

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

Effect of Synthesis Conditions

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Synopsis

The gamma radiation-induced graft copolymerization of methacrylic acid onto polypropylene fibers was investigated by simultaneous—irradiation technique. The effect of various synthesis conditions on the graft content was studied. At a constant dose, the percent grafting was found to be higher at low dose rate. For all the dose rates, a linear increase in the grafting was observed up to 0.25 Mrad, beyond which the grafting levelled off. Percent grafting also increased continuously with increasing monomer concentration up to 4.0 mol/L, but a linear increase in grafting was observed only up to 2.0 mol/L. The initial rate of grafting increased with the increase in dose rate and monomer concentration. The dependence of rate of grafting on dose rate and monomer concentration was found to be 0.70 and 1.71, respectively. The effect of liquor ratio upon grafting was also studied.

INTRODUCTION

Polypropylene fiber has certain disadvantages in its properties which has impeded its growth in commercial use. These include poor moisture absorption and inability to takeup dye. The major reason for these drawbacks are hydrocarbon nature of the fiber and lack of presence of any reactive site on it. Of the various attempts made to overcome these drawbacks, graft copolymerization of a suitable vinyl monomer onto the polymer backbone has proved to be an attractive means to impart some advantageous properties into this polymer, without affecting most of its original properties.¹ Several grafting initiating techniques, such as chemical,²⁻⁷ mechanical,⁸ photochemical,⁹⁻¹⁷ and radiation,¹⁸⁻²⁴ have been used for the purpose. However, gamma ray radiation-induced graft copolymerization has shown to be the most promising method, and a number of vinyl monomers including styrene,²⁵ butadiene,²⁶ ethyl vinyl ether,²⁷ and methylmethacrylate²⁸ have been grafted onto polypropylene, by using this technique.

The present investigation involves the graft copolymerization of methacrylic acid onto polypropylene fibers by simultaneous-irradiation technique using Co⁶⁰ as the source of gamma rays.

EXPERIMENTAL

Materials

Polypropylene, grade E 0035, manufactured by Indian Petrochemicals Corp. Ltd., Gujarat, India, was used for the graft copolymerization studies.

The fiber (undrawn) was prepared by melt spinning of polypropylene using a laboratory model melt spinning unit at 240°C and soxhlet-extracted with acetone for 12 h. The fiber was dried and stored in a desiccator over fused calcium chloride.

Methacrylic acid monomer, supplied by E. Merck, was purified by double distillation at 70°C/20 mm Hg²⁹ and stored at refrigerator temperature. Reagent grade benzene supplied by Glaxo Laboratories (India) Ltd. was distilled in an all glass apparatus. Methanol and solvent ether were used without any further purification.

Radiation Source

The irradiation of samples was carried out in a Co⁶⁰ gamma chamber (900 and 4000 C), supplied by Bhabha Atomic Research Center, Bombay, India. Variation in dose rates was achieved by the use of lead attenuators of different thickness.

Grafting Procedure

Graft copolymerization was carried out in standard joint Corning tubes of 11.5 × 2.8 cm size under nitrogen atmosphere. A weighed amount of the melt-spun polypropylene fiber was put in benzene, taken in the glass tube, and the whole system was left as such for 24 h in order to attain the equilibrium swelling of the fiber. Methacrylic acid monomer was added just before the exposure of the samples. The tube was placed into the radiation chamber for a desired period. After the exposure was over, the tube was removed, and the polymerization was stopped by the addition of a large volume of solvent ether to the reaction mixture. The whole mass was filtered and washed several times with solvent ether to remove any residual monomer. The product was then dried to constant weight under vacuum at 60°C. The homopolymer was removed by soxhlet extraction with methanol for 24 h. The residual polymer was dried under vacuum at 60°C and weighed. Homopolymer was precipitated out from the solution by the addition of excess of solvent ether and dried under vacuum at 60°C.

