

Radiation-Induced Graft Copolymerization of Methacrylic Acid onto Polypropylene Fibers VI. Dyeing Behavior

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Synopsis

The dyeing behavior of polypropylene-*g*-polymethacrylic acid fibers prepared by graft copolymerization of methacrylic acid onto polypropylene fibers by gamma-ray irradiation was evaluated for their dyeability characteristics using two basic dyes, rhodamine B and methylene blue. An increase in the dye uptake and moisture regain with the increase in graft content was observed. Such behavior has been attributed to the hydrophilicity imparted to polypropylene fiber by the presence of polar carboxyl groups in polymethacrylic acid grafts. The dependence of rate of dyeing on the percentage graft was evaluated. The diffusion coefficient of the fiber showed an increase with the increase in graft content and has been related to the structural changes occurring during grafting.

INTRODUCTION

Polypropylene fiber has been commercially successful due to its cheapness, low density, chemical resistance, and excellent mechanical properties. However, high crystallinity and lack of any polar site in the fiber makes it very difficult to dye using existing classes of dyes.

A considerable amount of work has been carried out on graft copolymerization of vinyl monomers onto polypropylene with a view to improving its dyeability.¹⁻⁵ Sundardi^{6,7} has shown that grafting of hydrophilic monomers onto polypropylene fiber results in a marked increase in moisture regain and dyeability of the fiber. Interestingly, Simionescu et al.⁸ carried out grafting of benzidine on polypropylene fibers in alcoholic medium. The fibers thus obtained were diazotized and coupled with resorcinol, chromotropic acid, and β -naphthol to produce fibers of different colors.

This investigation aims at studying the effect of methacrylic acid grafting on the dyeing characteristics of polypropylene fiber.

EXPERIMENTAL

Materials

Polypropylene (E 0035), supplied by Indian Petrochemicals Corporation Ltd., Gujrat, India, was melt spun to get the monofilament. Methacrylic acid (Merck) was vacuum distilled at 70°C and 20 mm Hg⁹. Benzene and methanol (Glaxo Laboratories) were dried and distilled before use. Two basic dyes used for the study were rhodamine B, C.I. Basic Violet 10 (ICI), and methylene blue, C.I. Basic Blue 9 (BDH).

Grafting Reaction

Grafting of methacrylic acid onto polypropylene fiber was carried out in benzene and methanol at a monomer concentration varying in the range of 1–4 mole/L.^{9,10} The fiber was exposed to gamma radiation from a ⁶⁰Co source at dose rates of 24, 86, and 106 rad/s. A total dose of 0.1–0.3 Mrad was used in the present study. All the exposures were carried out under nitrogen atmosphere. After the desired period, fiber was taken out and Soxhlet extracted with methanol for 24 h to remove homopolymer. The grafted fiber, that is, polypropylene-*g*-polymethacrylic acid, was dried and weighed.

Dyeing and Dye Uptake

Dyeing was carried out at a pH of 5.5, keeping a material to liquor ratio of 1:500 at 100°C for various time periods in a high-temperature beaker dyeing machine. The dye concentration was kept at 1.0 g/L. The dyed sample was taken out and rinsed with fresh water followed by soap solution to remove any adhering dye on the fiber surface.

The dye uptake of the fiber was measured using a Unicam SP-600 spectrophotometer. The dye was extracted from the fiber in dimethylformamide, the extract was made up to known volume, and the optical density of the solution was measured. The dye content was calculated from a previously constructed calibration curve.

The diffusion coefficient of various samples was obtained using the expression¹¹

$$D = \frac{\pi a^2}{16t} \left[\frac{C_t}{C_\infty} \right]^2$$

where D is diffusion coefficient, a is the radius of fiber, C_t is dye uptake at time t , and C_∞ is the equilibrium dye uptake. In the present study C_∞ was taken as the dye uptake at 16 h.

