Photoinduced Graft Copolymerization of Nylon 6 Fibers with Acrylamide. II. Characterization and Evaluation of Properties

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Synopsis

Nylon 6-g-polyacrylamide graft copolymer prepared by photoinduced initiation was characterized and some of its properties were evaluated. Intrinsic viscosity of the graft copolymer increased continuously with percent grafting. Thermal stability decreased corresponding to the increase in add-on %. The moisture regain, diameter, and density showed an increase with percent grafting. The acid dyeability of the graft copolymer decreased with increase in graft level, whereas the disperse dye uptake increased initially up to a graft add-on of 28.9% and then showed a decrease.

INTRODUCTION

Graft copolymerization of nylon with vinyl monomers leads to an appreciable improvement in its properties. Jancso and Laszlo[1] reported that acrylamide-grafted nylon fabrics approach natural fibers moisture uptake. Dye uptake is satisfactory, but tear strength decreases continuously with grafting. In an another study it was reported[2] that the product shows improved weather resistance, wet crease recovery, and dye uptake. Nylon 6-g-polyacrylamide also show improved sewing resistance and water absorbency.[3] However, the thermal stability of the product decreases slightly.[4]

Recently we reported[5] the photoinduced graft copolymerization of nylon 6 fibers with acrylamide and the effect of reaction conditions on grafting. The present investigation is undertaken to evaluate the effect on structure and properties due to grafting a hydrophilic monomer (acrylamide) to a hydrophobic substrate (nylon 6).

EXPERIMENTAL

Materials

Various nylon 6-g-polyacrylamide samples with different percent grafting were obtained by grafting nylon 6 with acrylamide under different reaction conditions, as reported previously.[5]

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CCC 0021-8995/83/072217-09$01.90

Characterization

Fructose Estimation

The estimation of freshly prepared fructose solution and fructose solution treated under UV radiation was done by Fehling's solution method.[6]

Intrinsic Viscosity

The intrinsic viscosity $[\eta]$ of the parent, UV-treated nylon 6 and the grafted samples was determined at $30 \pm 0.1°C$ using Ubbelohde viscometer. 50–70 mg of the sample was dissolved in 25 cc of 98% sulfuric acid.

Diameter

The diameter of the parent and the grafted samples was measured using a projection microscope with a magnification of 250 times. Fifty readings were taken for each sample.

Density

The density of the parent and the grafted samples was measured at $65 \pm 2\%$ RH and $25 \pm 2°C$ by flotation method.[7] The column was prepared with xylene (density = 0.866) and carbon tetrachloride (density = 1.595).

Properties

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the parent, grafted nylon 6, polyacrylamide and 91.2% blend was carried out on a Stanton Redcroft TG-750 Thermobalance in nitrogen atmosphere. The samples were heated at a uniform heating rate of 10°C/min from room temperature to 800°C. Primary thermograms were obtained by plotting residual weight against temperature. From the thermograms, the initial decomposition temperature (IDT), the temperature corresponding to 50% weight loss (T_{50}), and the integral procedural decomposition temperature (IPDT) were calculated.

Moisture Regain

The moisture regain was measured by vacuum desiccator method. The fibers (0.3–0.4 g) were conditioned for 6 h at $65 \pm 3\%$ RH and $25 \pm 2°C$ temperature. After conditioning, the fibers were weighed and stored in a vacuum oven overnight and then in a vacuum desiccator containing P_2O_5 until a constant weight was obtained. From the original and dry weight of the fibers, moisture regain was calculated.

Dye Uptake

The dye uptake of the parent and the grafted samples was measured using (1) acid dye—Naphthalene Scarlet 4 RS (C.I. Acid Red 18); (2) disperse dye—Cibacet Red 2G (C.I. Disperse Red 17).

The fibers were dyed in aqueous medium under infinite dye bath conditions. The purified dye was dissolved in hot water (3% solution). For acid dyeing, the pH was adjusted to 5.5 using acetic acid and sodium acetate, whereas for disperse dyeing the dispersing agent (29 m/L) was added under continuous stirring. After this, distilled water was added in both types of dyeing to make up the dye bath. The material to liquor ratio was 1:500.

