dose rate. Since the yields determined in the initial level of grafting are very low, the accuracy of measurement is not high. Besides, an autoacceleration is observed even in the initial stage. Hence, a definitive kinetic scheme cannot be suggested. The effect of temperature on the rate of grafting is minimal and only a small positive energy of activation is observed.

**Vinyl acetate.** From Table I it is observed that the grafting yield increases with increase in the concentration of the monomer.

**Acrylonitrile.** When using acrylonitrile in DMF solution and  $M/50$   $\text{CuSO}_4$  as scavenger, it was observed that, in addition to grafting, there was always a certain amount of homopolymer formation with its precipitation. This can be explained as being due to the chain transfer from the polymer to the monomer leading to homopolymer formation. The chain transfer constant  $C_m$  is known from literature and is found to be  $2.6 - 3.0 \times 10^{-5} \text{ dm}^3 \text{ M}^{-1} \text{ s}^{-1}$  (11).

If the radical  $\text{CH}_3-\overset{\text{CN}}{\underset{|}{\text{C}}}\dot{\text{H}}$  is not scavenged by  $\text{Cu}^{++}$  it adds on to the monomer to form a homopolymer. Infrared spectra of acrylonitrile grafted polymer (Fig. 3) shows two peaks at  $2262$  and  $1613 \text{ cm}^{-1}$  characteristic of the nitrile group. In addition, there are peaks of medium intensity observed at  $1666$  and  $3268 \text{ cm}^{-1}$ , indicating the presence of  $-\text{C}=\text{N}-$  bands. The data in

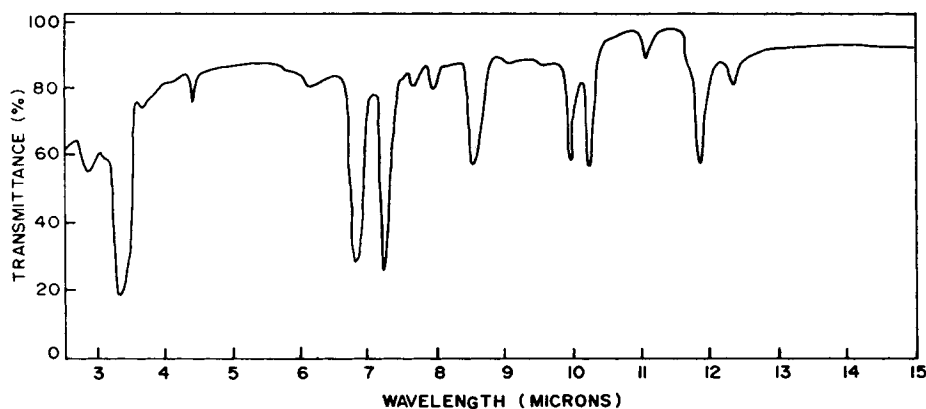


Fig. 3. Infrared spectra of polypropylene fibers grafted with acrylonitrile.

Table II for the grafting of acrylonitrile at various temperatures show that the yield decreases with increase in temperature. This leads us to believe that predominant chain transfer to the monomer is taking place instead of propagation or chain transfer to the backbone polymer leading to an increase in grafting. This suggests that, in addition to usual chain transfer to the monomer that normally takes place at  $\cdot\text{C}=\text{C}$ , transfer could also be taking place through  $-\text{C}=\text{N}$ . This leads to the end group being  $-\text{C}=\text{NH}$ .

#### Moisture Content of the Grafted Polypropylene (PP fibers)

The moisture content of the grafted polypropylene fibers are shown in Figure 4. In general, increasing the amount of graft on polypropylene fibers increases the amount of moisture regain, showing the hydrophilicity of the fibers grafted with these monomers.

TABLE II  
Amount of Methacrylic Acid and Acrylonitrile Grafted onto Polypropylene at Various Temperatures<sup>a</sup>

Total dose (M rad)	Methacrylic acid 30% V/V % Graft			Acrylonitrile 20% V/V % Graft		
	Temperature °C			Temperature °C		
	27	37	47	27	37	47
0.15	—	0.7	0.76	—	—	—
0.20	—	1.5	1.05	—	—	—
0.225	2.15	—	2.40	—	—	—
0.250	—	2.33	—	—	—	—
0.300	3.12	3.53	4.08	2.35	0.8	0.5
0.450	—	—	—	2.80	1.9	1.25
0.600	—	—	—	3.2	3.5	2.33
0.750	—	—	—	3.4	4.4	1.99
0.900	—	—	—	4.9	5.4	3.00

<sup>a</sup>Dose rate 0.3 M rad/h.

