Radiation-Induced Graft Copolymerization of Methacrylic Acid onto Polypropylene Fibers. III. Characterization

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Synopsis

Polypropylene-g-polymethacrylic acid graft copolymer, prepared by simultaneous-irradiation technique, was characterized to determine the structural changes, occurring in the copolymer. The presence of polymethacrylic acid graft in the copolymer was ascertained by infrared spectroscopy. Crystallinity of the grafted fibers, as deduced from X-ray diffraction pattern, showed a decrease with the increase in graft level in the fiber. Such a behavior has been attributed to the dilution of crystalline fraction of polypropylene by the incorporation of amorphous polymethacrylic acid chains in the fiber matrix, without disrupting the original crystallites of the backbone polymer. The density of the grafted samples showed a continuous increase with the increase in percent graft. However, the diameter did not change up to 16% graft content, beyond which an increase in the diameter was observed. This increase in diameter has been related with the sharp increase in disperse dye uptake of the grafted fiber at higher levels of grafting.

INTRODUCTION

A graft copolymer results from the chemical linkage of a growing macromolecular chain with the preformed polymer, thereby producing a branched structure.[1] The interaction of grafted moiety with the polymer backbone, nature of bonding, and the distribution of the graft chains strongly influence the properties of a graft copolymer. It, therefore, is of interest to determine the composition and structural changes in a copolymer, induced by graft copolymerization and to correlate them with the polymer properties.

Terada[2] carried out the grafting of 1-phthalimido-1,3-butadiene onto polypropylene by thermal mastication. It has been shown that the percentage of grafted monomer against feed can be determined by ultraviolet spectroscopy. Microinterferometry[3] has been successfully used for the determination of transversal distribution of the graft concentration, thus providing a qualitative tool to characterize a graft copolymer. Ohshika[4] studied the graft copolymerization of vinyl monomers onto chlorinated polypropylene, using benzoyl peroxide and UV rays as initiator and used infrared spectroscopy to prove that various monomers, such as acrylic acid, methyl methacrylate, acrylonitrile, and vinyl acetate can be grafted onto polypropylene. Similar technique has been used by Ikeda et al.[5] to characterize polypropylene fabric grafted with acrylic acid.

The present investigation aims to evaluate structural changes induced

in polypropylene as a result of graft copolymerization of methacrylic acid by simultaneous-irradiation technique.

EXPERIMENTAL

Materials. Various polypropylene-g-polymethacrylic acid (PP-g-PMAA) samples with different graft content were prepared by simultaneous irradiation-induced graft copolymerization of methacrylic acid onto polypropylene fibers, under different reaction conditions, as reported previously.[6,7]

Infrared Spectroscopy. The infrared spectra (IR) were measured on a Perkin-Elmer Model 580 B Infrared Spectrophotometer in the range of 400°–400 cm⁻¹.

X-Ray Diffraction. X-ray diffraction pattern (intensity vs. diffraction angle plot) was recorded in the range of diffraction angle $2\theta = 10$–$32°$ on a Philips X-ray diffractometer equipped with a scintillation counter. CuK_α radiation ($\lambda = 1.54$ Å) was used for these X-ray diffraction measurements. The X-ray diffractograms were obtained using following experimental conditions:

filament current = 30 mA
voltage = 40 kv
scanning speed = 1°/min

The degree of crystallinity of polypropylene was evaluated from the X-ray diffraction pattern by separating the crystalline and amorphous portions under the diffraction pattern, according to the method, reported in literature.[8,9] The intensity (I) vs. diffraction angle (2θ) plots were converted into Is^2 vs. s curves and the degree of crystallinity (X_{cr}) was calculated from the diffractogram, according to the following expression[8,9]:

$$X_{cr} = \frac{\int_0^\infty s^2 I_{cr}(s) \, ds}{\int_0^\infty s^2 I(s) \, ds} \cdot K \tag{1}$$

where $I_{cr}(s)$ is the coherent intensity in the crystalline peaks and Is is the total coherent intensity scattered. s is the scattering vector, represented as $s = (2/\lambda) \sin\theta$. K is the correction factor and, due to its uncertainty, has been taken as unity for evaluating the comparative study of the crystallinity.

