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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Mukherjee, A. K. and Goel, H. R.(1982) 'Grafting Vinyl Monomers onto Nylon 6 Fiber. I. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Fiber by Photoirradiation', *Journal of Macromolecular Science, Part A*, 17: 4, 545 – 557

**To link to this Article:** DOI: 10.1080/00222338208062407

**URL:** <http://dx.doi.org/10.1080/00222338208062407>

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## Grafting Vinyl Monomers onto Nylon 6 Fiber. I. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Fiber by Photoirradiation

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### ABSTRACT

Graft copolymerization of MMA onto nylon 6 fiber by UV radiation was studied at 70°C using various water alcoholic systems: water-methanol, water-ethanol, and water-n-propanol. The effects of monomer concentration, time, and the medium were investigated. The graft yield is greatly enhanced by increasing the monomer concentration and reaction time. The extent of grafting is affected by the medium of grafting and is in the following order: water-methanol > water-ethanol > water-n-propanol.

### INTRODUCTION

Graft copolymerization of various vinyl monomers onto nylon 6 fiber using different types of initiation techniques has been carried out by several workers. Some of the monomers used have been styrene [1-3], acrylic acid [4, 5], and methyl methacrylate [5-7]. Initiation has been done by using chemical initiator (e.g., persulfate [1]) as well as by irradiation. Irradiation methods used include initiation by argon blow discharge [8], radiation [9, 10], and electron

beam [ 11-13]. In the present study radiation from a carbon arc lamp has been used as the source for photoirradiation for grafting methyl methacrylate (MMA) onto nylon 6 fiber in the presence of several alcoholic solvents and water.

## EXPERIMENTAL

### Materials

Nylon 6. Monofilament of 12.4 denier as supplied by Shree Synthetics Ltd., Ujjain, has been used.

Methanol, ethanol, n-propanol, and benzene as supplied by BDH Laboratories, Bombay, were distilled prior to use.

Double distilled water was used.

MMA as supplied by Koch Light Laboratories was purified and distilled prior to use using the standard technique.

### Photoirradiation Source

A carbon arc lamp type 18F supplied by Atlas Electric Devices Co. (Chicago, Illinois) as fitted inside a fadometer was used.

### Grafting Technique

One gram of nylon 6 fiber was immersed in the water alcohol mixture and monomer in a suitable standard joint Corning glass flask under nitrogen atmosphere. The material-to-liquor ratio was maintained as required. The samples were then exposed to the light source on a rotating plate in an enclosed chamber maintained at 70°C.

After the desired time interval the reaction was stopped by pouring six to eight times the methanol volume into the reaction mixture. The residue was collected by filtration followed by repeated washing with methanol and drying in vacuum at 40°C to constant weight.

The homopolymers was removed by Soxhlet extraction with benzene for 12 h using the standard method [ 14]. The residue was dried under vacuum at 40°C to constant weight.

The % graft add-on (GAO) and total polymer yield % (TPY) were calculated as follows:

$$\text{Graft add-on } \% = \frac{\text{Dry wt of the grafted sample} - \text{dry wt of the sample}}{\text{dry wt of the sample}} \times 100$$

$$\text{Total yield \%} = \frac{\text{wt of homopolymer + wt of the monomer added to the yarn}}{\text{wt of the monomer}} \times 100$$

## RESULTS AND DISCUSSION

Grafting of nylon 6 fiber was carried out using MMA as monomer in the presence of a carbon arc lamp as the source for photochemical initiation in the presence of water-methanol, water-ethanol, and water-n-propanol as reaction medium using a 1:1 water:alcohol ratio at 70°C.

To ascertain that whether MMA undergoes thermal polymerization in water, an initial experiment was carried out at 70°C for 3 h using a liquor ratio of 1:26 of MMA:water in the absence of any light source. No polymerization occurs, as has also been found by other workers [15]. In another experiment only MMA was exposed to the photo source while using the same reaction conditions. In this case also, no polymerization took place. In a separate experiment using a UV spectrophotometer it was found that a wavelength below 290 m $\mu$  is unable to pass through Corning glass. Thus the effective wavelength for the present study is only above 290 m $\mu$ . Other workers have found similar results [21].