Percent grafting and grafting efficiency were calculated as follows³⁰:

$$\begin{aligned} \% \text{ grafting} &= \frac{\text{wt grafted poly(methacrylic acid)}}{\text{original wt fiber}} \times 100 \\ \% \text{ grafting efficiency} &= \frac{\text{wt grafted poly(methacrylic acid)}}{\text{wt grafted poly(methacrylic acid)} + \text{wt homopolymer}} \\ &\times 100 \end{aligned}$$

The equilibrium swelling was determined by the procedure adopted by Wilson³¹ and has been represented as percent swelling, i.e.,

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

RESULTS AND DISCUSSION

The melt-spun polypropylene fiber used for the present study had an average diameter of 0.094 mm, as measured by a "Projectina" microscope. An average of 25 samples showed a variation of $\pm 5\%$. The role of benzene, during grafting, was not only to provide a homogeneous medium for methacrylic acid monomer, but also to act as a swelling agent for polypropylene fiber, so as to make available increased surface area for grafting.

A plot of percent swelling of the fiber in benzene against time has been shown in Figure 1. It can be seen from the plot that the maximum swelling of 8.8% is attained in a time period of 10 h. However, a constant time of 24 h was used for each experiment. The use of benzene as a swelling agent for polypropylene fiber has been reported by others also.^{28,32}

Polypropylene fibers were grafted using 2.0 mol/L concentration of monomer in benzene, to a total dose of 0.25 Mrad and material to liquor ratio of 1:75 (w:v). Grafting was studied at 30°C under different dose rates, viz., 24, 86, and 106 rad/s. The results have been presented in Figure 2.

At constant dose of irradiation, grafting was found to be higher at lower dose rates. The increasing dose rates resulted in a decrease in the percent grafting. A similar behavior has been found for other systems also.³³ It has been established earlier that the number of radical species formed during irradiation is directly proportional to the dose rate.³⁴ As the irradiation results in the formation of both monomeric as well as polymeric radical species, the former may react either with the polymer backbone (grafting) or with other monomer molecules (homopolymerization).³⁵ During the grafting, monomer molecules will continuously diffuse into the fiber matrix. At higher dose rate, the relative number of radicals present in the system will also be higher. However, the rate of diffusion of monomer to the grafting sites will not alter. Under such circumstances, the greater availability of free radicals will increase the rate of homopolymerization. This will cause

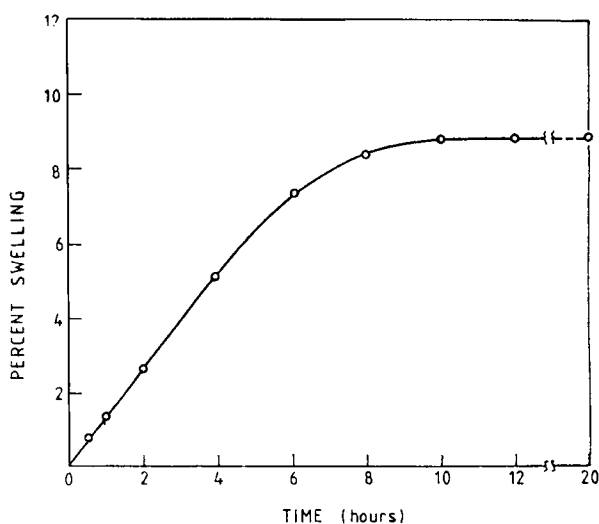


Fig. 1. Effect of time on the percent swelling of polypropylene fibers in benzene.

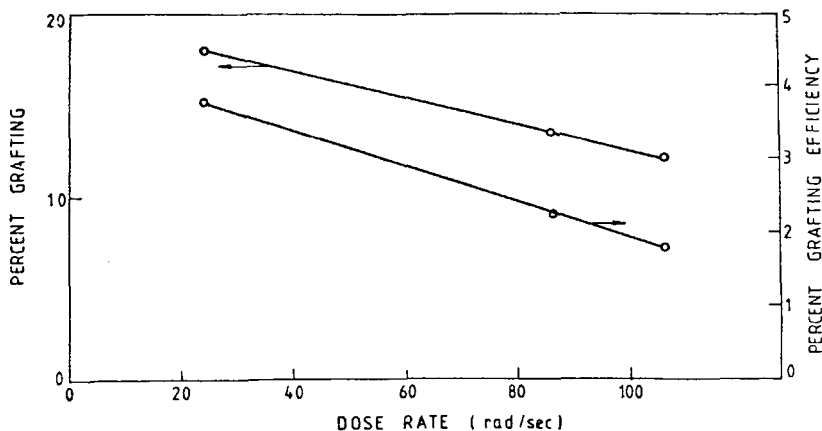


Fig. 2. Effect of dose rate on the percent grafting and grafting efficiency of polypropylene fibers: monomer concentration, 2.0 mol/L; liquor ratio, 1:75.

