

NOTE

Photoinduced Graft Copolymerization of Nylon 6 Fibers with Acrylamide. I. Effect of Synthesis Conditions

INTRODUCTION

The graft copolymerization of nylon 6 with vinyl monomers has been studied extensively.¹⁻⁴ Nylon 6-*g*-polyacrylamide (nylon 6-*g*-PAam) has been prepared using different techniques. Teichmann and Uhlig^{5,6} used $Mn_4(P_2O_7)_3$, prepared by reaction of MnO_2 with H_3PO_4 , as the initiator in the graft copolymerization of nylon 6 with acrylamide. Varma and Ravisankar^{7,8} prepared nylon 6-*g*-PAam using a ceric ion-sulfuric acid system. The wrinkle resistance of polyamide fiber sheets was improved by contacting the electron-beam-irradiated fiber sheets with Aam to graft the latter to the sheets.⁹

The present work is aimed at grafting Aam to nylon 6 fibers in the presence of an aqueous fructose solution at 70°C under nitrogen atmosphere using photo-chemical initiation and studying the effect of synthesis conditions on grafting.

EXPERIMENTAL

Materials

The nylon 6 monofilament of 12.4 denier was obtained from Shree Synthetics Ltd., Ujjain, M.P., India.

The monomer acrylamide (SISCO Research Laboratories) of extra pure grade was used. The fructose (E. Merck) of molecular weight 1.8×10^2 was used.

Methanol (BDH, England) was used as the precipitant.

An Atlas 400 W Mercury Vapour Lamp made in Britain was used as a photochemical source.

Graft Copolymerization

One gram conditioned nylon sample was immersed in a solution of fructose and acrylamide in water, nitrogen was bubbled for 15 min through the solution, and then the reaction flask was kept under UV radiations at 70°C. After the desired time period, the reaction was terminated by the addition of large amount of methanol. The reaction mixture was filtered, and the residue was washed several times with methanol and dried to constant weight under vacuum at 40°C.

Homopolymer present either as a surface deposition or as an internal deposition was removed by hot water washings under continuous stirring. The product free of homopolymer was then dried in vacuum at 40°C.

Various grafting parameters such as percent conversion, percent grafting, grafting efficiency (GE), and percent homopolymer were evaluated. Percent grafting was calculated as the percent increase in weight over the original weight of the sample.

$$\text{grafting \%} = \frac{\text{wt grafted sample} - \text{wt sample}}{\text{wt sample}} \times 100$$

RESULTS AND DISCUSSION

Nylon 6 was graft-copolymerized with Aam in the presence of an aqueous fructose solution using photochemical initiation at 70°C under nitrogen atmosphere.

A preliminary experiment was carried out without any fructose and light source. No polymerization was found, indicating that Aam does not undergo thermal polymerization at the temperature (70°C) of the system.

In another experiment, no polymerization occurred at 70°C using the lamp source in the presence of fructose solution. This shows that Aam does not undergo homopolymerization in the absence of nylon.

TABLE I
Effect of Reaction Time on Acrylamide Grafting to Nylon 6 Fibers^a

Sample no.	Reaction time (h)	Acrylamide conversion (%)	Acrylamide grafting (%)	Grafting efficiency (%)	Homopolymer yield (%)
A ₁	2	40.0	27.0	33.8	66.2
A ₂	4	57.0	39.3	34.5	65.5
A ₃	6	65.9	53.2	40.4	59.6
A ₄	10	75.7	41.7	27.5	72.5

^a Nylon 6 = 1 g, acrylamide concn = 28.2 mmol/g nylon 6, fructose concn = 5 mmol/L, temp = 70°C, liquor ratio = 1:20.

Effect of Synthesis Conditions on Grafting

Effect of Reaction Time

The effect of reaction time on grafting is shown in Table I. The rate of acrylamide conversion increased continuously with reaction time, whereas percent grafting and GE first increased and then showed a decrease. It appears that at higher conversion autoacceleration sets in, showing a sudden increase in the homopolymer yield and resulting in a decrease in percent grafting and GE.

