

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

Effect of Solvents

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Synopsis

Graft copolymerization of methacrylic acid onto polypropylene fibers by simultaneous-gamma ray irradiation technique was carried out. The effect of various solvents on grafting was studied. The results have been presented in terms of swelling behavior of polypropylene fiber and the extent of homopolymerization. An accelerative effect upon the rate of grafting was observed when benzene was partly replaced by methanol. At the dose rate of 24 rad/s and monomer concentration of 3 mol/L, a maximum in the rate of grafting was observed with 40% methanol fraction in the benzene-methanol mixture. However, a further increase in the methanol fraction in the solvent mixture resulted in a sharp decrease in the rate of grafting. No grafting was observed in pure methanol. This behavior has been explained in terms of the inhibitory action of methanol for polymerization of methacrylic acid and the extent of swelling of polypropylene fiber in various compositions of benzene-methanol mixture.

INTRODUCTION

Radiation-induced graft copolymerization of vinyl monomers onto various polymers has been extensively studied.¹⁻³ The use of solvents as diluent has been observed to show a marked influence on the extent of grafting by radiation technique.⁴⁻⁷ Odian et al.⁸⁻¹⁰ studied the kinetics of graft copolymerization of styrene on several polymers, such as nylon, polyethylene, and polypropylene. A substantial increase in grafting was observed when styrene monomer was diluted with methanol. The authors attribute it to the onset of the "Tromsdorff effect" in the system. The studies of Machi et al.¹¹ on the polyethylene-styrene system in methanol as a diluent do not agree that such an effect is operative. The increase in grafting has been explained in terms of concentration of sorbed monomer and viscosity of the amorphous region of swelled polyethylene. Several studies of solvent effects in the grafting onto polypropylene have been reported.^{12,13} Recently, an accelerative effect of methanol in the grafting of styrene on polypropylene has been reported by Ang et al.¹⁴ They observed the Tromsdorff peak at 30% monomer concentration, but a shifting of the peak to higher monomer concentration was noted when divinylbenzene and sulfuric acid were used as additives. Therefore, the interaction between the polymer matrix and the monomer-solvent mixture strongly influences the kinetics of the grafting in one way or the other. The use of proper solvent may produce a pronounced accelerative effect on the rate of grafting,¹⁵ but the conditions under which the process is influenced may vary depending upon the architecture of macromolecule and the type of monomer being grafted.

EXPERIMENTAL

Materials

Polypropylene grade E 0035, used for grafting, was supplied by Indian Petrochemicals Corp. Ltd., Gujarat, India. The monofilament was prepared by melt spinning of the polymer in a laboratory model melt spinning unit at 240°C. The fiber was Soxhlet extracted with acetone for 12 h and dried under vacuum at 50°C.

Methacrylic acid (MAA) monomer, supplied by E. Merck, was purified by distillation at 70°C/20 mm Hg¹⁶ and stored at refrigerator temperature.

Benzene (Glaxo Laboratories India, Ltd.), methanol, dimethyl formamide, chlorobenzene, ethyl methylketone (all E. Merck), and water were distilled before use. Solvent ether was used as received, without any further purification.

Radiation Source

The irradiation of samples was carried out in a Co⁶⁰ gamma Chamber (4000 Ci), supplied by Bhabha Atomic Research Center, Bombay, India.

Grafting Procedure

Graft copolymerization of methacrylic acid onto polypropylene fiber was carried out according to the procedure reported earlier.¹⁷ The swelling measurements were carried out by immersing the fiber in the solvents for different time intervals. The fiber was taken out from the solvents and quickly pressed between two Whatmann no. 1 filter papers and weighed. The increase in weight was taken as percent swelling. In the case of the benzene-methanol mixture, a constant period of 24 h was used. Percent grafting and percent swelling were calculated using the following expressions^{18,19}:

$$\% \text{ grafting} = \frac{\text{wt grafted polymethacrylic acid}}{\text{original wt fiber}} \times 100$$

$$\% \text{ swelling} = \frac{\text{wt swollen fiber} - \text{original wt fiber}}{\text{original wt fiber}} \times 100$$

RESULTS AND DISCUSSION

Variation in the graft yield with increasing concentration in different solvents has been presented in Figure 1. All the grafting experiments were carried out at the dose and dose rate of 0.25 Mrad and 24 rad/s, respectively, and a liquor ratio of 1:75 (w:v).

