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Grafting Vinyl Monomers onto Nylon 6 Fiber. IV. Graft Copolymerization of Ethyl Methacrylate onto Nylon 6 Fiber by Photoirradiation

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ABSTRACT

Grafting of nylon 6 fiber was carried out using ethyl methacrylate (EMA) as the monomer in various water-alcohol systems (i.e., water-methanol, water-ethanol and water-n-propanol; water-alcohol ratio 1:1) at 70°C using a carbon arc lamp as the source of photochemical initiation. Percent graft add-on (% GAO) increases continuously and linearly with an increase in monomer concentration irrespective of the media used. The % GAO, however, decreases with an increase in the alkyl chain length of the alcohol used in the following order: water-methanol > water-ethanol > water-n-propanol. With an increase in the time period of grafting, % GAO and total polymer yield (% TPY) increase continuously in all three media whereas the grafting efficiency (GE) first increases and then falls after reaching a maximum level. Although a similar trend is maintained in the three systems, there is a decrease in overall % TPY and % GAO from the water-methanol system to the water-n-propanol system through the water-ethanol system.

INTRODUCTION

Various attempts have been made to modify nylon 6 fiber via graft copolymerization using several vinyl monomers [1-6]. Grafting has advantages over other methods because by choosing suitable monomers one can impart additional properties without affecting the basic properties of the fiber.

In our previous papers [7, 8], graft copolymerization of methyl methacrylate onto nylon 6 fiber using a UV radiation source in the presence of various water-alcohol systems have been reported.

In the present study ethyl methacrylate (EMA) was grafted onto nylon 6 fiber in the presence of several alcoholic systems using a photoirradiation source for initiation.

EXPERIMENTAL

Methanol, ethanol, n-propanol, the monomer EMA, and the nylon 6 fiber used for this study are the same as mentioned in our previous papers [7-9]. The grafting technique was the same as used previously [7].

RESULTS AND DISCUSSION

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

Certain preliminary experiments were conducted to ascertain whether EMA undergoes thermal polymerization at 70°C in water medium. It was found that no thermal polymerization of EMA takes place at this temperature when using a 3-h time period in the absence of any light source. It was further observed that when either water or alcohol (methanol, ethanol, or n-propanol) was used alone as the medium, no grafting takes place. However, grafting occurred when water-alcohol (ratio 1:1) was used with all three alcohols. Thus this system (water-alcohol ratio 1:1) was used as media during this study.

Effect of Monomer Concentration on GraftingWater-Methanol (1:1 Ratio)

Nylon 6 fiber was grafted using EMA as monomer in a water-methanol solution at a ratio 1:26 (1 mL of EMA and 25 mL of water-methanol) for 90 min using a carbon arc lamp as the photosource at four different monomer concentrations (from 9.1 to 22.75 mmol/g nylon). The results are presented in Table 1 and Fig. 1.