Effect of Acrylamide Concentration

Table II shows the effect of acrylamide concentration on grafting. The percent grafting and GE increased continuously with monomer concentration. The percent conversion initially increased, but at a higher concentration of acrylamide it showed a decrease.

With increase in monomer concentration rate of grafting increases whereas the rate of homopolymer formation decreases, resulting in a continuous increase in GE. Polyacrylamide formed at a higher concentration of acrylamide perhaps is of low molecular weight, which may be partially soluble in the nonsolvent, leading to a decrease not only in the homopolymer percent yield but also in total percent conversion.

Effect of Fructose Concentration

The effect of concentration of fructose on grafting was studied in the range of 5–15 mmol/L. The results are presented in Figure 1.

It may be seen from the results that in the absence of fructose around 41% grafting was obtained, indicating that fructose does not initiate the grafting and Aam can be grafted using photochemical initiation in water medium. Similar results have been obtained by Hiroshi et al.¹⁰ in the graft copolymerization of nylon with styrene in methanol solution by photochemical initiation in the absence of photosensitizer.

When fructose was used during the grafting at low concentration (5 mmol/L), an increase in percent conversion, percent grafting, and homopolymer percent yield over those of the reaction conducted

TABLE II
Effect of Acrylamide Concentration on Acrylamide Grafting to Nylon 6 Fibers^a

Sample no.	Acrylamide concn (mmol/g nylon 6)	Acrylamide conversion (%)	Acrylamide grafting (%)	Grafting efficiency (%)	Homopolymer yield (%)
B ₁	14.1	41.2	15.4	37.4	62.6
B ₂	21.1	53.3	31.0	38.8	61.2
A ₃	28.2	65.9	53.2	40.4	59.6
B ₃	56.3	49.2	91.3	46.3	53.7

^a Nylon 6 = 1 g, fructose concn = 5 mmol/L, liquor ratio = 1:20, temp = 70°C, time = 6 h.

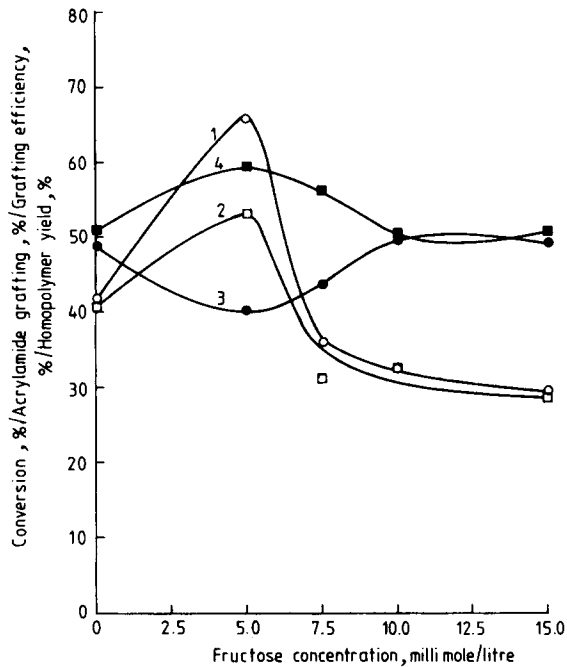


Fig. 1. Effect of fructose concentration on grafting. Nylon 6 = 1 g, acrylamide concn = 28.2 mM/g nylon 6, liquor ratio = 1:20, temp = 70°C, time = 6 h: (1) conversion (%); (2) acrylamide grafting (%); (3) grafting efficiency (%); (4) homopolymer yield (%).

without fructose was observed. However, GE showed a decrease. It seems that fructose increases the rate of grafting as well as homopolymerization. Probably, there is a greater increase in the rate of homopolymer formation than the grafting, resulting in a decrease in GE.