Moisture Regain

Moisture regain of the fiber was measured at a relative humidity (RH) of 65% and at $26 \pm 2^\circ\text{C}$. A saturated solution of sodium nitrate in water was used to achieve the relative humidity of 65%.¹² The fiber was dried over P_2O_5 in a desiccator containing a saturated solution of sodium nitrate for 15 days. After such conditioning, the fiber was reweighed and moisture regain was calculated using the relationship¹²

$$\% \text{ Moisture regain} = \frac{(W - W_i)}{W_i} \times 100$$

where W_i is the weight of dry fiber and W is the weight of fiber after putting them over sodium nitrate solution,

RESULTS AND DISCUSSION

The dyeing behavior of ungrafted and methacrylic acid-grafted fiber with various graft levels is presented in Figures 1 and 2. From the results it may be seen that polypropylene has a negligible dye uptake even after 16 h of dyeing. On the other hand, the grafted samples show a considerable increase in the dye uptake. However, the rate of dye uptake starts decreasing at a faster rate beyond a dyeing time of 4 h and levels off at 16 h. To ensure the attainment of equilibrium dye uptake, the dyeing was carried out for 16 h.

An increase in the dye uptake with the increase in graft level may well be attributed to the increased interaction between the dye molecules and carboxyl groups present in the grafted chains. A plot between equilibrium dye uptake and the percentage graft is presented in Figure 3. From the results it may be seen that there is a linear increase in equilibrium dye uptake only up to 5.5% grafting, beyond which the increase becomes slower. The possibility of increased interaction between carboxyl groups at higher graft levels, which may occur through anhydride formation, may be ruled out because anhydride formation takes place at a temperature of $\approx 200^\circ\text{C}$,¹³ which is much higher than that used for dyeing. There of course remains a possibility of increasing steric factors with an increase in the graft level. Beyond a certain percentage of dye uptake, it may become increasingly difficult for the dye molecules to approach and react with the available carboxyl groups.

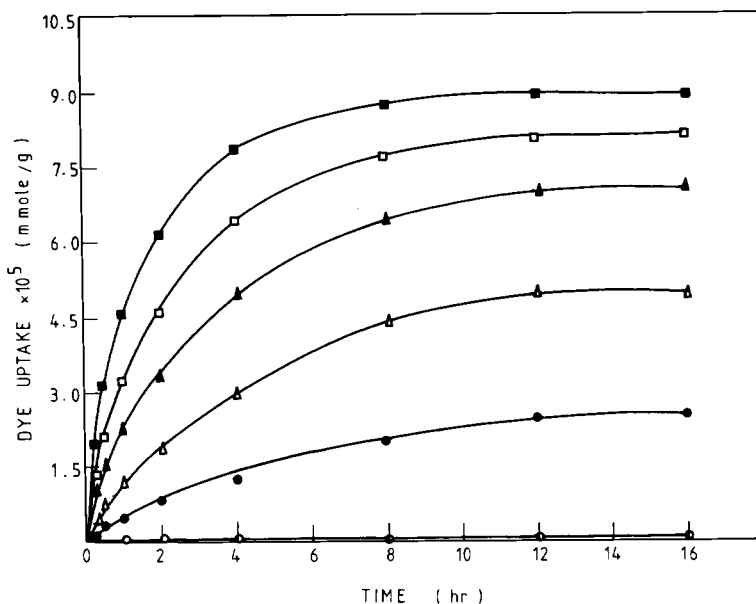


Fig. 1. Dyeing of polypropylene and polypropylene-*g*-polymethacrylic acid fibers with rhodamine B; (○) ungrafted PP fiber and PP-*g*-PMAA fibers with (●) 5.5% PMAA, (△) 11.5% PMAA, (▲) 21.0% PMAA, (□) 35.0% PMAA, (■) 50.0% PMAA.

The relation between diameter and equilibrium dye uptake for both the dyes is shown in Figure 4. Although diameter does not increase up to a graft level of 5.5%, the dye uptake shows a sharp increase. However, with further increase in graft level beyond 5.5%, an increase in diameter is accompanied by the increase in dye uptake, but in a different fashion than the increase when diameter remains same (below 5.5% graft).

The whole process of dyeing in an ionic system can be divided into three steps¹⁴: (1) adsorption of dye on the fiber, (2) diffusion of dye from the surface into the fiber, and (3) interaction of the dye with the dyeing site in the fiber.