Density. Density measurements for various PP-g-PMAA fibers were carried out at $26 \pm 2°C$, using a density gradient column (Davenport, London). The column was prepared using isopropanol (density = 0.783) and diethylene glycol (density = 1.115). The density of poly(methacrylic acid) was determined by making a film from solvent casting, using a column prepared from xylene (density = 0.857) and carbontetrachloride (density = 1.590).

The density of various samples was calculated by the following expression[10]:

$$\frac{1}{\rho} = \frac{(1-x)}{\rho_p} + \frac{x}{\rho_g} \tag{2}$$

where ρ is the density of copolymer, ρ_p and ρ_g are densities of ungrafted polypropylene and polymethacrylic acid, respectively, and x is the weight fraction of polymethacrylic acid, as obtained from $G/(1 + G)$ (G is the graft content). The densities ρ_p and ρ_g of polypropylene and polymethacrylic acid were used as 0.8975 and 1.3105 g/cm^3, respectively, as obtained from the density gradient column.

Diameter. Diameter of the fibers was determined using a projection microscope "Projectina." The diameter was calculated as an average of 25 values.

Dye Uptake. The dyeing of various samples with Dispersol Red B-3B (C.I. Disperse Red 11) was carried out in an aqueous medium under infinite dye-bath conditions, keeping the material to liquor ratio of 1:500. The dispersing agent was used to make the dye bath with a dye concentration of 1 g/L. Dyeing was carried out to a constant period of 16 h at 100°C. The fibers were then soaped with Sandozin N1S and washed with fresh water.

Dye uptake of the samples was measured using Unicam SP-600 spectrophotometer, by extracting the dye from the fiber in DMF.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The infrared spectra of samples have been shown in Figure 1. It can be seen from the figure that the spectra of original polypropylene is similar to that of irradiated polypropylene, which suggests that the exposure of polypropylene under the experimental conditions, does not bring about any detectable change in the polymer.

In the spectra of the grafted polypropylene samples, few peaks characteristic of polymethacrylic acid (PMAA) appear. The absorption in the region 1710 cm^{-1} may be ascribed to the carbonyl group of PMAA graft. Further, in the grafted samples, the intensity of few characteristic bands of polypropylene diminish and broadening of some other peaks takes place, showing that PMAA has been incorporated as a graft into the polypropylene matrix. Similar results have been obtained in the grafting of acrylic acid onto polypropylene fabric.[5]

The absorption in the region of 1170 cm^{-1} may be related to the crystalline nature of polypropylene fiber. In case of ungrafted fiber, spectra shows a doublet which consists of an intense band at 1170 cm^{-1} and a second band at 1152 cm^{-1}, occurring as a shoulder on the first one. Such a doublet has been assigned to the amorphous nature at 1156 cm^{-1}, occurring as a shoulder on the second more prominent band at 1167 cm^{-1}.[11] With the increase in PMAA content (essentially an amorphous polymer) in the grafted samples, the peak at 1152 cm^{-1} and 1170 cm^{-1} appear to merge together and its breadth increases. This appears to be due to the increase in the amorphous content in the grafted fiber.