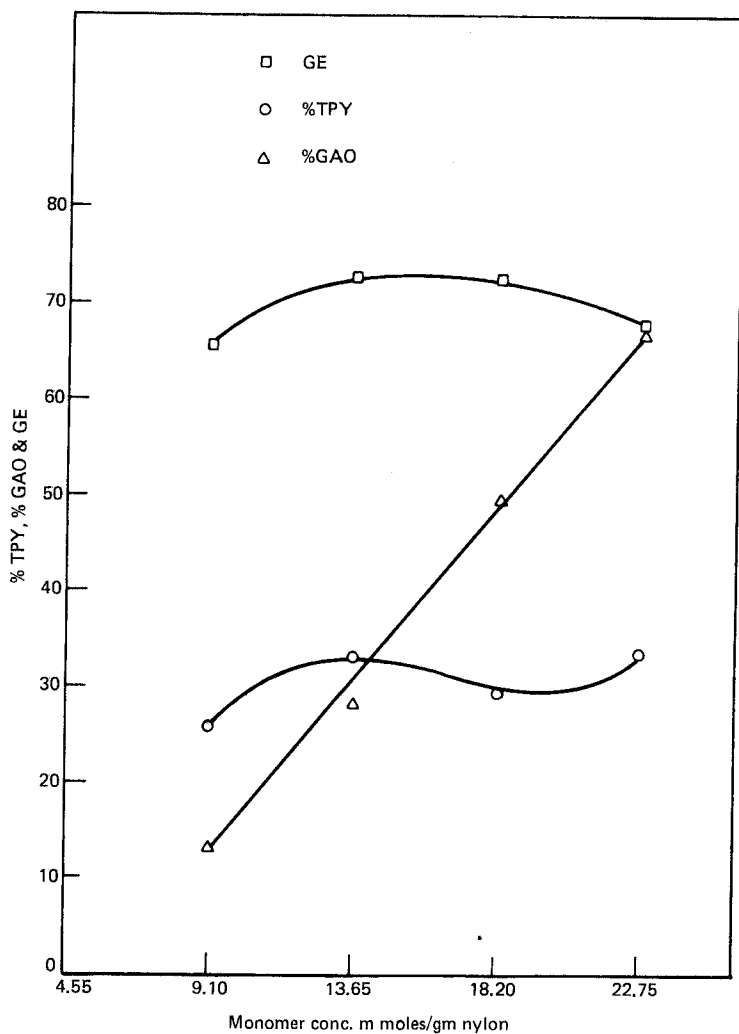


FIG. 1. Effect of monomer concentration on grafting of EMA onto nylon 6 fiber in water-methanol medium.

TABLE 1. Effect of Monomer Concentration on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (methanol) Medium^a

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.1	26.6	7.9	13.8	65.1
2	13.65	33.1	2.4	28.0	72.7
3	18.2	29.5	2.2	49.5	72.4
4	22.75	33.6	4.0	67.3	67.9

^aNylon fiber, 1 g; time, 90 min; 70°C; liquor ratio, EMA:water-methanol = 1:26.

From the results it may be seen that the % graft add-on (GAO) increases continuously and linearly with an increase in the monomer concentration. The grafting efficiency (GE) also increases slowly. However, there is not much increase in the % total polymer yield (TPY). This can be attributed to the fact that % TPY does not increase in proportion to the addition of monomer in the graft. The initial increase in grafting efficiency may be attributed to a decrease in homopolymerization with an increase of monomer concentration. Later on it might level off and even decrease at a very high concentration of the monomer. These results are similar to those obtained by other workers using several other vinyl monomers, e.g., acrylamide, acrylonitrile, acrylic acid, and styrene [3, 10, 11].

Water-Ethanol (Ratio 1:1)

EMA was grafted onto nylon 6 fiber using a water-ethanol medium at 70°C for 90 min and a liquor ratio of 1:26. The results are presented in Table 2 and Fig. 2.

From the results it is seen that the % GAO increases continuously with an increase in monomer concentration. The GE increase reaches a maximum value (76.5) and then falls. Not much change in % TPY is observed. These results are similar to those obtained in the water-methanol system. However, the rate of increase in % GAO with an increase in monomer concentration is less than in the water-methanol system.

Water-n-Propanol (Ratio 1:1)

EMA was grafted onto nylon 6 fiber using similar reaction conditions as used for the water-ethanol system. The results are presented in Table 3 and Fig. 3.