It appears from the results that grafting is highly dependent on the nature of solvent, for all monomer concentrations. Graft yield is higher when chlorobenzene was used as a medium for the system. However, graft yields are almost similar with benzene and toluene as diluents, but lower than that obtained with chlorobenzene. Further, using dichloroethane, ethylmethyl ketone, and water, the graft yields are relatively lower than those obtained in other solvents. For all the solvents except water, as the monomer con-

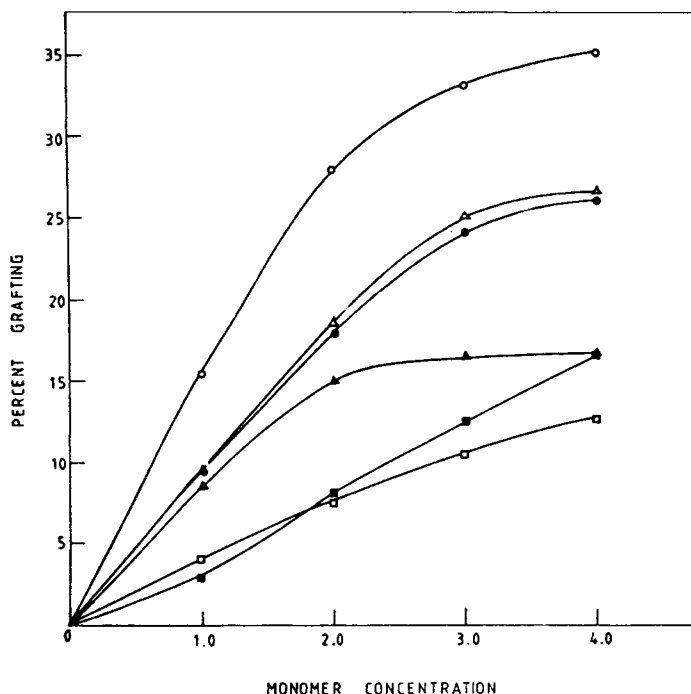


Fig. 1. Effect of monomer concentration on the percent grafting of polypropylene fibers in various solvents: dose rate, 24 rad/s; dose, 0.25 Mrad; liquor ratio 1:75; (○) chlorobenzene; (△) toluene; (●) benzene; (▲) dichloroethane; (□) ethylmethylketone; (■) water.

centration increases, grafting also increases linearly up to a monomer concentration of 20 mol/L, but, with further increase in monomer concentration, grafting levels off. This effect seems to be more pronounced with dichloroethane as diluent.

The effect of the solvents on grafting may be attributed to two factors, viz., (i) the extent of swelling of fiber in the solvent and (ii) the degree of homopolymerization during grafting.

The swelling behavior of polypropylene fiber in various solvents has been presented in Figure 2. It can be seen from the results that, irrespective of the solvent used for grafting, equilibrium swelling is attained in 10–12 h. However, a constant time of 24 h was used for each experiment.

Using dichloroethane as diluent, increasing graft yields are obtained with the increase in monomer concentration up to 3 mol/L, beyond which grafting does not increase. This behavior may be explained in terms of high degree of homopolymerization in dichloroethane, i.e., 92% as compared to 42.9% in benzene and 46% in chlorobenzene at the monomer concentration of 3 mol/L (Fig. 3). This results in the depletion of monomer, thus leaving behind very little methacrylic acid for grafting. When dichloroethane is replaced with water, almost a linear increase in the graft yield is obtained. The graft yield is even comparable to that with dichloroethane at higher monomer concentration. The initial grafting is definitely lower than with dichloroethane which seems to be due to the fact that, unlike dichloroethane, grafting takes place on the surface of the fiber only (as there is no swelling of polypropylene fiber in water).

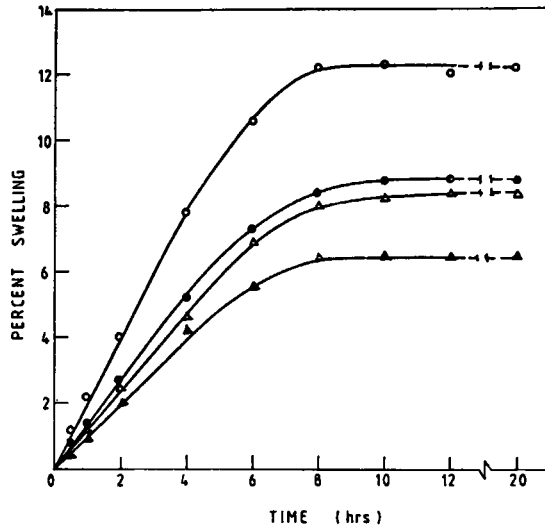


Fig. 2. Effect of time on the percent swelling of polypropylene fibers in various solvents: (○) chlorobenzene; (●) benzene; (△) toluene; (▲) dichloroethane.