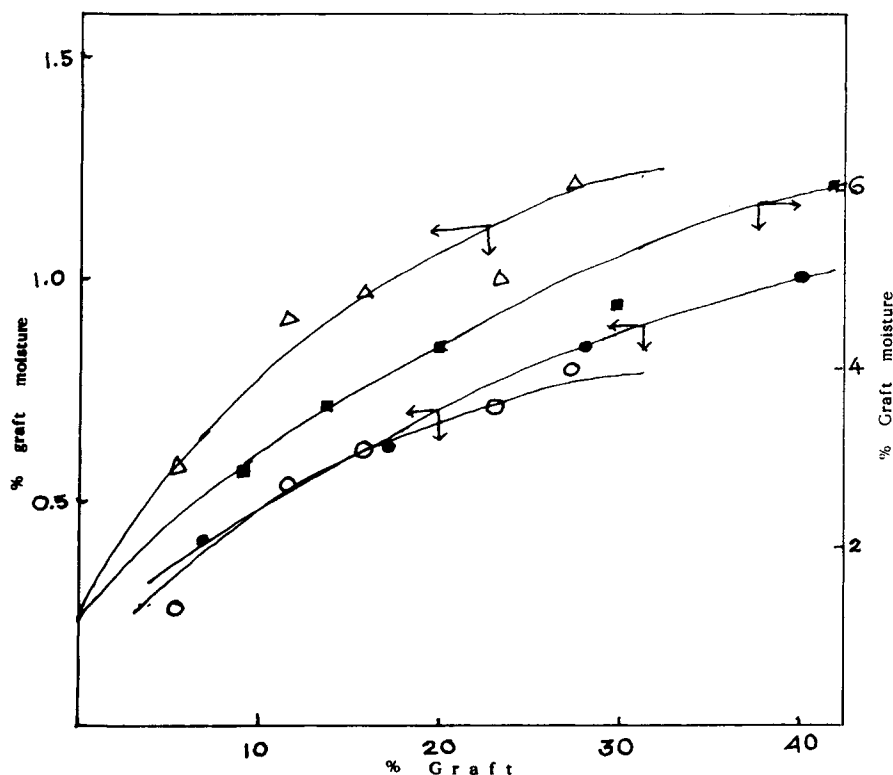


Fig. 4. Moisture uptake of grafted fiber: ( $\Delta$ ) PP-VA (hydrolyzed); ( $\circ$ ) PP-VA (unhydrolyzed); ( $\bullet$ ) PP-An; PP-MAA ( $\blacksquare$ ).

The increase in moisture regain was highest in case of methacrylic acid-grafted polypropylene fibers. Thus, at 29.7% methacrylic acid graft the moisture regain was raised to 4.7% from 0.2%, while the corresponding values for the vinyl acetate and acrylonitrile grafts were 0.8% and 0.9%, respectively. In the case of hydrolyzed vinyl acetate PP fibers it was around 1.21%. The results indicate that the presence of carboxylic group is responsible for the increase in the moisture uptake with methacrylic acid. Since the vinyl acetate and acrylonitrile polymers are not hydrophilic in nature, their grafting does not increase the moisture uptake to any great extent. Even with the hydrolyzed polyvinyl acetate-grafted material, the increase is not very much, except for a marginal increase. Perhaps all the acetate groups are not completely converted into hydroxyl groups.

#### Dyeability of the Grafted Polypropylene Fibers with Disperse Dyes

The control polypropylene fibers were not dyeable with disperse dyes under the conditions of study of the present investigation, namely 130°C and 1 h time of dyeing. In general, as is seen in Figure 5, the disperse dye content values increase as the amount of graft increases. The 18.8% vinyl acetate-grafted polypropylene fibers had dye content of 8.70 g/kg. in case of C.I.