In a dyeing process after an initial period, there is a diffusion-controlled phase followed by continuous dyeing phase. In the dyeing of PP-*g*-PMAA fiber, basic dye will react with the carboxyl groups present in the grafted chains. At a low level of grafting, below 5.5%, the dye will react with few but easily accessible carboxyl groups (at low graft levels, the grafting will be confined more to the fiber surface). As the graft level increases to incorporate more grafted chains, the backbone polymer chains will be pushed apart, thus increasing the diameter. For equilibrium dyeing to take place in such a sample, the dye molecule must diffuse through the fiber matrix before reaching and reacting with carboxyl groups. Hence the increase in diameter as well as diffusion phenomenon; both become responsible for the dye uptake behavior of the sample.

The relation between moisture regain and percentage graft is presented in Figure 5. Ungrafted polypropylene does not show any moisture regain

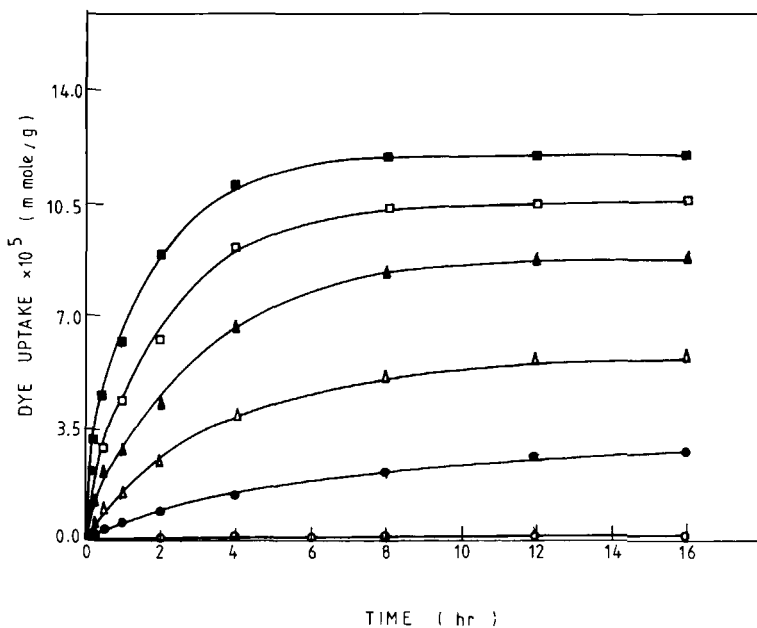


Fig. 2. Dyeing of polypropylene and polypropylene-*g*-poly(methacrylic acid) fibers with methylene blue; (●) ungrafted PP fiber and PP-*g*-PMAA fibers with (●) 5.5% PMAA, (△) 11.5% PMAA, (▲) 21.0% PMAA, (□) 35.0% PMAA, and (■) 50.0% PMAA.

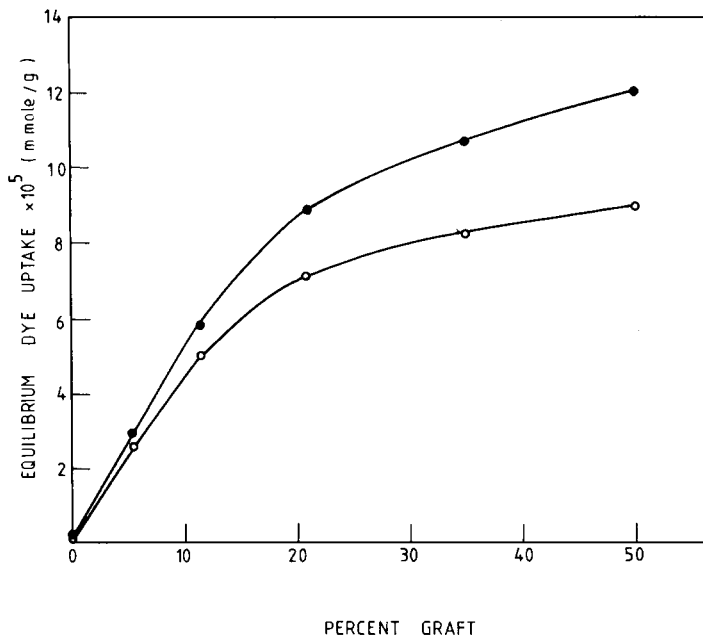


Fig. 3. Variation of equilibrium dye uptake with percentage graft in polypropylene-g-polymethacrylic acid fiber; (O) rhodamine B and (●) methylene blue.