X-Ray Diffraction

X-ray diffractograms of various samples have been presented in Figures 2 and 3. The diffraction curve of PMAA, recorded in the same region, does not show any diffraction peak, implying a completely amorphous structure
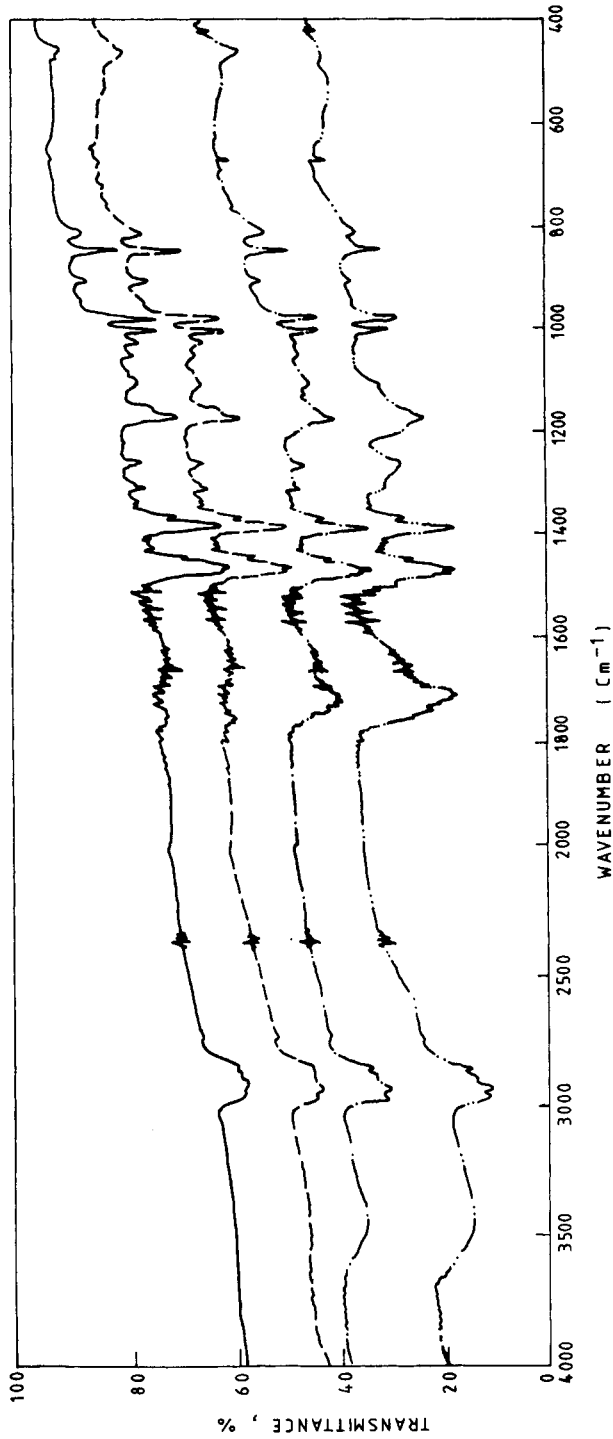
Fig. 1. Infrared spectra of polypropylene and polypropylene-*g*-polymethacrylic acid fibers: (—) ungrafted PP fiber; (-·-) irradiated PP fiber; and PP-*g*-PMAA with (—·—) 5.5% PMAA and (—···—) 21% PMAA.