### Effect of Monomer Concentration on Grafting

#### Water-Methanol System

Nylon 6 fiber was grafted using MMA as the monomer in a water-methanol solution (1:1 ratio) and a liquor ratio 1:26 (1 mL MMA, 25 mL of water-methanol) at 70°C for 90 min and using a carbon arc lamp as the photo source at four different monomer concentrations. The results are presented in Table 1 and Fig. 1.

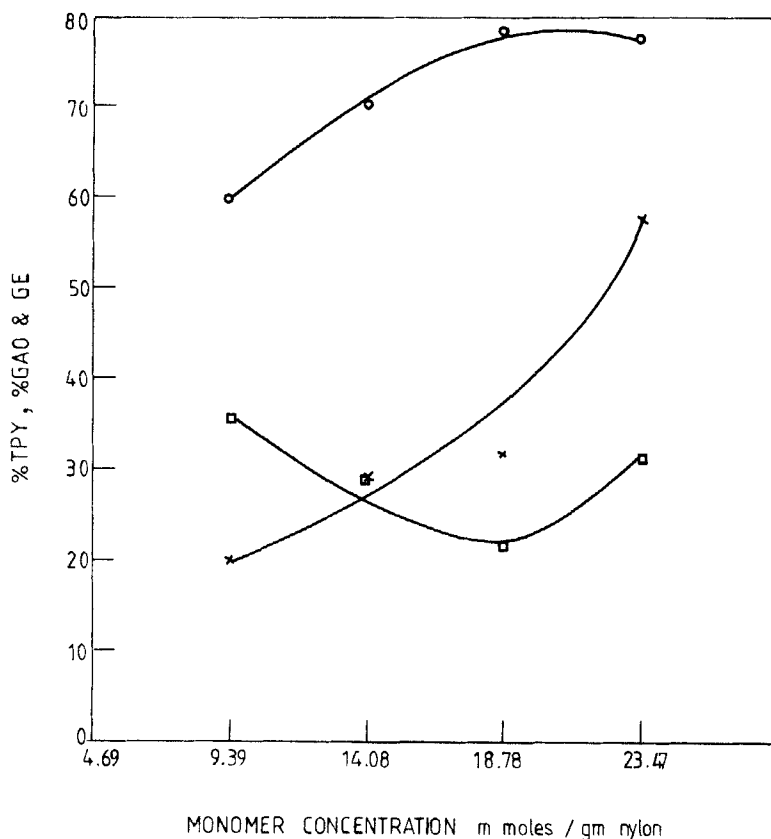
From the results it may be seen that the GAO increases continuously with an increase in monomer concentration. The grafting efficiency also increases, reaches a maximum, and then remains practically unchanged. However, there is not much increase in the % TPY. This can be attributed to the fact that the TPY % does not increase in proportion to the addition of monomer. Since the % TPY is directly related with the amount of the monomer used, the overall % TPY does not change much. The increase in the grafting efficiency is due to the decrease in homopolymerization as we proceed to higher doses of the monomer concentration.

Several workers have found a similar effect in graft add-on % by increasing the monomer concentration [16-18].

**TABLE 1. Effect of Monomer Concentration on Grafting of MMA onto Nylon 6 fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>**

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.39	35.7	14.3	20.1	60.0
2	14.08	29.0	8.5	28.9	70.6
3	18.78	21.7	4.7	32.0	78.5
4	23.47	31.5	6.8	58.0	78.4

<sup>a</sup>Water-methanol ratio: 1:1. Nylon fiber: 1 g. Time: 90 min. Temperature: 70°C. Liquor ratio: MMA:water-methanol: 1:26.