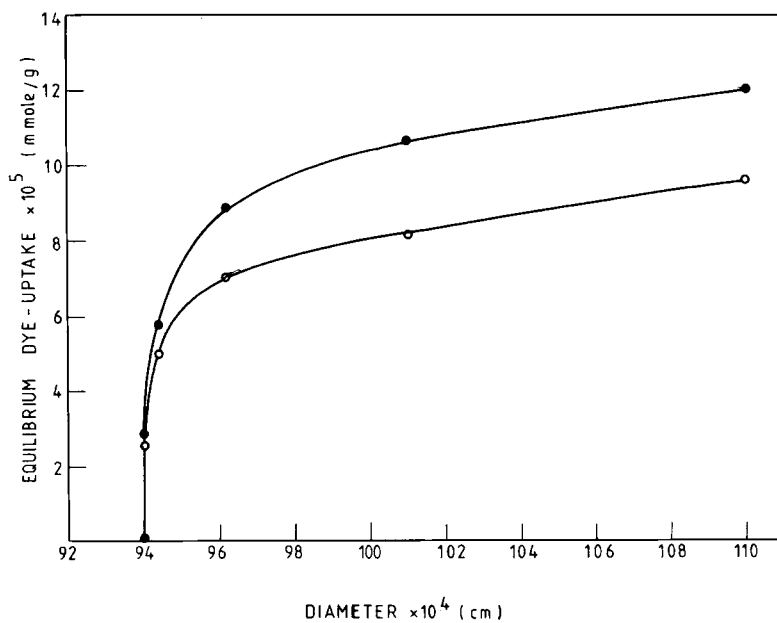


Fig. 4. Variation of equilibrium dye uptake with diameter of polypropylene-g-polymethacrylic acid fiber; (O) rhodamine B and (●) methylene blue.

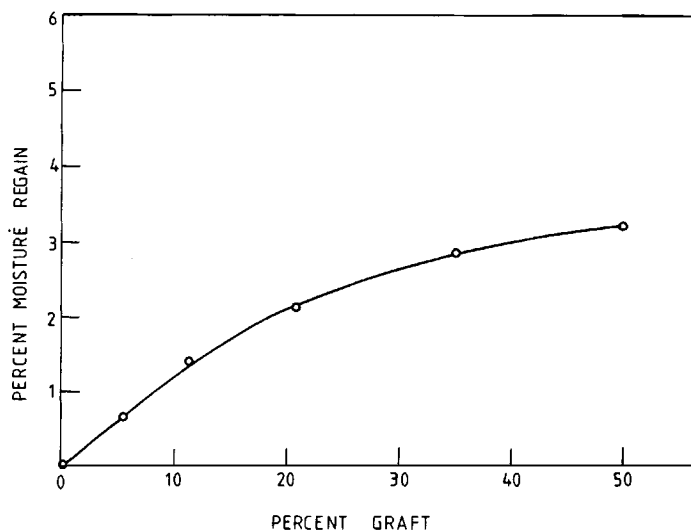


Fig. 5. Variation of moisture regain with percentage graft in polypropylene-*g*-polymethacrylic acid fiber.

at 65% RH, but it increases with the increasing percentage graft in polypropylene. An increase in the moisture regain of polypropylene fiber by the grafting of acrylic monomers has been reported by Lokhande et al.¹⁵ This is essentially due to the hydrophilic nature of the monomer used for grafting, which increases the hydrophilicity of the fiber by the incorporation of polar carboxyl groups into the fiber matrix and accounts for an increase in the moisture regain from 0.0% for polypropylene to 3.2% for the fiber with 50% graft content. Sundardi⁶ has also reported similar behavior for polypropylene fibers grafted with vinyl and acrylic monomers. This increased hydrophilicity appears to have a considerable contribution to an increase in the dyeability of the polypropylene fiber with basic dyes. This is also evident from the linear relationship between moisture regain and equilibrium dye uptake of both the dyes (Figure 6). However, methylene blue shows a higher dye uptake than rhodamine B. This should be due to the structure of the dye concerned and needs further study to elucidate the facts.