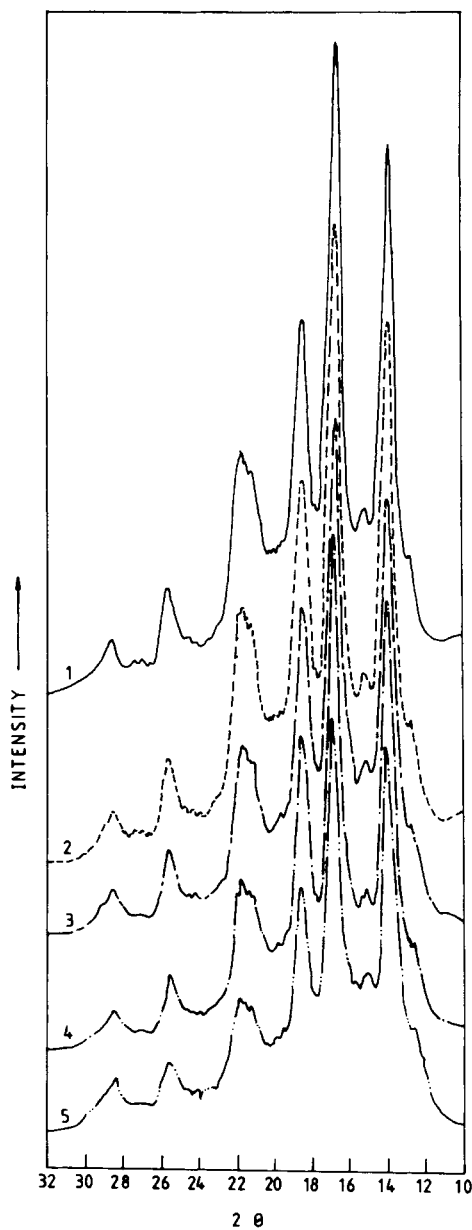
Fig. 2. X-ray diffractograms of polypropylene and polypropylene-*g*-polymethacrylic acid fibers: (—) ungrafted PP fiber; (--) irradiated PP fiber; PP-*g*-PMAA fiber with (— - —) 11.5% PMAA, (— · —) 21% PMAA, and (— · · —) 40% PMAA.
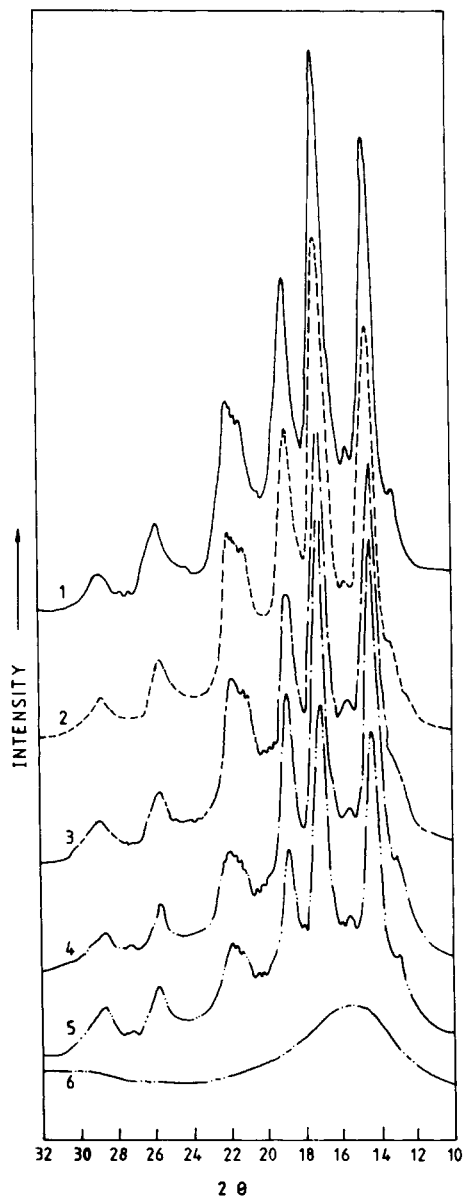
Fig. 3. X-ray diffractograms of polypropylene-g-polymethacrylic acid fibers: (—) 5.5% PMAA; (--) 16% PMAA (— ·—) 28% PMAA; (— · —) 35% PMAA; (— · · —) 50% PMAA; (— · · · —) PMAA.