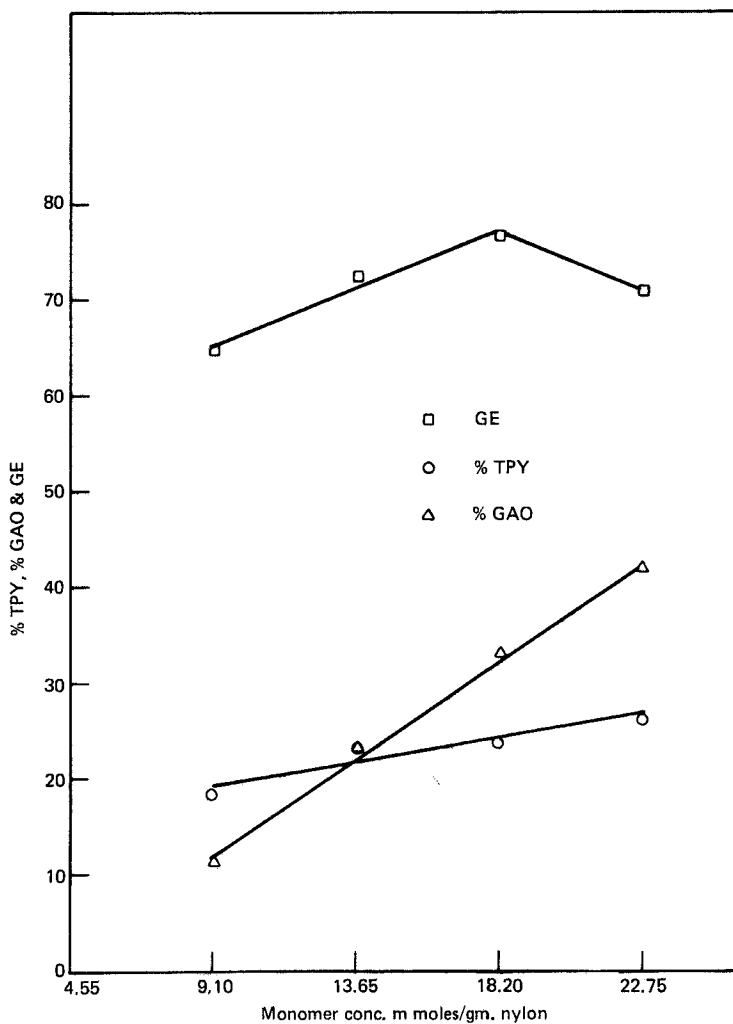


FIG. 2. Effect of monomer concentration on grafting of EMA onto nylon 6 fiber in water-ethanol medium.

TABLE 2. Effect of Monomer Concentration on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (ethanol) Medium^a

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.1	19.8	6.5	11.0	65.1
2	13.65	23.3	6.4	23.1	72.4
3	18.2	23.7	5.5	33.0	76.5
4	22.75	26.2	7.7	42.1	70.0

^aNylon fiber, 1 g; time, 90 min; 70°C; liquor ratio, EMA:water-methanol = 1:26.

TABLE 3. Effect of Monomer Concentration on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (n-propanol) Medium^a

No.	Monomer concentration (mmol)	% TPY	% HPY	% GAO	GE
1	9.1	17.7	5.6	8.9	63.6
2	13.65	16.1	4.6	15.7	71.3
3	18.2	16.7	3.2	24.6	80.9
4	22.75	21.5	5.1	37.2	76.1

^aNylon fiber, 1 g; time, 90 min; 70°C; liquor ratio, EMA:water-n-propanol = 1:26.

These results are similar to the results obtained in the water-ethanol system. The overall yield %, % GAO, and % HPY, however, are comparatively less than obtained in the above two cases. This seems to be the effect of the medium.

The following order of the media with respect to % TPY, % GAO, and GE is obtained: Water-methanol > water-ethanol > water-n-propanol.

It seems that the alcohols used in the above system take an active part in determining the efficiency of the reaction, which follows the following order: Methanol > ethanol > n-propanol.