The typical plots of dye uptake (C_t) versus \sqrt{t} for various grafted samples are shown in Figures 7-9. The results can be summarized as

$$C_t = m \sqrt{t}$$

where C_t is dye uptake, m is the slope (rate of dyeing), and t is the time. A similar relation has been found in dyeing of basic dyeable polyacrylonitrile fiber.¹⁶ The rate of dyeing values for different fibers are presented in Table I. An increase in the rate of dyeing with increasing graft content is due to a higher number of carboxyl groups and increase in diameter with the increasing graft levels. The variation of rate of dyeing with percentage graft is shown in Figure 10. The plots for both rhodamine B and methylene blue

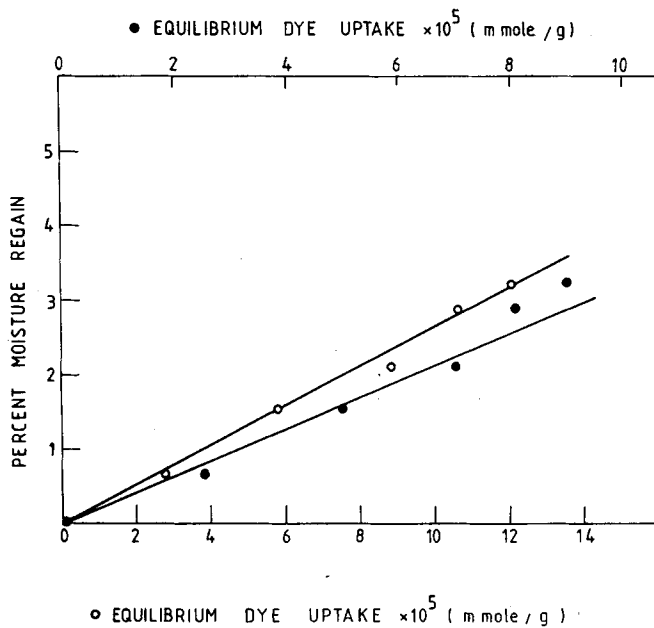


Fig. 6. Relation between moisture regain and equilibrium dye uptake; (○) rhodamine B and (●) methylene blue.

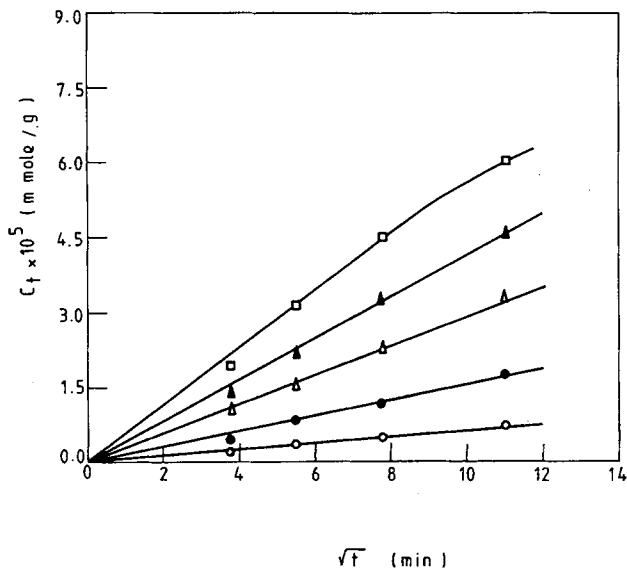


Fig. 7. C_t versus \sqrt{t} for rhodamine B on polypropylene-g-polymethacrylic acid fibers; (○) 5.5% PMAA, (●) 11.5% PMAA, (△) 21.0% PMAA, (▲) 35.0% PMAA, and (□) 50.0% PMAA.