**FIG. 1. Effect of monomer concentration on grafting. Nylon 6 fiber = 1 g; liquor ratio (water-methanol 1:1) 1:26; time 90 min; temperature 70°C. (□) % total polymer yield (TPY). (×) % Graft add-on (GAO). (○) Grafting efficiency (GE).**

TABLE 2. Effect of Monomer Concentration on Grafting of MMA onto Nylon 6 Fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.3	28.1	10.2	16.2	61.3
2	14.0	22.5	6.0	23.2	73.1
3	18.7	25.2	5.1	37.8	79.6
4	23.4	28.1	8.3	46.6	70.4

<sup>a</sup>Water-ethanol ratio: 1:1. Nylon fiber: 1 g. Time: 90 min. Temperature: 70°C. Liquor ratio: MMA:water-methanol: 1:26.

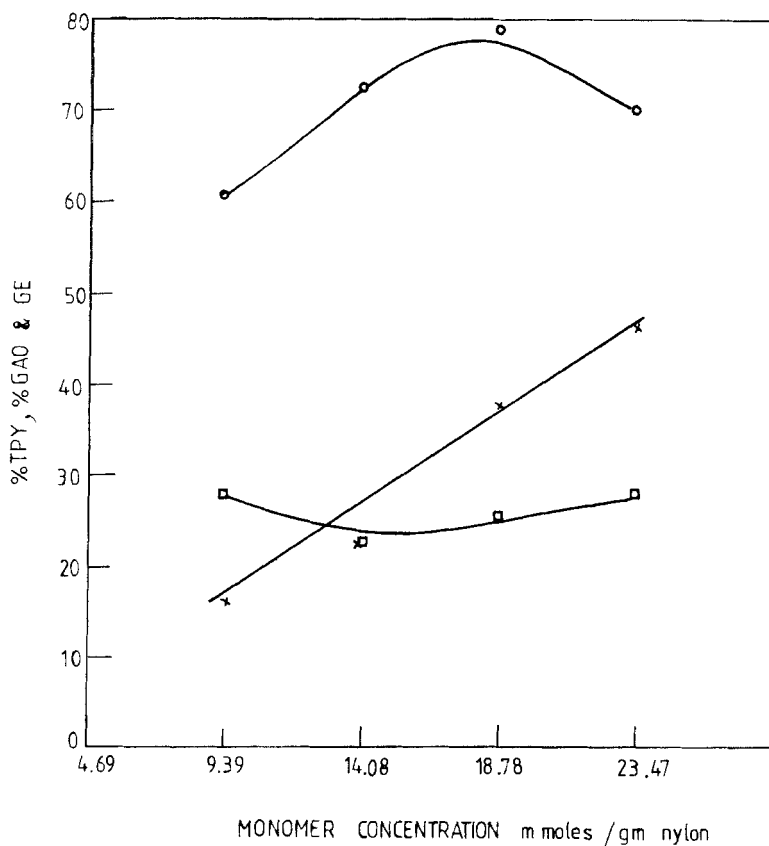


FIG. 2. Effect of monomer concentration on grafting. Nylon 6 fiber = 1 g; liquor ratio (water-ethanol 1:1) 1:26; time 90 min; temperature 70°C. (□) % total polymer yield (TPY). (×) % graft add-on (GAO). (○) Grafting efficiency (GE).

**TABLE 3.** Effect of Monomer Concentration on Grafting of MMA onto Nylon 6 Fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.3	18.2	6.8	10.7	62.3
2	14.0	17.9	3.8	19.8	78.3
3	18.7	18.9	3.6	28.7	80.8
4	23.4	26.3	7.9	43.2	69.7

<sup>a</sup>Water-propanol ratio: 1:1. Nylon fiber: 1 g. Time: 90 min. Temperature: 70°C. Liquor ratio: MMA-methanol: 1:26.