a relative decrease in the grafting reaction as well as grafting efficiency. Similar results have been obtained by other workers.³⁶

The extent of graft copolymerization as a function of time at various dose rates is shown in Figure 3. All the plots pass through the origin, indicating that the grafting proceeds without any induction period. Similar behavior has been observed for the poly(ethylene-styrene) system.³⁷ The slopes of all the straight lines remain constant over a long period and then start levelling off. There is no autoacceleration effect noticeable in the range of dose rates studied. The lack of autoacceleration effect not only indicates a smooth grafting reaction, but also shows a lack of high degree of viscosity changes in the polymerization mix during the reaction. One of the obvious reasons should be that the homopoly(methacrylic acid) formed, being insoluble in

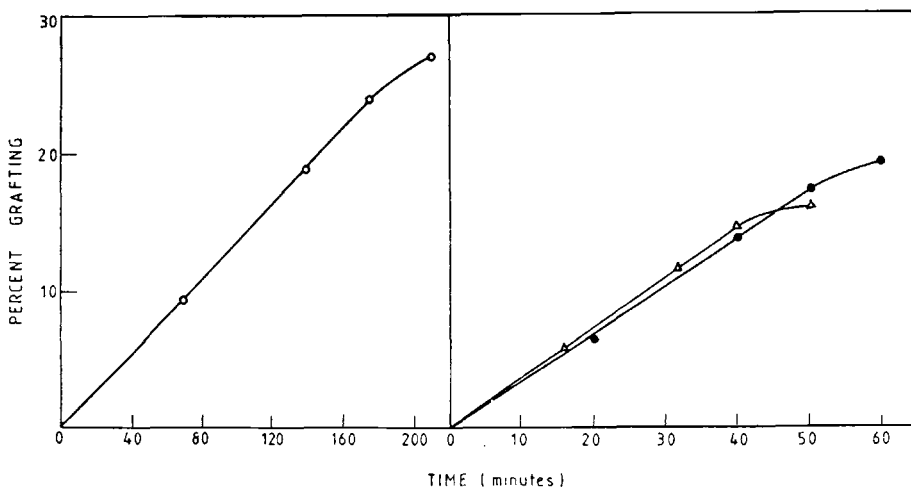


Fig. 3. Effect of time on the percent grafting of polypropylene fibers at various dose rates: monomer concentration, 3.0 mol/L; liquor ratio, 1:75; (○) 24 rad/s; (●) 86 rad/s; (△) 106 rad/s.

the reaction mixture, precipitates out from the mix and hence has a very little contribution in increasing the viscosity of the reaction mix.

Table I shows the rates of grafting (R_g) at various dose rates. The log-log plot of the rate of graft copolymerization vs. dose rate of irradiation is shown in Figure 4. The straight line thus obtained has a slope of 0.70. The results can be summarized in the following form:

$$R_g \propto [I]^{0.70}$$

The dependence of rate of grafting on the dose rate has been determined in several other systems and a very wide range of dependence, namely, between 0.31 and 0.90 has been reported.^{26,38,39} A proposed mechanism operating for the present system was presented later.

The effect of total dose upon grafting at various dose rates is shown in Figure 5. All the reactions were carried out at a monomer concentration of 3.0 mol/L and a liquor ratio of 1:75. A total dose up to 0.30 Mrad was used at three different dose rates, viz., 24, 86, and 106 rad/s.