50 mg of the material was immersed in 25 cc of the dyestuff solution at 40°C and the temperature of the dyebath solution was raised to 100°C in $\frac{1}{2}$ h. The dyeing was continued at this temperature for 75 min. The material was then washed and soaped with Sandozin NIS for 30 min.

Dye uptake was measured by dissolving 10 mg of the dyed sample in 5 mL of formic acid, followed by determining the optical density of this solution using a Beckmann DK 2A Ratio Recording Spectrophotometer. The dye content was calculated using a previously constructed calibration curve.

RESULTS AND DISCUSSION

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

Intrinsic Viscosity

Intrinsic viscosities of nylon 6-g-polyacrylamide samples of different polyacrylamide contents were determined in 98% H_2SO_4 at 30 ± 0.1°C. The results are presented in Table I. Changes in $[\eta]$ with percent grafting are shown in Figure 1.

It can be seen from the results that there is a decrease in intrinsic viscosity of nylon 6 when it is treated with a photo source. This may be due to degradation. It is well known[8] that nylon 6 undergoes degradation when exposed to UV light.

TABLE I
Effect of Percent Grafting on Intrinsic Viscosity of Nylon 6-g-Polyacrylamide[a]

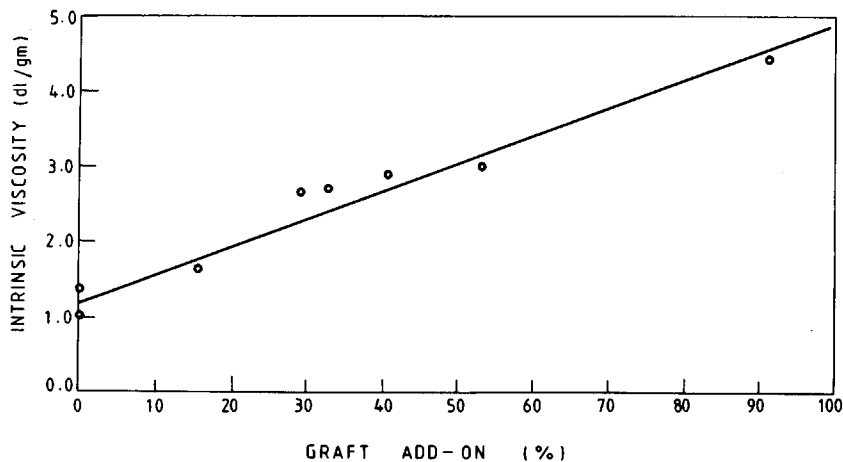| Sample no.	Graft add-on (%)	Intrinsic viscosity (dL/g)
1	Parent	1.32
2	Nylon treated with photo source for 6 h	0.98
3	15.3	1.65
4	28.9	2.68
5	32.8	2.73
6	40.7	2.85
7	53.2	3.02
8	91.2	4.48

[a] Grafting time = 6 h.

Fig. 1. Effect of percent grafting on intrinsic viscosity of nylon 6-*g*-polyacrylamide.

However, with increase in percent grafting the intrinsic viscosity increases continuously.

Intrinsic viscosity increases linearly on increasing the monomer concentration (Fig. 2).

Intrinsic viscosity of the graft copolymer also increases up to a fructose concentration of 5 mmol/L and then decreases (Fig. 3).   The trend in this curve is similar to that of the curve between fructose concentration and graft add-on % (Fig. 4).   This similarity indicates that increase in fructose concentration leads
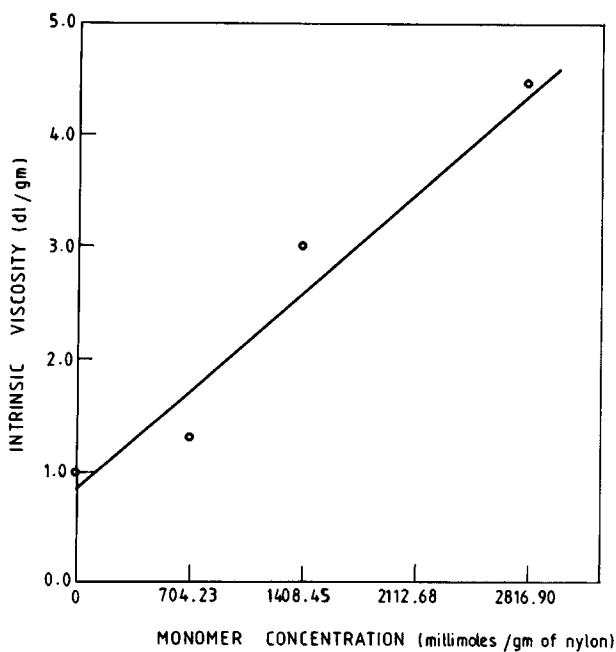