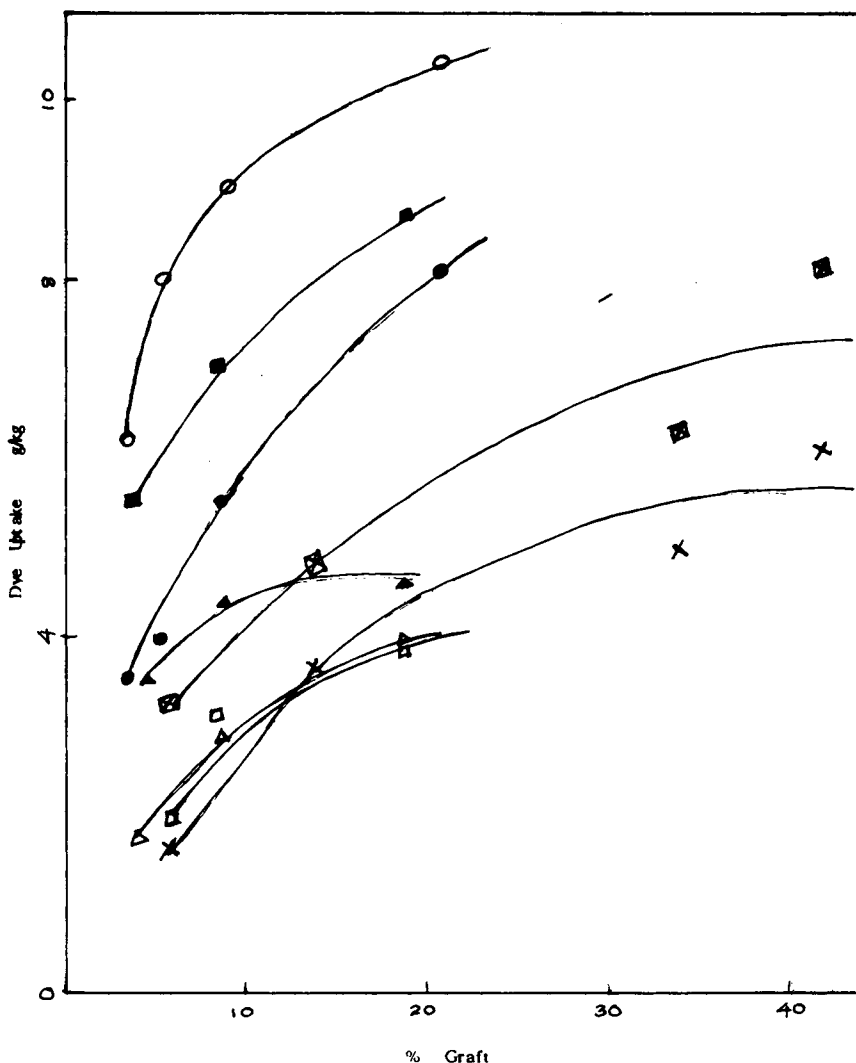


Fig. 5. Dispersion dye uptake of grafted fibers: ( $\Delta$ ) PP-AN CI Disperse Red 82, ( $\bullet$ ) PP-AN-Disperse Red 15, ( $\times$ ) PP-MAA CI Disperse red 82, PP-MAA-Disperse Red 15, ( $\blacksquare$ ) PP-VA (unhydrolyzed) CI Disperse Red 82, ( $\square$ ) PP-VA (hydrolyzed) CI Disperse Red 82, ( $\triangle$ ) PP-VA (hydrolyzed) CI Disperse Red 15, ( $\blacktriangle$ ) PP-VA (unhydrolyzed) CI Disperse Red 15.

Disperse Red 82, and for the same amount of graft 4.6 g/kg. of C.I. Disperse Red 15. The effect of hydrolysis of acetyl groups of vinyl acetate-grafted material is to decrease the dye uptake as seen from the value of 3.9 g/kg and 3.95 g/kg of fibers in case of C.I. Disperse Red 82 and C.I. Disperse Red 15, respectively. The dyeability imparted to the polypropylene fibers is a result of the opening of the polymer structure during grafting reaction. The opening of the polymer structure is probably dependent on the amount of graft introduced into the fibers. The decrease in the amount of dye content as a result of hydrolysis of acetyl groups in vinyl acetate-grafted polypropylene fiber is as a result of the increase in the hydrophilicity of the fiber.