From the results, it may be seen that, for all dose rates, there is a linear increase in the percent grafting with increasing dose of irradiation up to 0.25 Mrad, beyond which there is a marked fall in the rate of grafting and a tendency to level off. Similar behavior in poly(vinyl chloride-methacrylic

TABLE I
Initial Rates of Graft Copolymerization for Different Dose Rates

Dose rate (I) (rad/s)	$R_g \times 10^7$ (mol/L s)	$\log I$	$\log R_g \times 10^7$	Order of dependence
24	105	1.3802	2.0212	0.70
86	265	1.9345	2.4232	
106	287	2.0253	2.4579	

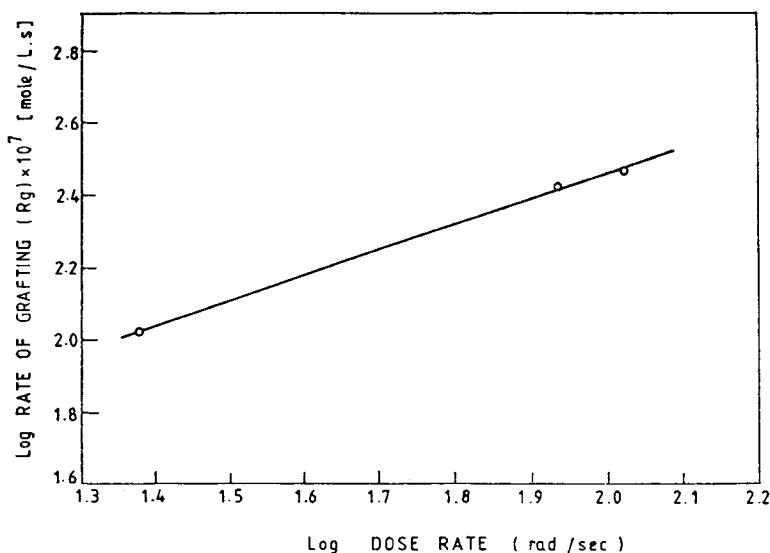


Fig. 4. Log-log plot of graft copolymerization rate (R_g) vs. dose rate.

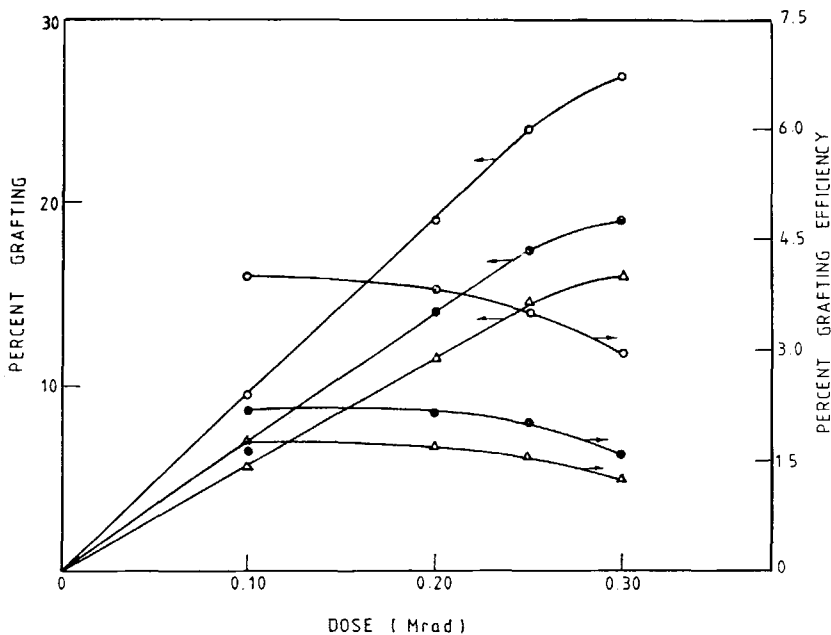


Fig. 5. Effect of total dose of irradiation on the percent grafting and grafting efficiency at various dose rates: monomer concentration, 3.0 mol/L; liquor ratio, 1:75; (○) 24 rad/s; (●) 86 rad/s; (△) 106 rad/s.

acid) system has been reported by Singh.³⁶ However, at a comparable total dose, the percent grafting is higher at lower dose rates. On the other hand, the grafting efficiency does not show any appreciable fall up to a total dose of 0.20 Mrad, but beyond that there is a considerable fall in grafting efficiency.