of this component. The overall crystallinity calculated from these diffraction patterns thus represents the crystallinity of the polypropylene component and has been plotted against weight fraction of polymethacrylic acid in Figure 4.

The results show that the crystallinity decreases with the increase in the percent graft in the fiber. Since the crystalline reflections in the diffraction patterns of the grafted samples occur at identical diffraction angles as in polypropylene and no additional diffraction peak occurs in the grafted samples, it appears that PMAA is present as an amorphous phase only and the crystalline regions are contributed by the polypropylene sequences. The crystallinity may then be expressed in terms of a parameter "apparent crystallinity" $(X_{cr})_{app}$ of the PP-*g*-PMAA fibers; thus

$$(X_{cr})_{app} = \frac{X_{PP}}{1 + G} \tag{3}$$

where X_{PP} is the crystallinity of the ungrafted polypropylene and G is the graft content. The crystallinity of original polypropylene fiber was found to be 52.10% from X-ray measurements. The crystallinity values of various samples are in good agreement with those derived by using eq. (3) and gives a linear relationship between $52.10/(1 + G)$ vs. weight fraction of PMAA in the grafted fiber (Fig. 4).

These results suggest that the inherent crystallinity of the backbone polymer, i.e., polypropylene, is not impeded by the graft copolymerization of methacrylic acid and the grafting occurs only in the amorphous areas, without disrupting the crystallinity of the fiber. The decrease in the overall crystallinity of polypropylene then appears only due to dilution of crystalline fraction by the incorporation of amorphous PMAA chains into the fiber matrix.[12]
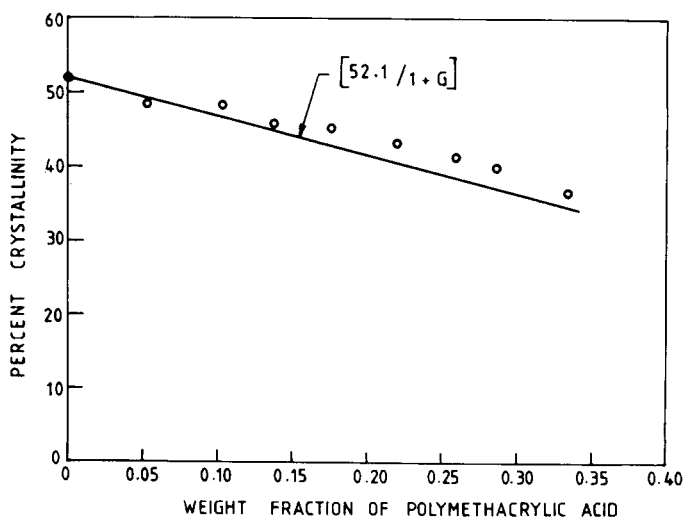

Fig. 4. Variation of percent crystallinity with weight fraction of polymethacrylic acid in polypropylene-*g*-polymethacrylic fiber.

Density

The density values of various PP-g-PMAA samples have been presented in Figure 5. It can be seen from the figure that the density increases with the increase in the graft content of PMAA. However, a linear increase in the density was observed only up to 16% graft level. The observed density values are higher than the calculated values [using the mixture rule relation, eq. (2)] except at higher graft levels, where the observed densities are much lower than their calculated values. Such a behavior of increase in density with the increase in the extent of grafting has been observed in other systems also.[13,14]

As a result of grafting of polypropylene fibers, an increase in density appears quite reasonable because of the higher density of the grafted moiety, i.e., PMAA, (1.3) than that of original polypropylene. A linear increase in the density of polyethylene with increasing degree of grafting up to 74% has been reported in polyethylene-g-styrene system.[15] But, in the present system, it appears that, up to 16% graft level, the diffusion process during the grafting reaction is not much affected and the grafting takes place in the interlamellar regions.[16] However, with further increase in grafting, the deviation from linear relationship may be attributed to the creation of a higher specific volume due to the pushing apart of polymer chains, so as to accomodate more PMAA grafts.[13] Similar behavior has been observed for polyethylene-g-styrene system,[16] where the density increases continuously with the increasing graft levels, but beyond 20% grafting the change is not rapid.

Diameter

The diameter of various samples has been presented in Figure 6. The results show that the diameter of the fiber remains almost unaffected up
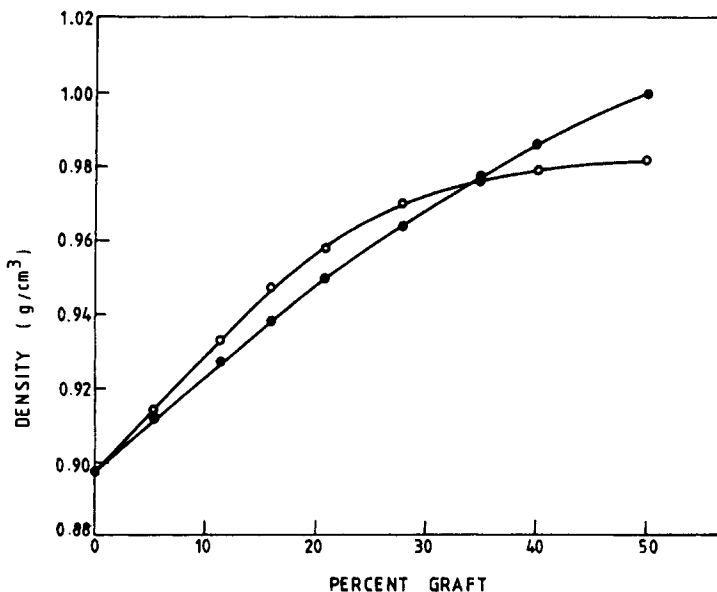