#### Water-Ethanol System

MMA was grafted onto nylon 6 fiber using 1 g nylon in a liquid ratio of 1:26 for 90 min at 70°C in a water-ethanol medium (1:1 ratio). The monomer has been varied fourfold from 9.39 to 23.47 mmol/g nylon. The results are presented in Table 2 and Fig. 2.

From the results it is seen that the % GAO increases continuously. The grafting efficiency increases, reaches a maximum value, and then falls. However, there is not much change in % TPY. The results are similar to those obtained with the water-methanol system. The HPY% decreases and hence the grafting efficiency increases.

#### Water-n-Propanol System

MMA was grafted onto nylon 6 fiber using a monomer concentration of 9.39 mol to 24.37 mmol/g nylon, a liquor ratio of 1:26, for 90 min at 70°C in a water-n-propanol medium (1:1 ratio). The results are presented in Table 3 and Fig. 3.

From the results it is seen that the % GAO increases continuously. The grafting efficiency (GE) increases, reaches a maximum value, and then falls. As also seen in the above two cases, there is not much of a change in the % TPY. However, the % HPY decreases, allowing the GE to increase.

From all the above results it is seen that % TPY, % GAO, and % HPY changes in the following order depending upon the nature of alcohol used: methanol > ethanol > n-propanol. This order is in complete agreement with the dielectric constant values [19] of these alcohols:

	Methanol	Ethanol	n-Propanol
$\epsilon$ at 25°	32.6	24.3	20.1

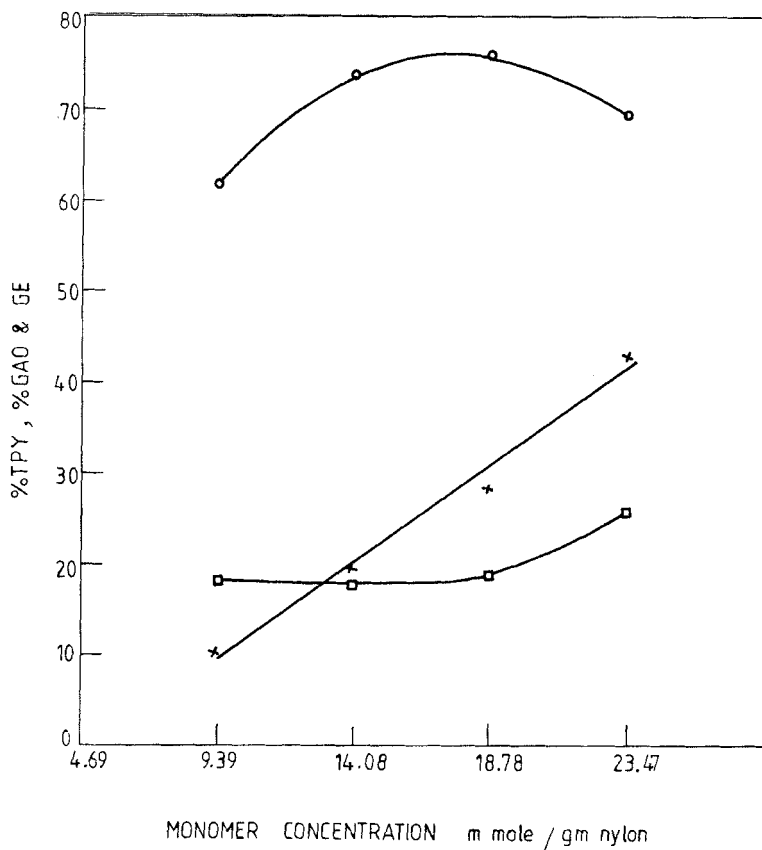


FIG. 3. Effect of monomer concentration on grafting. Nylon 6 fiber = 1 g; liquor ratio (water-propanol 1:1) 1:26; time 90 min; temperature 70°C. (□) % total polymer yield (TPY). (×) % graft add-on (GAO). (○) Grafting efficiency (GE).