With increase in the concentration of fructose, however, a decrease in percent conversion, percent grafting, and homopolymer percent yield was observed. The rate of homopolymer formation decreases more rapidly than grafting, leading to an increase in GE. Thus, maximum grafting can be achieved only at low concentrations of fructose.

In the present study, no change in the reducing power of fructose treated with photosource for 6 h was observed. This indicates that fructose acts only as an agent for energy transfer and does not undergo photodecomposition. Similar results have been obtained in the methyl methacrylate-fructose-MeOH system.¹¹

Effect of Liquor Ratio

The effect of the ratio of the polymer to liquid on grafting was studied in the range of 1:20–1:60. The results are summarized in Table III.

TABLE III
Effect of Liquor Ratio on Acrylamide Grafting to Nylon 6 Fibers^a

Sample no.	Liquor ratio	Acrylamide conversion (%)	Acrylamide grafting (%)	Grafting efficiency (%)	Homopolymer yield (%)
A ₃	1:20	65.9	53.2	40.4	59.6
C ₁	1:30	46.6	40.9	43.9	56.1
C ₂	1:45	40.0	25.0	31.3	68.7
C ₃	1:60	34.0	14.0	20.6	79.4

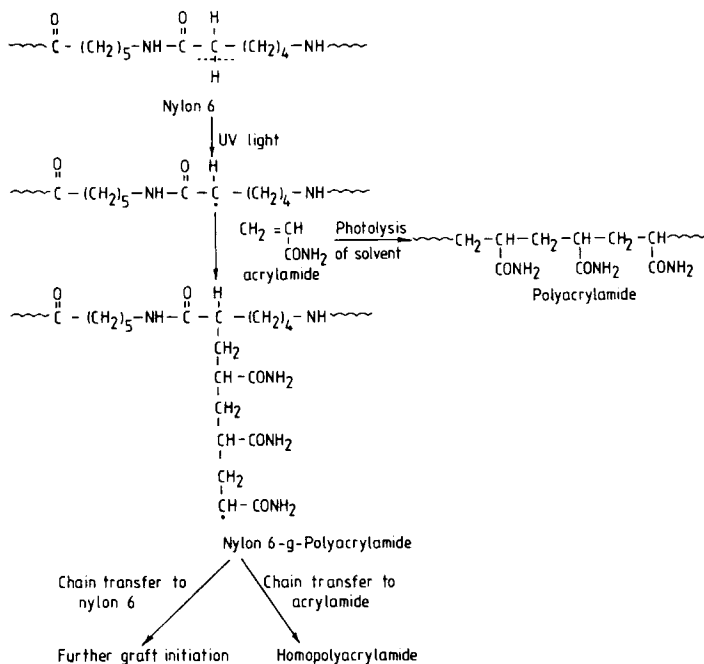
^a Nylon 6 = 1 g, acrylamide concn = 28.2 mmol/g nylon 6, fructose concn = 5 mmol/L, temp = 70°C, time = 6 h.

With an increase in liquor ratio there was a continuous decrease in all the grafting parameters. However, the homopolymer percent yield showed an increase with the liquor ratio.

As the solution becomes more dilute, the distance between the polymer chains increases, reducing the chances of grafting. This results in decreasing all the grafting parameters. An increase in the rate of homopolymer formation may be due to an increase in the photolysis of the solvent with dilution, which initiates the homopolymerization.

Mechanism of Graft Copolymerization

The grafting of Aam on nylon 6 is carried out by photochemical initiation. The UV light ($\lambda > 300$ nm) produces radical sites on nylon 6 backbone. The grafting of Aam is initiated from these sites. Homopolymerization is initiated by H and OH radicals formed from photolysis of the solvent and also by chain transfer to monomer:



Scheme 1

In conclusion, this study suggests that, to obtain a high percent grafting of acrylamide to nylon 6, the reaction must be carried out at high concentrations of acrylamide, small liquor ratio, and low fructose concentration for a moderate time period. However, more evidence is required to arrive at a definite conclusion in this regard and "work is in progress."

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