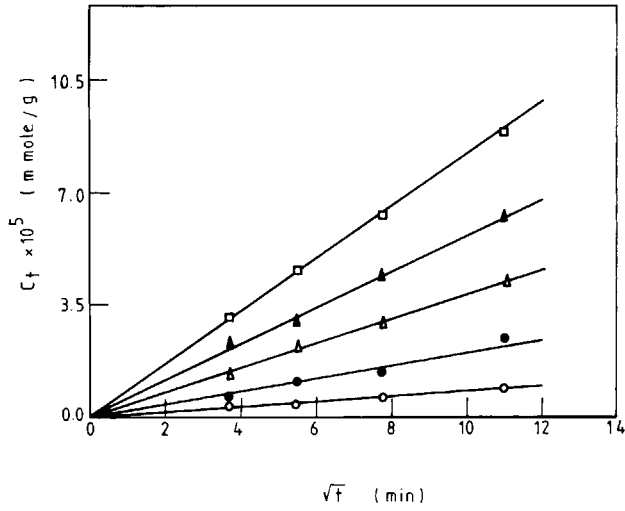


Fig. 8. C_t versus \sqrt{t} for methylene blue on polypropylene-*g*-polymethacrylic acid fibers; (○) 5.5% PMAA, (●) 11.5% PMAA, (△) 21.0% PMAA, (▲) 35.0% PMAA, and (□) 50.0% PMAA.

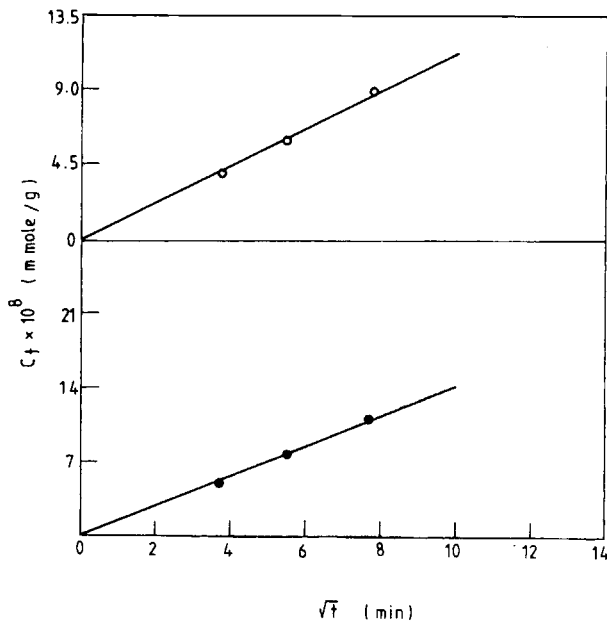


Fig. 9. C_t versus \sqrt{t} for ungrafted polypropylene fibers; (○) rhodamine B and (●) methylene blue.

TABLE I
Rates of Dyeing for Polypropylene-*g*-Polymethacrylic Acid Fibers

Percentage graft	$m \times 10^6$ (mmole/g min ^{1/2})	
	Rhodamine B	Methylene blue
Ungrafted PP	0.0113	0.0141
5.5	0.0649	0.7930
11.5	1.5800	1.9504
21.0	2.8251	3.8250
35.0	4.0870	5.7250
50.0	5.7752	7.9251

are linear over the whole range of graft levels studied. The dependence of rate of dyeing on the percentage graft can thus be represented as

$$Y = 0.229 + 0.112X$$

for Rhodamine B and

$$Y = 0.157 + 0.158X$$

for Methylene Blue. These equations should be considered valid within the grafted range studied. The slope values for rhodamine B (0.112) and methylene blue (0.158) indicate that the rate of dyeing varies at a faster rate for methylene blue dyeing than for rhodamine B. The extrapolated intercept values, that is, the rate of dyeing at 0.0% graft (ungrafted PP), however, does not coincide with the rate of dyeing of ungrafted polypropylene. This appears partially due to the change in voids and structural parameters of the fibers during grafting. These changes will have their own contributions in increasing the dyeing characteristics by regulating diffusion of the dye in the polymer matrix. This contribution will be over and above the dye

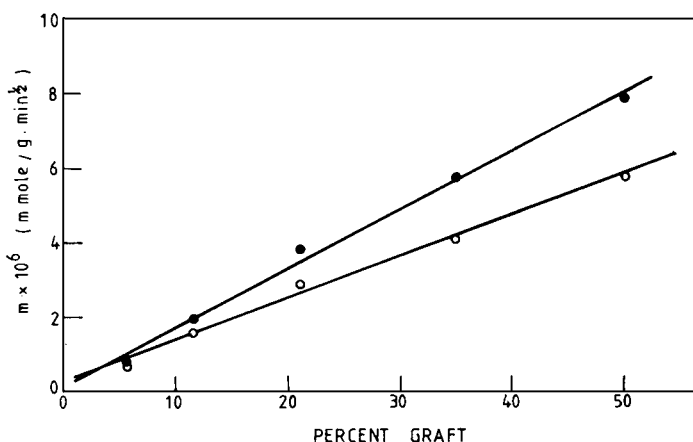


Fig. 10. Variation of rate of dyeing with percentage graft in polypropylene-*g*-polymethacrylic acid fiber; (○) rhodamine B and (●) methylene blue.

affinity imparted due to the incorporation of carboxyl groups in the polymer.