TABLE 4. Solubility of MMA in the Water-Alcohol System

Temperature (°C)	% Solubility (v/v) of MMA		
	Methanol-water	Ethanol-water	n-Propanol-water
25	23	29	21
50	37	34	25
70	46	36	27

TABLE 5. Effect of Time on Grafting of MMA onto Nylon 6 Fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	34.6	14.8	18.6	57.1
2	90	35.6	14.2	20.1	60.0
3	120	40.1	12.2	26.2	69.4
4	150	46.1	9.1	34.7	80.1
5	180	45.8	15.2	28.3	65.6

<sup>a</sup>Water-methanol ratio: 1:1. Nylon fiber: 1 g. Monomer concentration: 9.39 mmol/g nylon. Temperature: 70°C. Liquor ratio: MMA:water-methanol: 1:26.

It appears that the energy transfer becomes easier with increasing dielectric constant values for polymerization.

However, it should also be noted that all these alcohols are solvents for the monomer but nonsolvents for the polymer. The solubility data of MMA in these solvents is presented in Table 4. The solubility of MMA decreases in the same order as the dielectric constant values. Hence, with an increase in solubility of the monomer in the medium, polymerization can take place more homogeneously and as a result the % TPY increase. The % graft add-on also increases for the same reason.

Similar results were obtained by Nayak and co-workers with wool fibers [20].

#### Effect of Time on Grafting

MMA was grafted onto nylon 6 fiber using a monomer concentration of 9.39 mmol/g nylon in a liquid ratio of 1:26 at 70°C in a

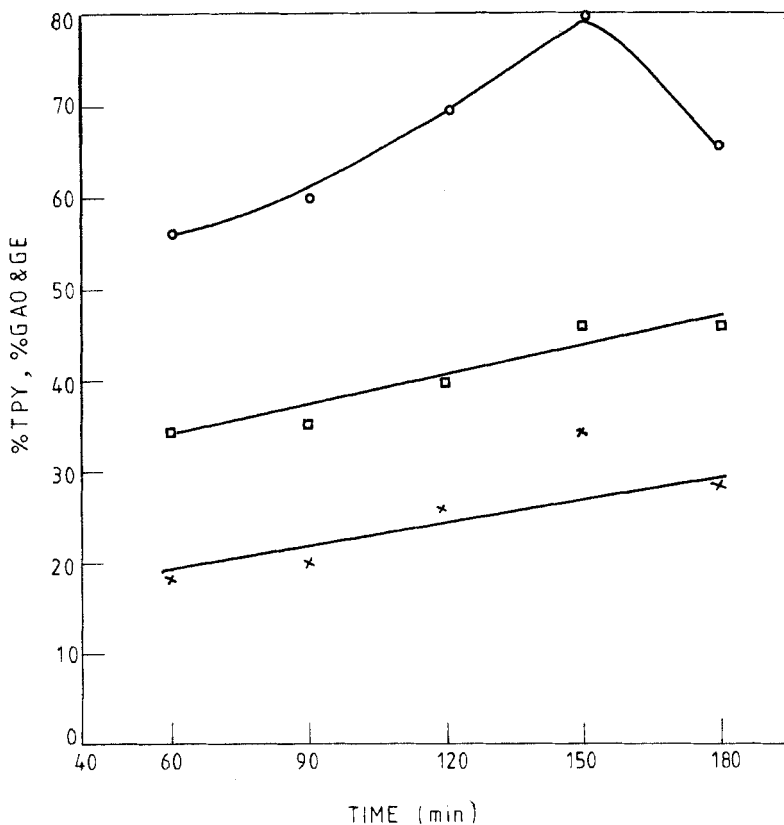


FIG. 4. Effect of reaction time on grafting. Nylon 6 fiber = 1 g. Monomer concentration = 9.39 mmol/g nylon. Temperature 70°C; liquor ratio (water-methanol 1:1) 1:26. (□) % total polymer yield (TPY). (x) % Graft add-on (GAO). (○) Grafting efficiency (GE).