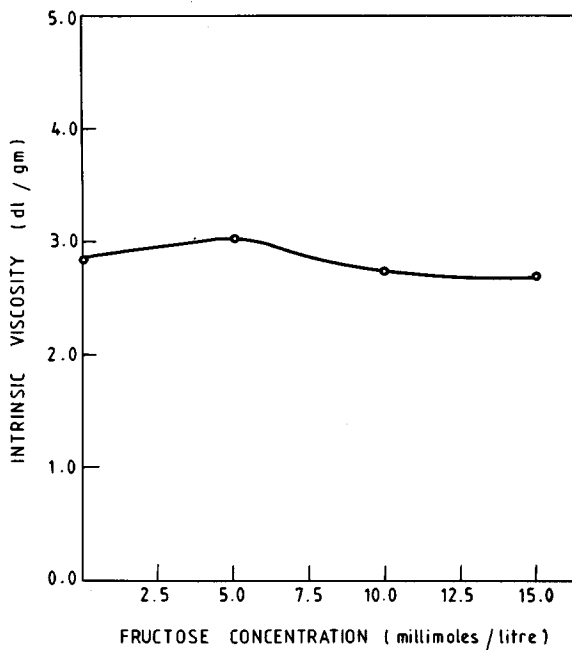Fig. 2. Variation in intrinsic viscosity with monomer concentration.

Fig. 3. Variation in intrinsic viscosity with fructose concentration.

to either increase in the rate of termination or decrease in the rate of grafting. However, as the grafting decreases with increase in fructose concentration, the later course seems to be more prevalent than the first.   However, it is not possible
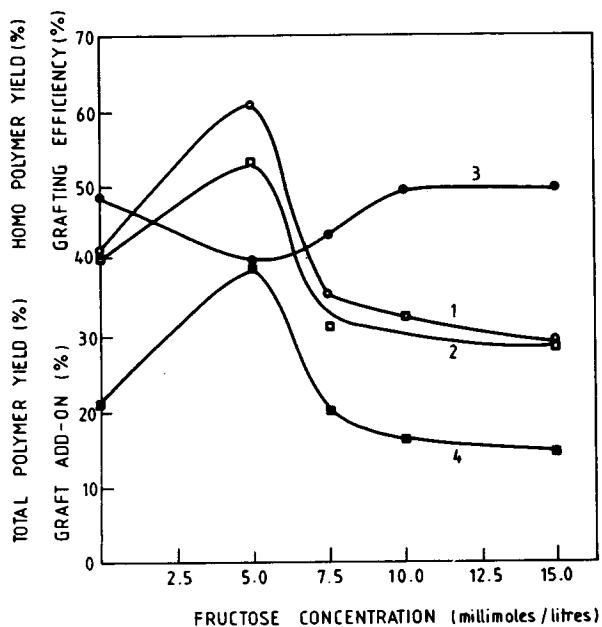

Fig. 4. Effect of fructose concentration on grafting parameters: (1) total polymer yield (%); (2) graft add-on (%); (3) grafting efficiency (%); (4) homopolymer yield (%).

TABLE II
Thermogravimetric Analysis of Nylon 6, Nylon 6-g-Polyacrylamide Samples, Polyacrylamide, and Nylon 6/Polyacrylamide Blend

Graft add-on (%)	IDT (°C)	T_{50} (°C)	IPDT (°C)
Parent	365	440	432.5
Nylon treated with photo source for 6 h	365	427	432.5
Polyacrylamide	187	405	416.5
Blend of nylon and 91.2% polyacrylamide	275	374	390.0
15.3	333	440	431.5
28.9	328	425	427.7
31.4	327	421	426.5
39.3	320	414	420.5
40.9	320	437	419.0
53.2	315	414	414.7
91.2	300	410	416.5

to say whether increase in fructose concentration affects the rate of grafting or not.