The diffusion coefficient (D) of various fibers is shown in Figure 11. An increase in the diffusion coefficient with the increasing graft content in the fiber was observed. It appears that the structural changes, such as denier and crystallinity of the fiber, have their own contribution to this increase in diffusion coefficient. The relation of diffusion coefficient with the denier of the fiber is presented in Figure 12. There is a steady increase in D with increase in denier. However, the increase is linear only in the initial phases. This may be expected because the denier of the fiber increases linearly with increase in graft content. Similar behavior has been observed by other workers.^{16,17}

In the initial stages, dyeing can directly take place on the samples, and the thicker the fiber, the more amenable is the structure for dye uptake. With progressive dyeing, diffusion of the dye takes place directly in the polymer segments, which are in the mobile phase due to the thermal agitation. Thus, the Hole (sufficient free volume) becomes large enough so that the segment and the dye can move freely.¹⁸⁻²⁰

Diffusion is obviously a function of the ease of penetration of the dye molecules through the noncrystalline regions of the fiber. The dyeing will thus be facilitated by the decrease in the degree of molecular order in the fiber. With the decrease in apparent crystallinity due to grafting, the dye molecules can easily approach the reactive sites in the unordered regions. Figure 13 reflects how the diffusion coefficient is dependent upon the crys-

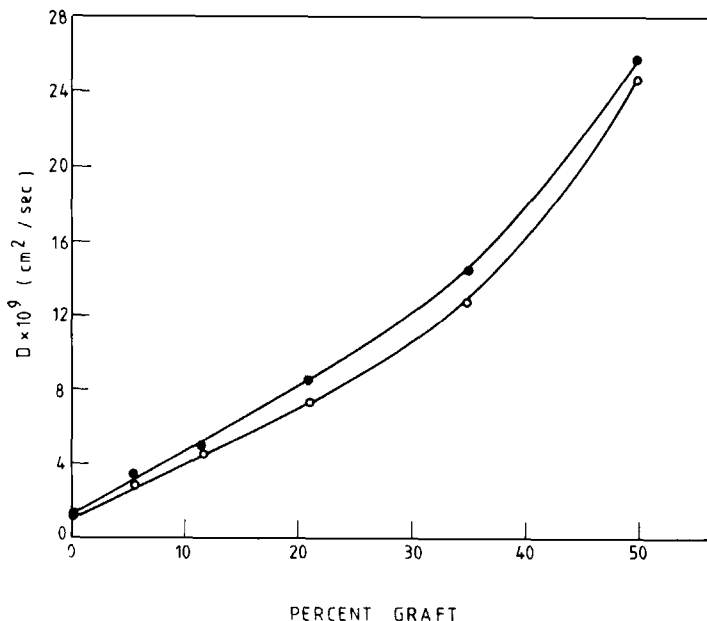


Fig. 11. Variation of diffusion coefficient with percentage graft in polypropylene-g-poly-methacrylic acid fiber; (○) rhodamine B and (●) methylene blue.