TABLE 6. Effect of Time on Grafting of MMA onto Nylon 6 Fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	25.7	12.5	12.3	51.0
2	90	28.1	10.8	16.2	61.3
3	120	35.2	10.4	23.2	70.1
4	150	40.1	13.7	24.8	65.7
5	180	43.2	13.7	27.7	68.2

<sup>a</sup>Water-ethanol ratio: 1:1. Nylon fiber: 1 g. Monomer concentration: 9.39 mmol/g nylon. Temperature: 70°C. Liquor ratio: MMA: water-methanol: 1:26.

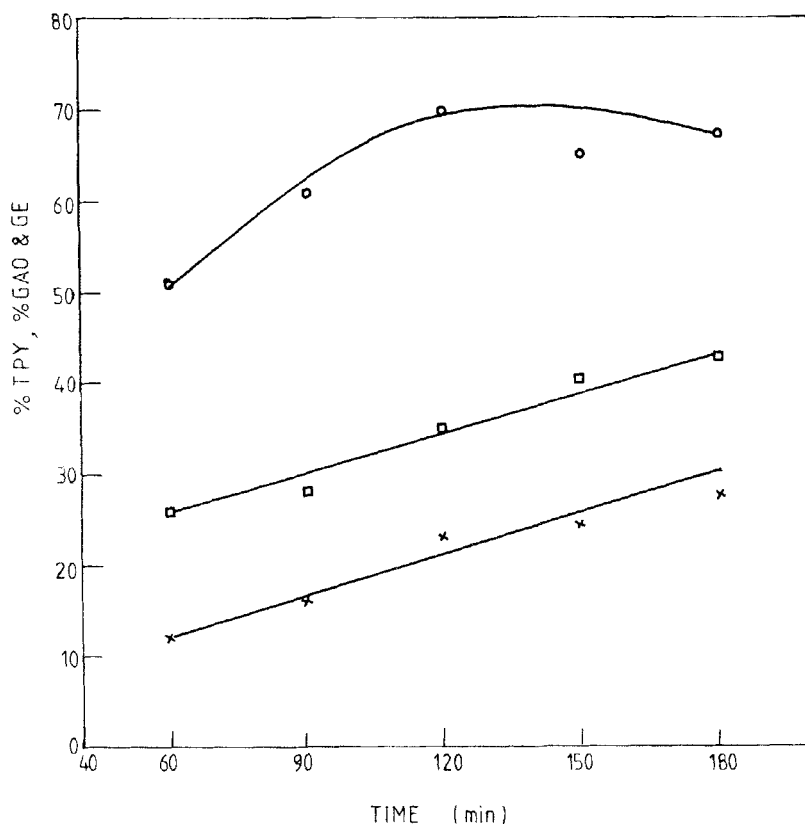


FIG. 5. Effect of reaction time on grafting. Nylon 6 fiber = 1 g. Monomer concentration = 9.39 mmol/g nylon. Temperature 70°C; liquor ratio (water-ethanol 1:1) 1:26. (□) % total polymer yield (TPY). (×) % graft add-on (GAO). (○) Grafting efficiency (GE).

water-methanol medium (1:1 ratio). The results are presented in Table 5 and Fig. 4. In this case the variation of time is fivefold from 60 to 180 min.

From the results it is seen that % TPY and % GAO increase for 150 min and thereafter decrease. The grafting efficiency also increases, reaches a maximum, and then falls.

#### Water-Ethanol System

Nylon 6 fiber was grafted with MMA using 1 g of nylon in a water-ethanol system with Liq. ratio 1:26 at 70°C in a water-ethanol medium (1:1 ratio). The results are presented in Table 6 and Fig. 5.