Fig. 5. Variation of density with percent graft in polypropylene-g-polymethacrylic acid fiber: (○) observed density and (●) calculated density.
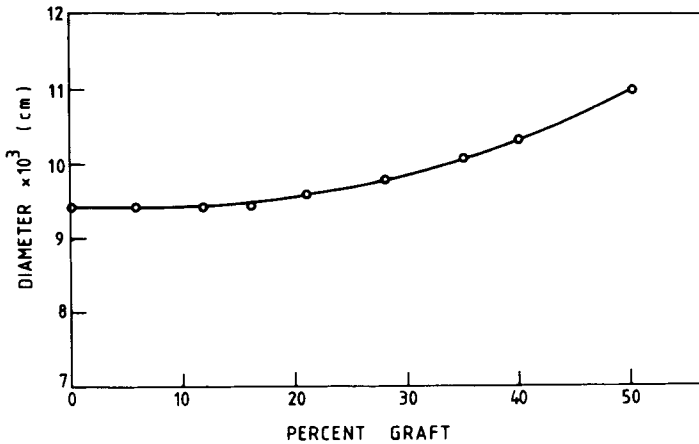
Fig. 6. Variation of diameter with percent graft in polypropylene-*g*-polymethacrylic acid fiber.

to 16% graft level, beyond which it increases continuously with the increase in the grafting up to 50%.

These results indicate a close relationship between the density and diameter of the fibers. Initially, the grafted PMAA is incorporated into the interlamellar region, it has produced no change in the diameter of fiber, but, obviously, density increases linearly. However, the diameter increases only beyond 16% graft level, where density behavior also deviates from linearity due to an increase in the specific volume of the fiber. Huang and Kanitz[16] has reported similar study involving the grafting of styrene to polyethylene film.

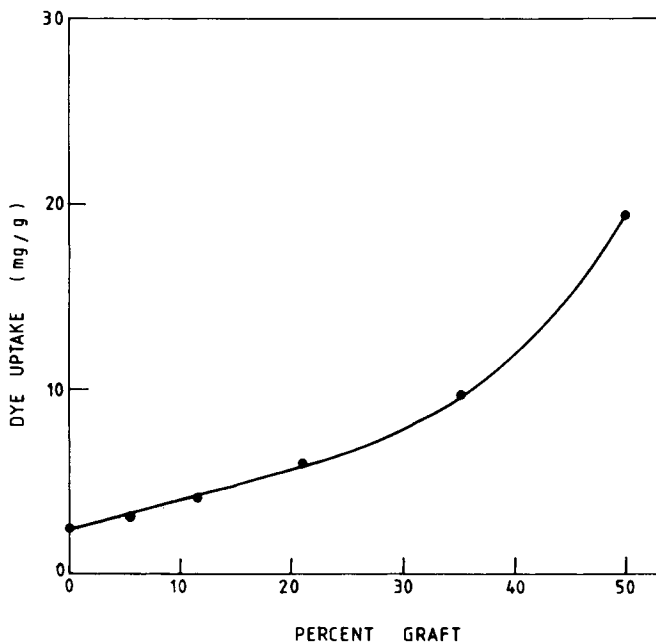

Fig. 7. Variation of dye uptake with percent graft in polypropylene-*g*-polymethacrylic acid fiber.

Dye Uptake

The dye-uptake values of various fibers with Dispersol Fast Red B-3 B has been presented in Figure 7. Initially, the grafted fibers show a slow increase in the dyeability with the increase in percent graft, in the fiber. This is followed by a sharp increase in the dye uptake at higher levels of grafting.

As the disperse dyeability is independent of the nature of the functional groups of the grafted polymer, but dependent upon the structural characteristics of the fiber, the initial increase in the dye uptake may be due to the decrease in the apparent crystallinity of the fiber. X-ray studies have shown that the apparent crystallinity decreases linearly with the percent graft (Fig. 4); its contribution in increasing the dye-uptake, therefore, may be kept constant. Under such circumstances, as long as the diameter of the fiber remains unchanged, dye uptake increases linearly. But, the significant effect contributing to a sharp increase in rate of dyeing at higher levels of grafting then appears, essentially from an increase in the diameter, which facilitates more penetration of dye molecules into the fiber matrix.

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