Thermogravimetric Analysis

The thermal properties of nylon 6-g-polyacrylamide were determined by studying their TGA thermograms. The results are presented in Table II.

It may be seen from the data (Table II) that there is no difference in IDT and IPDT values between nylon 6 and a photo-source-treated nylon sample. This indicates that there is no change in chemical nature during the degradation of nylon 6 which takes place by the effect of UV and light energy.

The IDT and IPDT values of the 91.2% grafted sample are higher than the corresponding values of a blend containing nylon and polyacrylamide in the same proportion. This confirms that grafting has taken place during the process.

The results in Table II also show that both IDT and IPDT decrease continuously with increase in graft add-on %. However, IPDT of the graft copolymers with >53.2% graft add-on remains almost unchanged. The decrease in thermal stability with increase in the graft add-on % has also been observed earlier.[4,9]

TABLE III
Moisture Regain, Diameter, and Density Values of Nylon 6 and Nylon 6-g-Polyacrylamide Samples

Graft add-on (%)	Moisture regain (%)	Diameter (cm $\times 10^{-3}$)	Density (g/cc)
Parent	4.01	3.87	1.141
15.3	4.96	4.90	1.189
28.9	5.30	5.50	1.215
31.4	5.65	5.70	1.204
39.3	6.09	6.55	1.207
40.9	6.18	6.70	1.207
53.2	6.87	6.95	1.231
91.2	9.08	9.90	1.248

Sample no.	Graft add-on (%)	Acid dye uptake	Disperse dye uptake
1	—	100.00	100.00
2	15.3	52.78	117.46
3	28.9	44.64	133.33
4	31.4	39.28	—
5	53.2	28.57	34.92
6	91.2	35.71	39.68

Moisture Regain, Diameter, and Density

Table III shows that with increase in graft add-on % the moisture regain increases continuously. This can be attributed to the hydrophilic nature of the monomer used and structural changes due to grafting.

Diameter of the fiber increases linearly with increase in grafting level (Table III). This may be due to the fact that the grafted polymer chains are to be accommodated in between the completely linear backbone chains which results in the pushing apart of the original linear nylon chains, resulting in an increase in diameter.

The density also shows a continuous increase with increase in graft add-on % (Table III). However, beyond 28.9% add-on the rate of increase in density decreases. It was observed in the case of acrylonitrile grafting[10] that the grafted
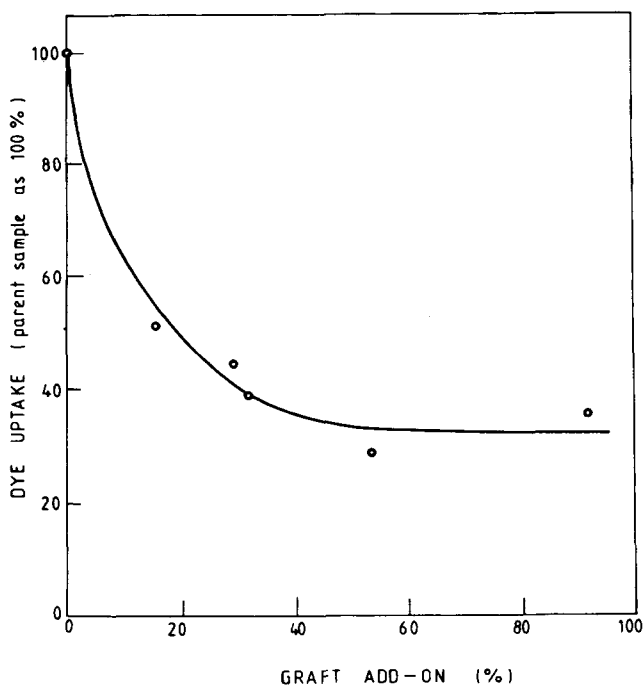