TABLE 7. Effect of Time on Grafting on MMA onto Nylon 6 Fiber in a 1:1 Water-Alcohol Mixture<sup>a</sup>

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	16.3	7.3	8.4	54.8
2	90	18.2	6.8	10.7	62.3
3	120	24.9	6.2	17.5	74.6
4	150	31.4	10.0	20.0	67.9
5	180	37.0	10.9	24.6	70.6

<sup>a</sup>Water-propanol ratio: 1:1. Nylon fiber: 1 g. Monomer concentration: 9.39 mmol/g nylon. Temperature: 70°C. Liquor ratio: MMA:water-methanol: 1:26.

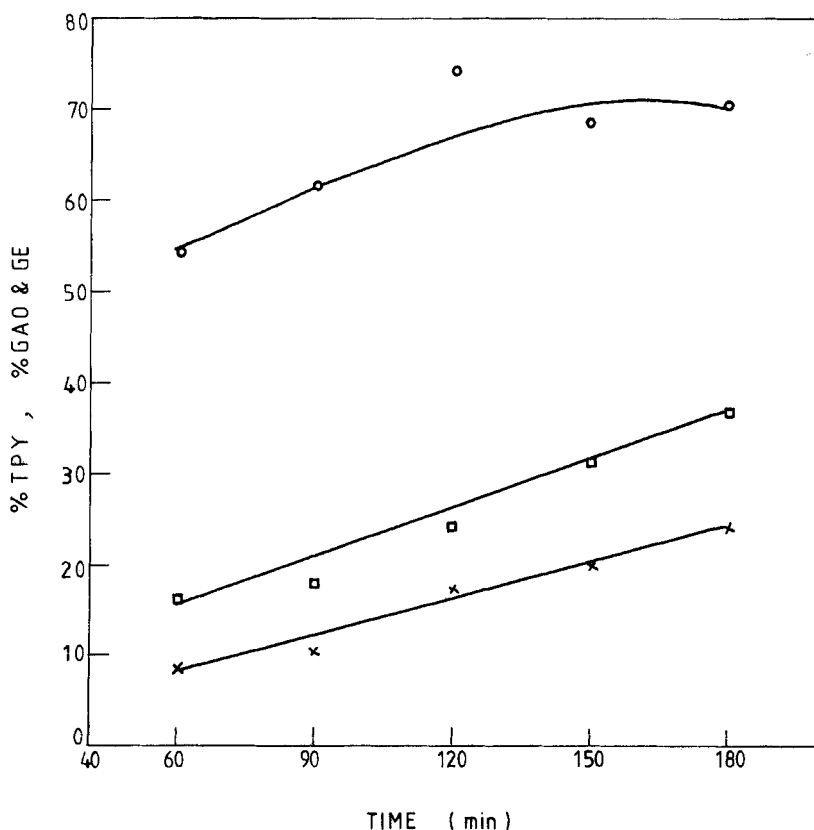


FIG. 6. Effect of reaction time on grafting. Nylon 6 fiber = 1 g. Monomer concentration = 9.39 mmol/g nylon. Temperature 70°C; liquor ratio (water-propanol 1:1) 1:26. (□) % total polymer yield (TPY). (×) % graft add-on (GAO). (○) Grafting efficiency (GE).

From the results it is evident that with the increase of time from 60 to 180 min, the % GAO and % TPY continuously increase whereas the GE increases, reaches a maximum, and then falls. However, the % HPY decreases for 120 min and then goes up again. Compared to the water-methanol system, in this system the overall GAO and TPY is less. With an increase in time, more monomer molecules react at the active sites available in the polymer chain. Hence the % TPY and % GAO increase continuously.

#### Water-n-Propanol System

Nylon 6 was grafted with MMA in a water-n-propanol system using a liquid ratio of 1:26 at 70°C. The results are presented in Table 7 and Fig. 6. From the results it is obvious that the % TPY and % GAO increase continuously in a fashion similar to the water-ethanol system. GE also increases and then falls. This is due to fall in % HPY. The fall in % GAO and GE in the case of the water-methanol system seems to be due to autoacceleration in the TPY curve (Fig. 4) [22].

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Accepted by editor January 15, 1981

Received for publication February 5, 1981