Like water, ethylmethyl ketone also does not swell polypropylene fiber. But, the graft yields are relatively lower as compared to those obtained in water. This might be due to comparatively higher extent of homopolymerization and hence more depletion of monomer in ethylmethyl ketone. However, toluene has been observed to produce a trend in grafting similar to that of benzene. Such a behavior may well be understood from the similar equilibrium swelling of polypropylene fiber in both solvents. The homo-

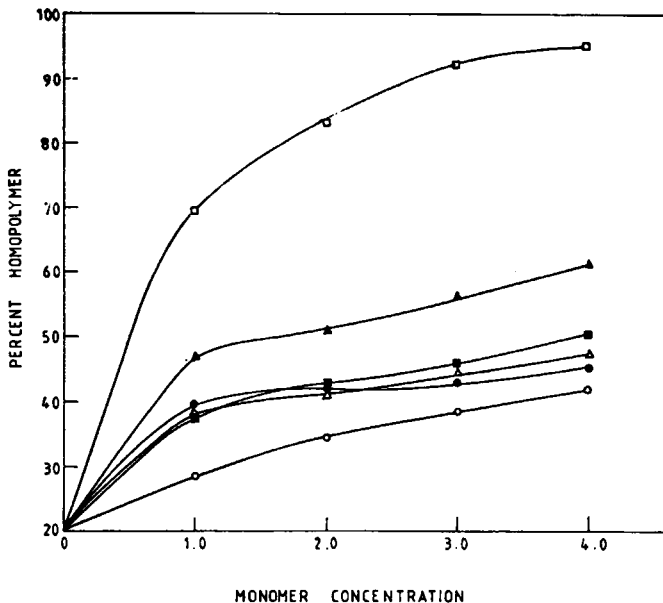


Fig. 3. Effect of monomer concentration on the percent homopolymer yield in various solvents: dose rate 24 rad/s; dose, 0.25 Mrad; liquor ratio, 1:75; (□) dichloroethane; (▲) ethylmethylketone; (■) chlorobenzene; (△) toluene; (●) benzene; (○) water.

polymer yields are also almost similar in both cases. In spite of an almost similar extent of homopolymerization, grafting in chlorobenzene gives higher yields than in benzene or toluene (Fig. 2).

The only significant effect of chlorobenzene dilution should then essentially be a higher degree of swelling of polypropylene fiber as compared to that occurring in other solvents, which permits more penetration of monomer into the polymer matrix. The contribution of swelling of polymer matrix by diluents to an increase in the grafting has been explored in other systems also.^{11,20}

An accelerative effect of methanol on the rate of grafting has been observed when benzene was partly replaced by methanol. The results have been presented in Figure 4. Using benzene as the only solvent, the graft yield is 24% (dose rate, 24 rad/s; dose, 0.25 Mrad and monomer concentration, 3 mol/L), while in pure methanol, grafting is completely inhibited. However, when a mixture of benzene and methanol was used, the rate of grafting was even higher than that in pure benzene and a maximum rate of grafting was observed at 40–50% methanol content in the solvent mixture. Addition of methanol to the system has also been observed to accelerate the rate of grafting in polyethylene–styrene–methanol system.²¹