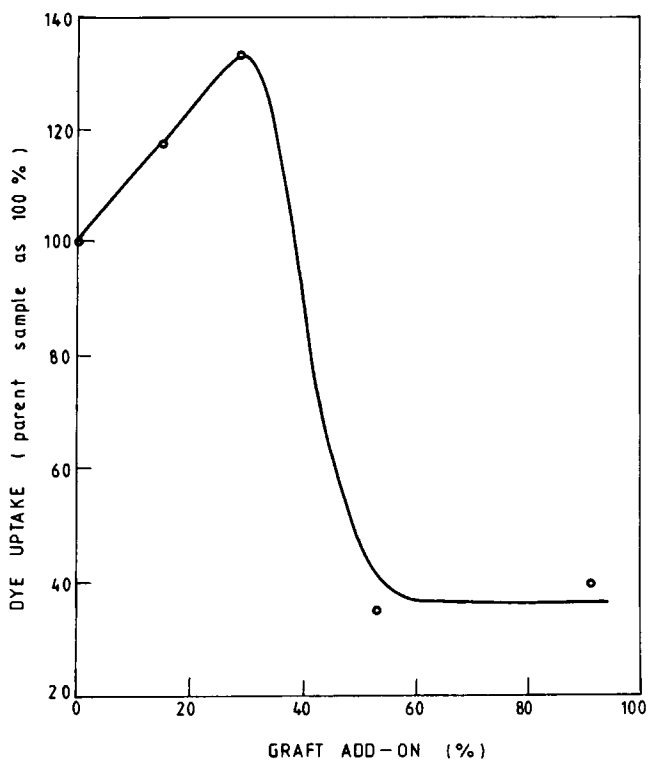Fig. 5. Acid dyeability of nylon 6-g-polyacrylamide samples.

Fig. 6. Disperse dyeability of nylon 6-*g*-polyacrylamide samples.

polyacrylonitrile chains remain mainly on the surface and only a part of these is used to fill up the voids of nylon 6 fibers. This leads to the changes in structural parameters of the original nylon, and hence a change in the density.
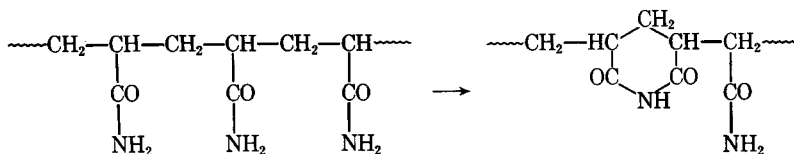
Dye Uptake

Nylon 6 fibers were grafted to various graft levels and the dye uptake of the grafted samples was evaluated taking ungrafted nylon 6 as having an arbitrary dye uptake value of 100 using acid and disperse dyes. The optical density values are presented in Table IV.

Acid Dye Uptake

It can be seen from Table IV that acid dyeability of the grafted samples decreases with increase in graft level. It has been observed earlier[11,12] that the acid dyeability of nylon 6-*g*-polyacrylamide decreases with increase in graft add-on % up to about 24%. However, in the present study there is a continuous decrease in the dye uptake, though at very high add-on % it becomes practically constant (Fig. 5). The main reason for reactive dye uptake should be sought in the change in chemical nature of parent nylon due to grafting. Acrylamide is known to give

a complex polymer containing amide and cyclic imide units.[13]   The structure of the grafted chains may be represented as follows:

$$\cdots CH_2-CH-CH_2-CH-CH_2-CH\cdots$$

(with CO—NH₂ substituents on each CH) → cyclic imide structure with $\cdots CH_2-HC$ ... $CH-CH_2\cdots$ and CO–NH–CO ring and CH₂, plus CO–NH₂

The cyclic units will not take part in the dyeing reaction and, moreover, can restrict the ease of approach of the dye to the reaction sites due to its bulky nature.

It is well known that protonation of amide group is pH dependent and does not take place at pH = 5.5 at which the dyeing was carried out.   Hence, the amide groups cannot contribute to the reactivity of the polymer towards acid dye.   The dye is then taken only by the nylon backbone chains as with increase in graft add-on % there is a proportionate decrease in the amount of nylon.

Disperse Dye Uptake

The results in Table IV and Figure 6 show that disperse dye uptake of the grafted samples increases initially up to a graft add-on of 28.9% and then decreases and becomes almost constant above 60% add-on.

Similar results have been observed by other workers.[1,3,14]   The disperse dye uptake is not dependent on the nature of the functional groups of the grafted polymers, but on the structural characteristics.   The initial increase in the dye uptake can be attributed to the increase in diameter of the grafted samples.   The subsequent decrease in dye uptake may be due to filling up more and more of voids and the amorphous regions of the nylon chains, thus leading to a decrease in the dye uptake.

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