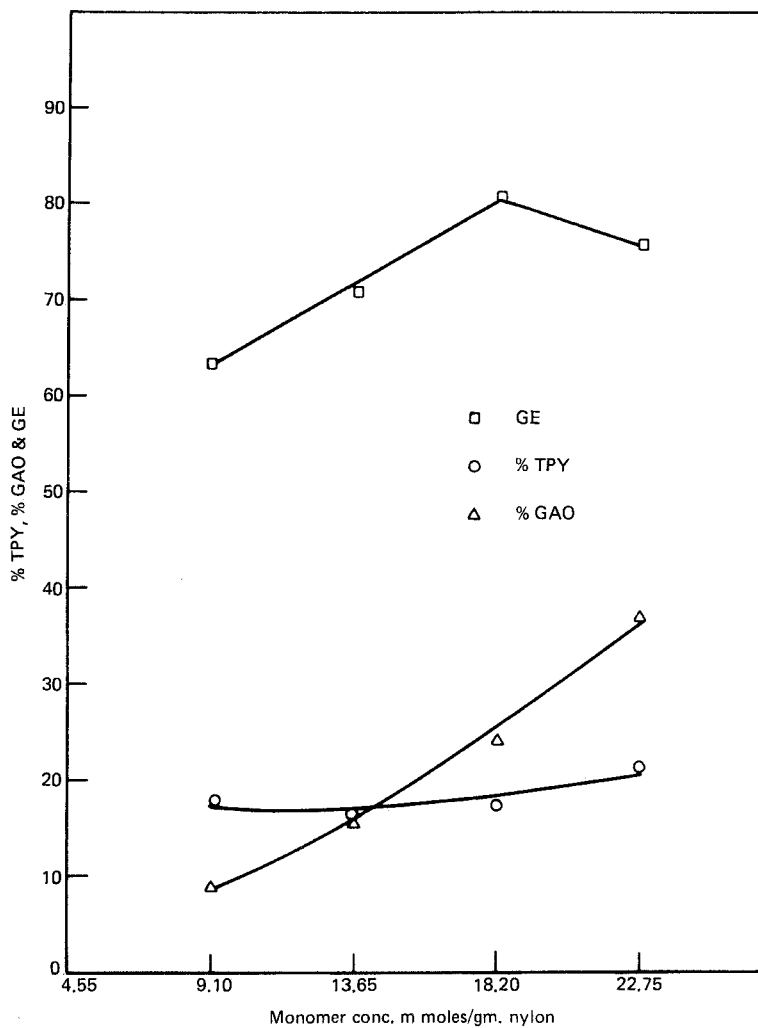


FIG. 3. Effect of monomer concentration on grafting of EMA onto nylon 6 fiber in water-n-propanol medium.

Effect of Reaction Time on Grafting

Water-Methanol (Ratio 1:1)

EMA was grafted onto nylon 6 fiber using 9.1 mmol/g nylon monomer concentration and a liquor ratio of 1:26 at 70°C for five different time intervals from 60 to 180 min in the water-methanol system. The results are presented in Table 4 and Fig. 4.

From the results it may be seen that % GAO and % TPY increase continuously whereas the GE increases at first and then falls after reaching its maximum level (74.3).

Water-Ethanol (Ratio 1:1)

Nylon 6 fiber was grafted with EMA using the water-ethanol system under the same conditions as used for the water-methanol system. The results are presented in Table 5 and Fig. 5.

From the results it is evident that with an increase in time from 60 to 180 min, the % GAO and the % TPY increase constantly whereas the GE increases, reaches a maximum (77.4), and then falls. Compared to the water-methanol system, the overall % GAO and % TPY are less in this system.

Water-n-Propanol (Ratio 1:1)

Nylon 6 fiber was grafted with EMA using the water-n-propanol system. The experimental conditions used here are similar to those used in the previous two cases. The results are presented in Table 6 and Fig. 6.

TABLE 4. Effect of Time on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (methanol) Medium^a

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	23.0	10.9	12.4	47.6
2	90	26.6	7.9	13.8	65.1
3	120	34.5	8.8	23.4	74.3
4	150	50.6	14.3	33.0	71.6
5	180	61.8	21.3	36.8	65.4

^aNylon fiber, 1 g; monomer concentration, 9.1 mmol/g nylon; 70°C; liquor ratio, EMA:water-methanol = 1:26.