The disperse dye content of the methacrylic acid-grafted (41.7%) and acrylonitrile-grafted fibers (20.7%) for C.I Disperse Red 15 and C.I. Disperse Red 82 are 6.08g/kg., 8.10 g/kg, and 10.4 g/kg and 8.05 g/kg of fibers, respectively. This again shows that the polymer structure is opened up as a result of grafting of methacrylic acid and acrylonitrile onto polypropylene fibers. It is interesting to note that the nature of graft also follows the same order for the increasing order of hydrophilicity.

### Dyeability of the Grafted Polypropylene Fibers with Cationic Dyes

The ungrafted as well as vinyl acetate-grafted and hydrolyzed vinyl acetate-grafted polypropylene were not dyeable with cationic dyes. The methacrylic acid-grafted as well as acrylonitrile-grafted polypropylene fibers

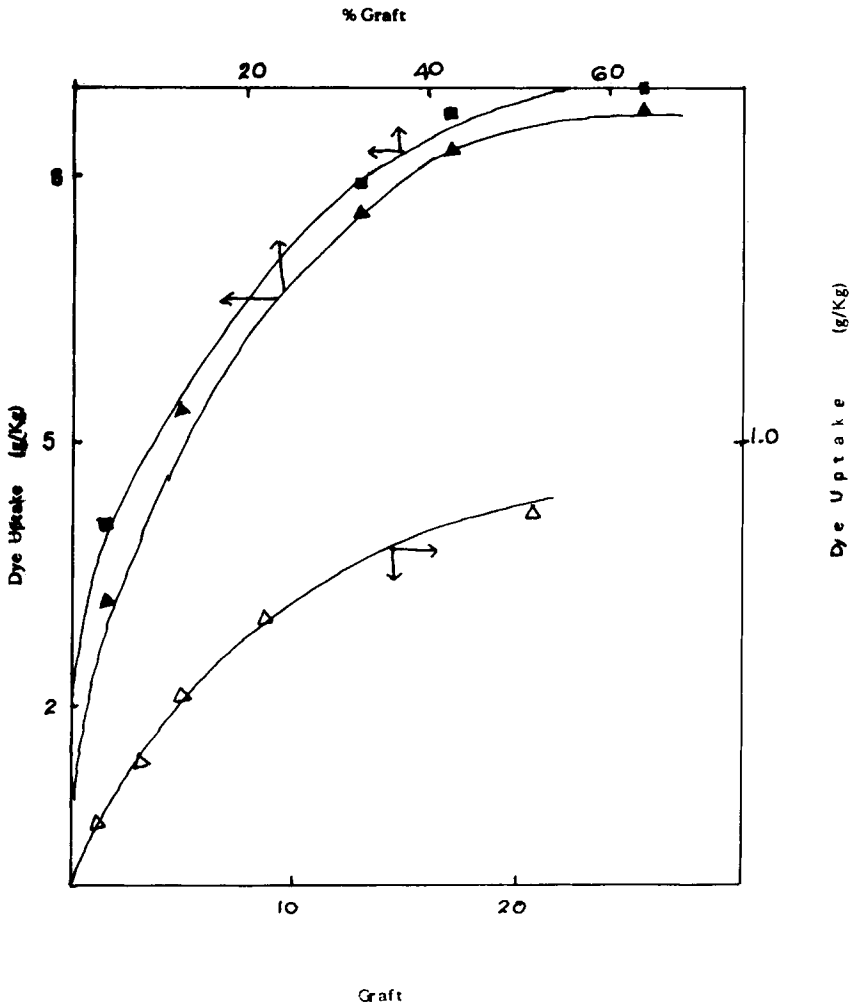


Fig. 6. Cationic dye uptake of grafted fibers: ( $\Delta$ ) PP-AN (CI basic orange 21), ( $\blacksquare$ ) PP-MAA (CI basic violet 16), ( $\blacktriangle$ ) PP-MAA (CI basic blue 3).



were imparted dyeability as a result of introduction of carboxyl and nitrile groups in the fiber structure. Both of these functional groups possess attraction for the cations of the cationic dye molecules which get fixed at these groups. The data are shown in Figure 6.

In conclusion, it can be said that a suitable monomer-grafted polypropylene has superior moisture and dye-uptake properties.

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