In the initial stages of polymerization, the amount of monomer available is higher at the grafting sites on polymer backbone. Hence, the monomer can diffuse very easily to the grafting sites and a smooth grafting reaction ensures. Further, the rate of homopolymerization is not much affected. Both these competing reactions proceed smoothly till a total dose of 0.20 Mrad has been reached. Beyond this, a slow decrease in grafting efficiency indicates that there is an increase in the rate of homopolymerization as compared to the rate of percent grafting. It appears that in our system, in spite of the higher homopolymer yield, the grafting is not affected up to 0.25 Mrad due to the regular accessibility of monomer to the grafting sites. Further, the increasing content of grafted polymethacrylic acid may also act as a barrier against the diffusion of monomer into the polymer matrix.⁴⁰ As a consequence, the rate of homopolymerization increases, resulting in a decrease in the grafting efficiency.

The relation of percent grafting with the monomer concentration is shown in Figure 6. Grafting was carried out at a constant temperature of 30°C, using a fourfold variation in monomer concentration and at the dose rate of 24 rad/s for four different total doses in the range of 0.10–0.30 Mrad.

The results show that, irrespective of the total dose, there is an increase in the percent grafting with the increase in monomer concentration. How-

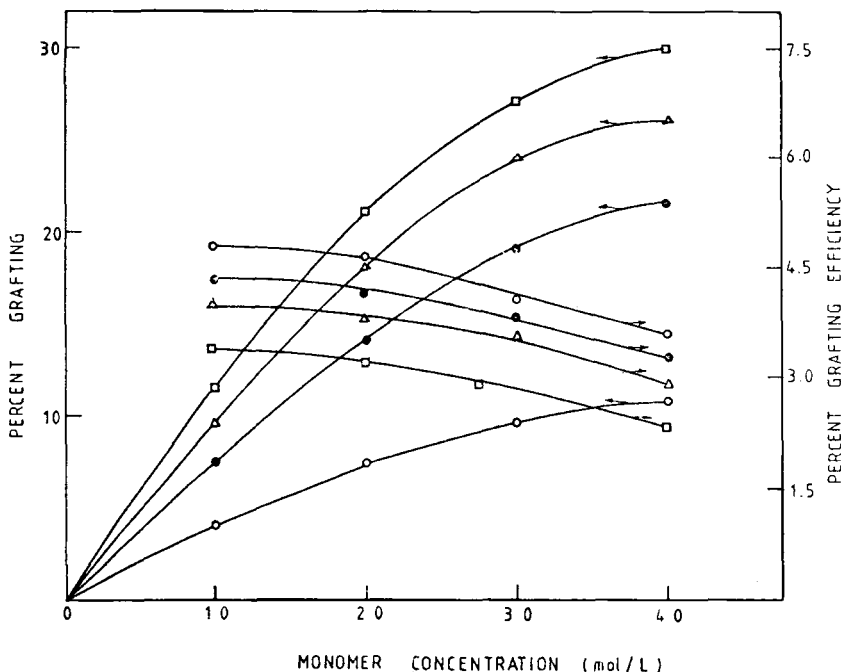


Fig. 6. Effect of monomer concentration on the percent grafting and grafting efficiency at various total doses of irradiation: dose rate, 24 rad/s; liquor ratio, 1:75; (○) 0.10 Mrad; (●) 0.20 Mrad; (△) 0.25 Mrad; (□) 0.30 Mrad.

ever, for all the doses, percent grafting increases linearly only up to 2.0 molar concentration of monomer, beyond which the grafting levels off. The grafting efficiency also decreases beyond the monomer concentration of 2 mol/L.

The results show a very general trend and have been found by other workers also.³⁵ During grafting, the monomer continuously diffuses into the polymer matrix, and the ability of polypropylene macroradical to capture the methacrylic acid would depend upon the availability of methacrylic acid molecules in their vicinity. Increased graft yields at higher monomer concentrations justify this behavior in the present system.