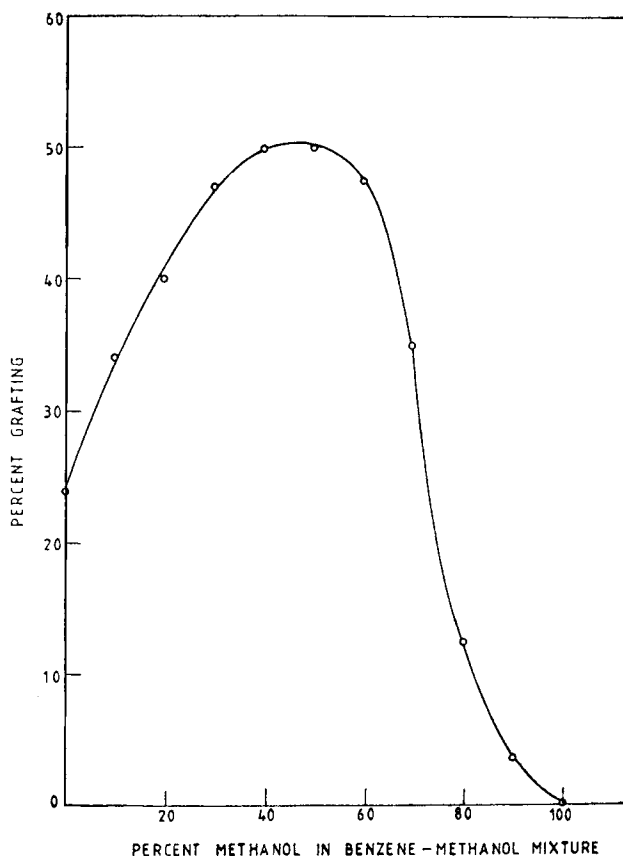


Fig. 4. Effect of methanol fraction in the benzene-methanol mixture on the percent grafting; dose rate 24 rad/s; dose, 0.25 Mrad; liquor ratio, 1:75.

Swelling behavior of polypropylene fibers in different compositions of benzene-methanol mixture is also shown in Figure 5. For each experiment, a constant time of 24 h was used to get the equilibrium swelling of fiber. A maximum swelling of 8.8% is achieved in pure benzene. However, the swelling decreases continuously and almost linearly with increasing methanol content in the solvent mixture. Absolutely no swelling was observed in pure methanol. The solubility parameter of benzene, a hydrocarbon solvent (9.2), is quite close to that of polypropylene (9.4), but the difference between solubility parameter values of polypropylene and methanol (14.5) is large²² and can account for this decrease in swelling of the fiber in a mixture of benzene and methanol.

A similar accelerative effect of methanol in the graft copolymerization of methyl methacrylate onto polypropylene film in benzene has been observed by Burchill et al.¹⁵ A maximum in the rate was obtained at 10% methanol content in benzene-methanol mixture. But, the grafting decreased with an increasing amount of methanol in the mixture. Authors attributed this behavior to the swelling of the film and polymer chain entanglement.

However, in the present system, polymethacrylic acid precipitates out from the reaction mixture, so that the viscosity of the reaction medium is not affected. Hence, the graft levels should be more regulated by the swelling of polypropylene fibers in the reaction medium. The swelling value of fiber does not change much up to a methanol content of 40% (by volume) in benzene-methanol mixture.

When methanol was used as a medium, absolutely no grafting was observed. Similar observation has been made for the grafting of methacrylic acid onto poly(vinyl chloride).²³ A separate experiment on methacrylic acid polymerization in methanol was carried out. It was found that methanol

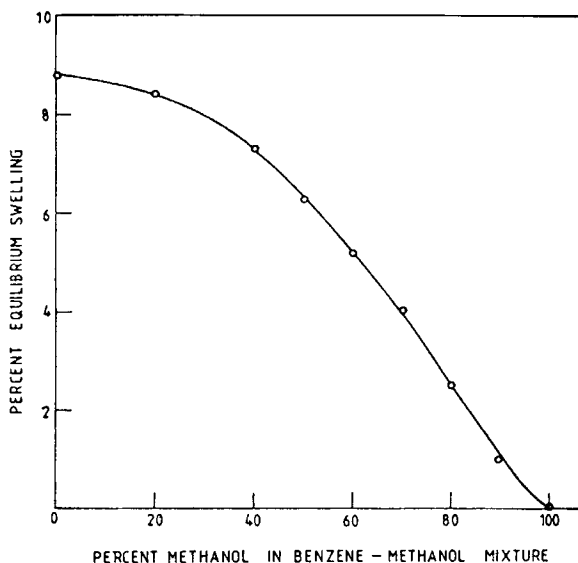


Fig. 5. Effect of the methanol fraction in the benzene-methanol mixture on the equilibrium swelling of polypropylene fibers.

completely inhibits the polymerization of methacrylic acid. It appears that methanol acts as inhibitor for external homopolymerization as well as surface grafting.

Hence, with the increasing content of methanol in the benzene-methanol mixture, the rate of homopolymerization decreases continuously. However, as the swelling of the fiber is not affected up to 40% methanol content, there is little likelihood of the rate of grafting being affected. Hence, this results in an apparent increase in the rate of grafting. It appears that methanol does not exert any inhibitory action inside the fiber matrix, because the amount of methanol content into the fiber matrix is too small to cause any inhibitory action.¹¹

As the methanol content in the solvent mixture exceeds 40% (by volume), the decrease in homopolymerization of methacrylic acid is also accompanied by a sharp decrease in the swelling of the fiber (Fig. 5). At 100% methanol content, the homopolymerization is completely inhibited and the fiber do not show any swelling. Under these conditions, the surface grafting is also inhibited, thus completely suppressing the grafting reaction.

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