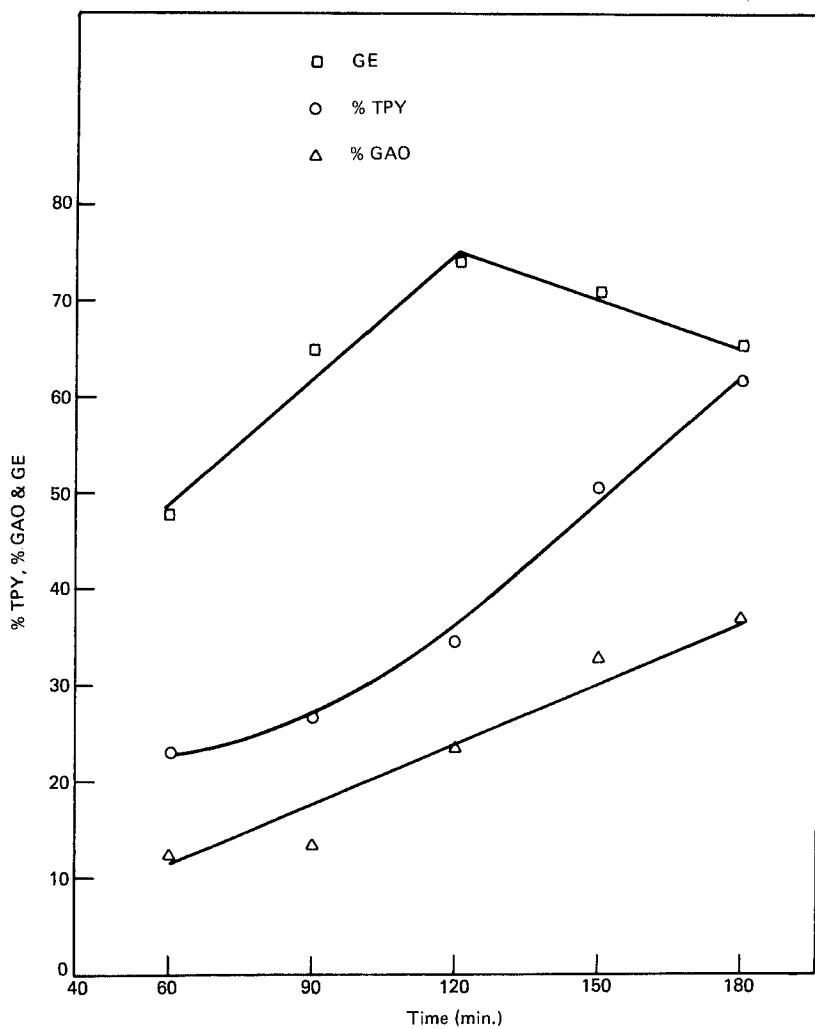


FIG. 4. Effect of time on grafting of EMA onto nylon 6 fiber in water-methanol medium.

TABLE 5. Effect of Time on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (ethanol) Medium^a

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	18.6	9.2	9.6	53.2
2	90	19.8	6.5	11.0	65.1
3	120	27.3	6.2	19.2	77.4
4	150	37.0	10.5	24.1	71.5
5	180	49.3	15.9	30.3	67.6

^aNylon fiber, 1 g; monomer concentration, 9.1 mmol/g nylon; 70°C; liquor ratio, EMA:water-ethanol = 1:26.

TABLE 6. Effect of Time on Grafting of EMA onto Nylon 6 Fiber in 1:1 Water-Alcohol (n-propanol) Medium^a

No.	Time (min)	% TPY	% HPY	% GAO	GE
1	60	15.4	9.1	7.8	48.4
2	90	17.7	5.6	8.9	63.6
3	120	26.9	8.6	16.7	68.1
4	150	38.9	12.6	23.9	67.5
5	180	50.7	8.0	30.0	54.3

^aNylon fiber, 1 g; monomer concentration, 9.1 mmol/g nylon; 70°C; liquor ratio, EMA:water-n-propanol = 1:26.

From the results it appears that with an increase in time, the % GAO and the % TPY go up constantly, whereas the GE increases, reaches a maximum value (68.1), and then falls. Similar results were also obtained in the above two cases.

Although a similar trend is maintained in all three systems, e.g., water-methanol, water-ethanol and water-n-propanol, there is a decrease in overall % TPY and % GAO as we move from the water-methanol system to the water-n-propanol system, giving the order of reaction: Water-methanol > water-ethanol > water-n-propanol.