The extent of grafting as a function of time at various monomer concentrations is shown in Figure 7. The slopes were calculated from the initial portions of the plots. The rates of grafting at various monomer concentrations have been presented in Table II. The log-log plot of graft copolymerization rate vs. monomer concentration at the dose rate of 24 rad/s is shown in Figure 8. A 1.71 order of dependence of the rate of graft copolymerization on monomer concentration was obtained from the slope of the plot. Hence, the kinetic equation for the observed dependencies of rate of graft copolymerization may be represented as

$$R_g \propto [I]^{0.70}[M]^{1.71}$$

This rate expression is not consistent with the first-order dependence of rate of grafting on monomer concentration. However, higher order of de-

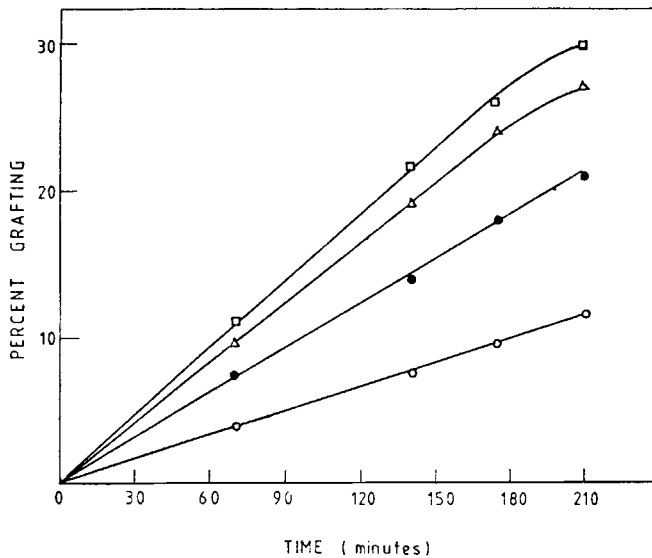


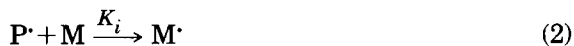
Fig. 7. Effect of time on the percent grafting at various monomer concentrations: dose rate, 24 rad/s; liquor ratio, 1:75; (○) 1.0 mol/L; (●) 2.0 mol/L; (△) 3.0 mol/L; (□) 4.0 mol/L.

pendence on monomer concentration has been reported by others also.⁴¹ Rabie and Odian³⁷ have reported a dependence of the grafting reaction on monomer concentration, to be higher than 1.5 in the poly(ethylene-styrene) gamma ray-irradiated system.

In the present system, the observed higher dependence of rate of grafting on monomer concentration and dose rate may well be explained in terms of the following scheme:



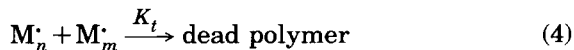
Initiation:



Propagation:



Termination:

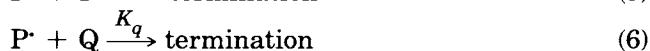
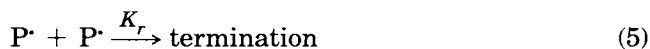


Any polymer swollen with the monomer or any other solvent presents a medium of very high viscosity. In the present system, benzene acts as a swelling agent for polypropylene fiber, and hence the grafting with such a matrix proceeds in a medium of very high viscosity. Under such circumstances, it may become increasingly difficult for monomer units to approach and react with the primary radicals. As a result, the rate of monomer addition to the primary radicals [eq. (2)] becomes slower than the radiolysis

TABLE II
Initial Rates of Graft Copolymerization for Different Monomer Concentrations

Monomer concentration [M] (mol/L)	$R_g \times 10^7$ (mol/L s)	$\log [M]$	$\log R_g \times 10^7$	Order of dependence
1.0	14.0	0.0	1.1461	1.71
2.0	52.0	0.3010	1.7160	
3.0	105.0	0.4771	2.0212	
4.0	161.0	0.6021	2.2068	

[eq. (1)]. Hence, due to this lowered rate of monomer addition to the primary polymeric radicals, the latter may terminate either by recombination [eq. (5)] or may undergo some unspecified process of destruction [eq. (6)]:



Here, Q may be any species involved in the destruction of primary radicals. Under such situation, the dose rate dependence may be expected to be greater than 0.5. The possibility of a radical destruction reaction with an impurity has been indicated by others also.⁴² Under the conditions when $K_q[Q] \gg K_i[M]$, the grafting rate will be 3/2 in monomer concentration. Alternatively, one can assume that radiolysis state is an equilibrium process.