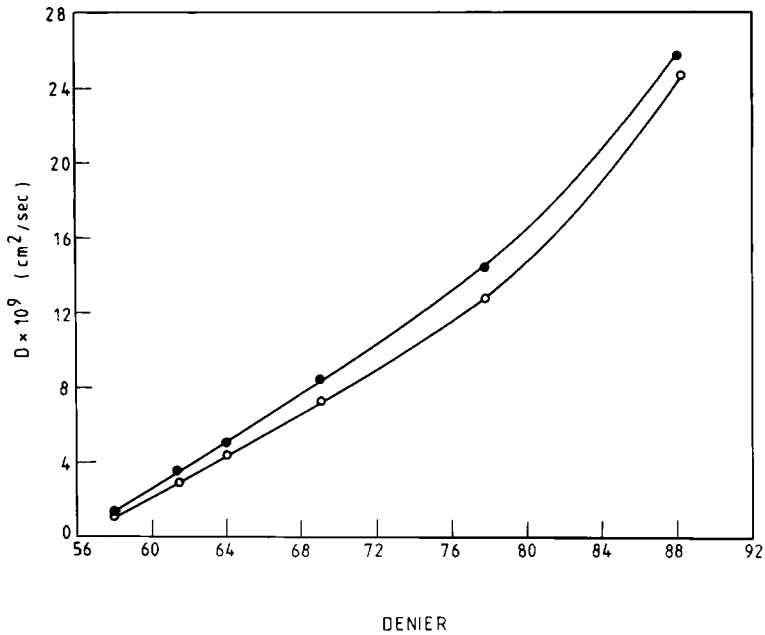


Fig. 12. Variation of diffusion coefficient with denier of polypropylene-*g*-polymethacrylic acid fiber; (○) rhodamine B and (●) methylene blue.

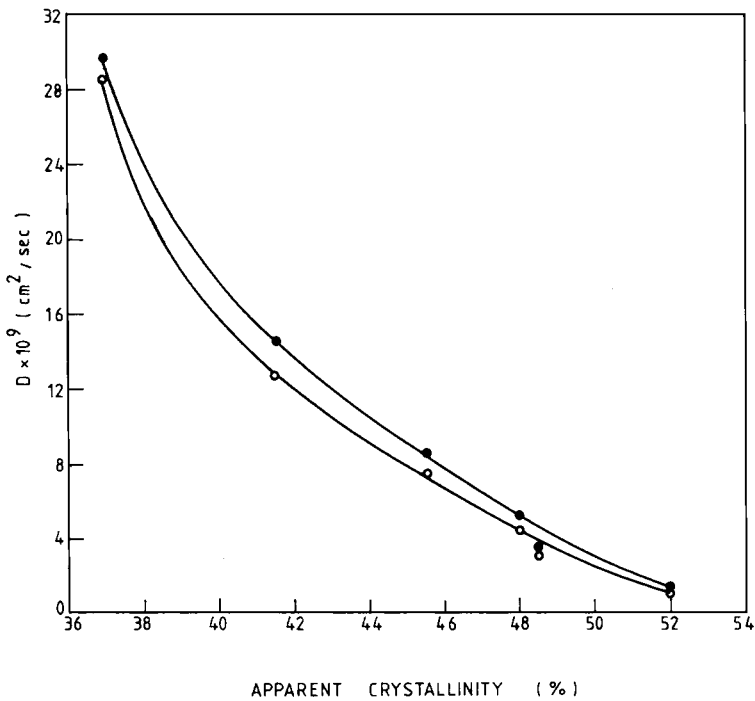


Fig. 13. Relation between diffusion coefficient and apparent crystallinity of polypropylene-*g*-polymethacrylic acid fiber; (○) rhodamine B and (●) methylene blue.

tallinity of the fiber. As the apparent crystallinity increases, the diffusion coefficient decreases irrespective of the dye taken.

However, the results do not provide a true relationship between dye uptake and apparent crystallinity. The decrease in crystallinity does not result from the destruction of the inherent crystalline region of the fiber by grafting. The graft copolymerization of methacrylic acid proceeds with the incorporation of amorphous PMAA chains in the noncrystalline region of the fiber, which in turn alter, the crystalline-amorphous ratio, thereby decreasing the degree of crystallinity.²¹ Therefore, it is essentially the dilution of inherent crystallinity of the fiber that appears as a decrease in crystallinity. The overall results are thus reflected in a sharp increase in diffusion coefficient at higher graft levels, that is, lower crystallinity.

CONCLUSIONS

The following conclusions may be drawn from the present investigation. The dyeability of polypropylene fibers for basic dyes could be achieved by the grafting of methacrylic acid. The rate of dyeing increases with the increase in graft level. The diffusion coefficient is simply related to the time period of dyeing. The dyeing is essentially a diffusion-controlled process. The rate of dyeing and, hence, the diffusion coefficient are also influenced by the thickness (denier), diameter, and crystallinity-amorphous ratio of the grafted samples.

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