With an increase in the reaction time period from 60 to 180 min,

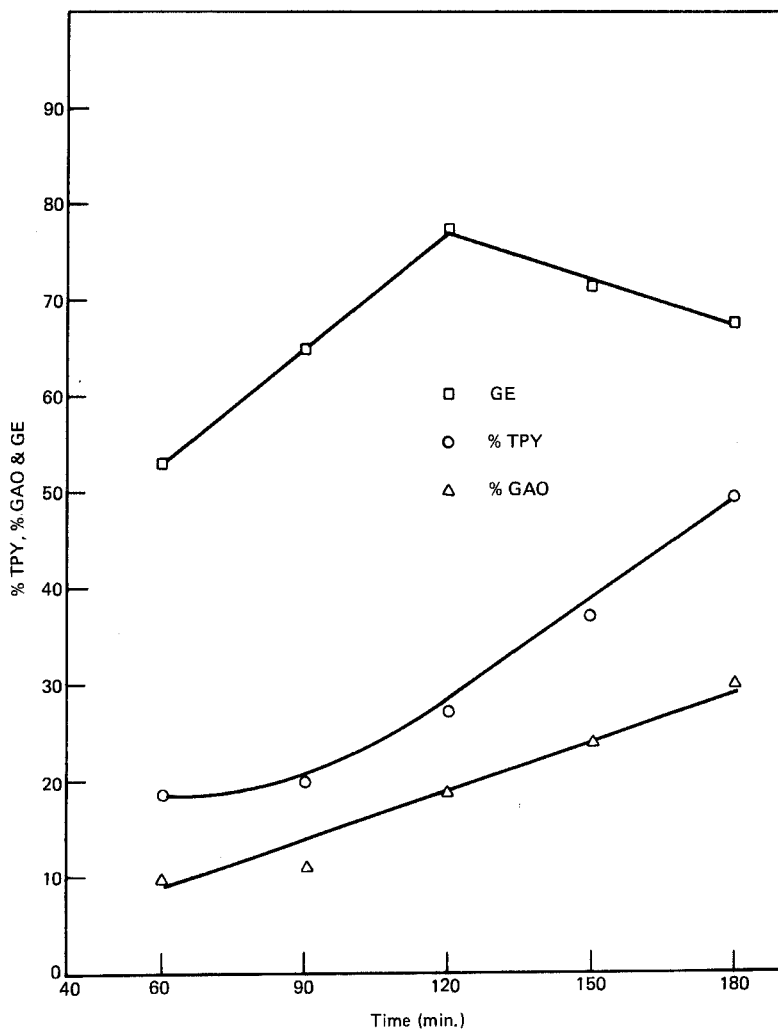


FIG. 5. Effect of time on grafting of EMA onto nylon 6 fiber in water-ethanol medium.

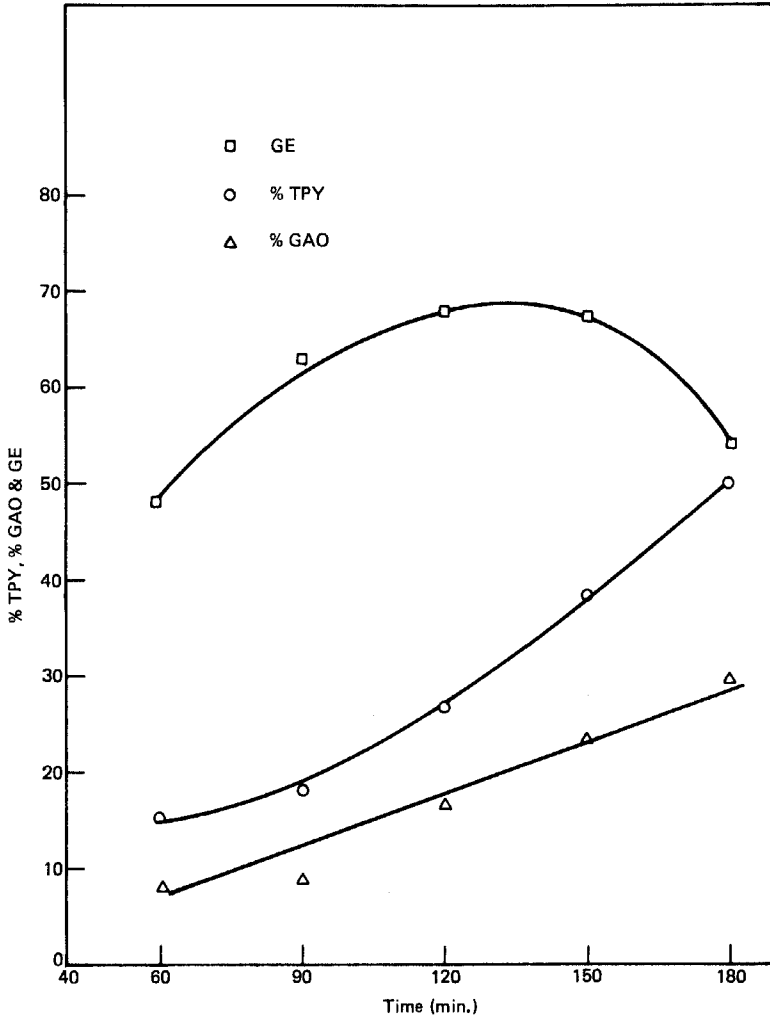


FIG. 6. Effect of time on grafting of EMA onto nylon 6 fiber in water-n-propanol medium.

monomer can polymerize for a longer period of time involving the active site, thus increasing the % TPY and the % GAO. This has been observed for all the media used. The maximum GE for these systems occurs at a reaction time of 120 min. This may be considered as the optimum reaction time for maximum grafting efficiency.

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