The variation of percent grafting with respect to the volume of monomer solution per gram of fiber, is shown in Figure 9. An increase in grafting was observed with increasing monomer solution. But the grafting efficiency

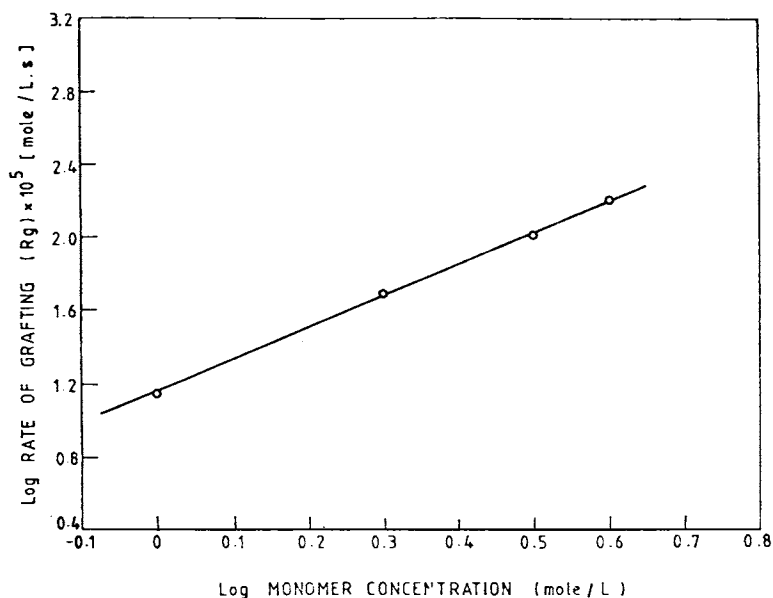


Fig. 8. Log-log plot of graft copolymerization rate (R_g) vs. monomer concentration.

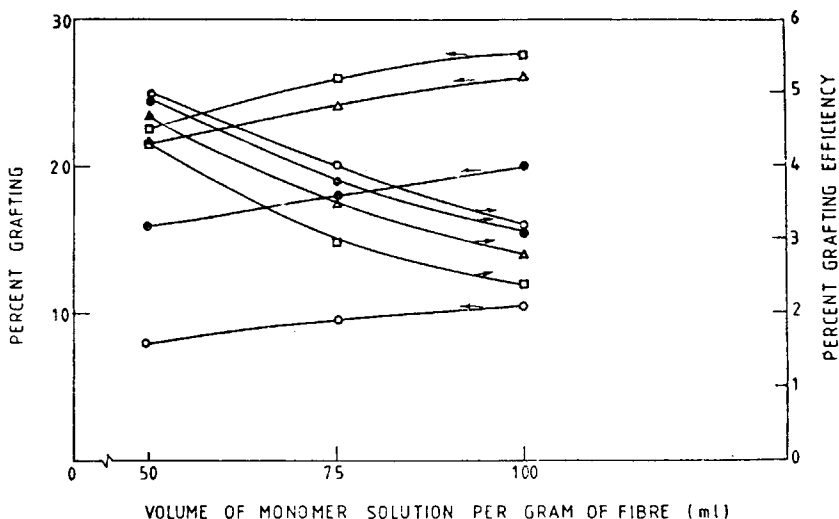


Fig. 9. Effect of liquor ratio on the percent grafting and grafting efficiency at various monomer concentrations: dose rate, 24 rad/s; dose, 0.25 Mrad; (○) 1.0 mol/L; (●) 2.0 mol/L; (△) 3.0 mol/L; (□) 4.0 mol/L.

decreased sharply. The increase in the percent grafting may be expected because, at higher volumes of monomer solution, the amount of free monomer required for grafting is also higher, thus reducing the effect of depletion of monomer concentration,⁴³ and the grafting proceeds with more monomer available to diffuse into the swollen polymer matrix. However, in spite of almost constant homopolymerization, percent grafting decreases with the increase in the liquor ratio. This behavior may be explained in terms of percent monomer conversion to graft, which decreases with the increasing amount of monomer solutions.

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