Free-Radical Grafting of 4-Vinyl Pyridine onto Nylon 6 Fiber

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ABSTRACT: The chemistry of free-radical graft copolymerization initiated with peroxomonosulfate (PMS)–thioglycolic acid (TGA) redox system has been investigated by using 4-vinyl pyridine (4VP) as a model for nylon 6 fiber in aqueous solution under nitrogen atmosphere. Effects of concentration of 4VP, PMS, TGA, nylon 6, time, and temperature on R_h and graft parameters were studied. The FTIR spectrum of nylon 6-*g*-4VP was reported. Water retention capacity (WRC) of the grafted fiber was tested. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3108–3113, 2002

Key words: 4-vinyl pyridine; grafting; redox initiation; nylon 6 fiber; FTIR spectroscopy

INTRODUCTION

Grafting provides a method of adding certain desirable properties to a fiber without greatly disturbing the strength and other mechanical properties of the fiber. Graft copolymerization usually is accomplished by generating radical sites on the first polymer backbone onto which the monomer of the second polymer is copolymerized. Many synthetic fibers are resistant to dyeing and this can be improved by grafting. Styrene-grafted nylon 6 fiber is insoluble in formic acid and *m*-cresol and shows good water repellency when >10% is grafted.[1] Water sorbency, heat resistance, and antistatic properties are improved when acrylic acid is grafted with nylon 6 fiber.[2,3] Gopalan and coworkers grafted poly(acrylonitrile) (PAN) onto wool,[4] poly(ethylene terephthalate) (PET),[5] nylon 6, and nylon 66.[6] Peroxomonosulfate (PMS)–Fe^{2+} redox-initiated graft copolymerization of poly(acrylamide) was made by Samal et al.[7] Poly(acrylic acid) was grafted onto dextran by using PMS-Ag^{+} redox system.[8] Methacrylic acid was grafted onto agar by using Ce^{4+} as an initiator.[9] Acrylic acid and methyl methacrylate were grafted onto starch, agar, and cellulose backbone by using various redox systems.[10–13] Free-radical grafting of itaconic acid onto LDPE was reported by Pesetskii and Kelar.[14] *t*-Butoxy radicals initiated the graft copolymerization of 4-vinyl pyridine (4VP) onto poly(propylene) fiber.[15] Kondo and coworkers[16] grafted methylmethacrylate onto cellulose film by an ultrasonic irradiation method in the presence of ceric salt.

In this article, we report on the results of graft copolymerization of 4VP onto nylon 6 fiber by using PMS–thioglycolic acid (TGA) redox system. The chemical grafting was confirmed by a FTIR spectroscopic method. The water retention capacity of the grafted nylon 6 fiber was tested.

EXPERIMENTAL

Materials

4-Vinyl pyridine [4VP; analytical reagent (AR), Aldrich] was distilled twice over KOH and CaH_2, respectively, under nitrogen atmosphere. Potassium PMS (E. Merck) and TGA (AR, SRL) were used as such. Nylon 6 (a donated sample from M/S. Madura Coats, Madurai) was used, after Soxhlet extraction with acetone to remove any adhering impurities, and was dried at room temperature.

Grafting procedure

Nylon 6 (W_1 g), a required amount of 4VP, TGA, and water were taken in a polymer tube and thermostated at 45°C for 30 min. Amounts used are defined in Table II. The solution was deaerated by passing pure nitrogen gas for 30 min. The polymerization was initiated by the addition of calculated volumes of preaerated PMS (using standard solutions). The time of adding the oxidizing agent, PMS, was taken as the starting time for the reaction (polymerization conditions were selected in such a way that no polymerization occurred in the absence of added oxidant). This was

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ascertained by a separate experiment. At the end of the reaction time, the reaction was arrested by immersing the reaction vessel into ice-cold water and blowing air into the reaction vessel. Here, all the graft copolymerization experiments were carried out at 45°C for 45 min.

The grafted nylon 6, along with homopolymeric [poly(4-vinyl pyridine) (P4VP)], was filtered from the reaction mixture using G4 sintered crucible, washed well with distilled water several times, dried at 80°C (for 4 h), and weighed to constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2 g). The mixture of the grafted nylon 6 fiber along with homopolymer, P4VP, was Soxhlet extracted with acetone or benzene for 24 h to separate the homopolymer. After the separation of the homopolymer, the grafted sample was dried at room temperature and weighed to constant weight (W_3 g). The difference in ($W_3 - W_1$) gives the weight of the grafted P4VP. The difference in ($W_2 - W_3$) gives the weight of the homopolymer, P4VP, formed. The above experimental approach hence provides a way to follow the kinetics of both graft copolymerization and simultaneous homopolymerization.

Rate measurements

Rate of grafting (R_g), rate of homopolymerization (R_h), % grafting, and % grafting efficiency were calculated as follows:

$$\%\ \text{grafting} = \frac{(W_3 - W_1)}{W_1} \times 100$$

$$\%\ \text{grafting efficiency} = \frac{(W_3 - W_1)}{\text{weight of monomer used } (W_4)} \times 100$$

$$R_g = \frac{(W_3 - W_1)}{VtM} \times 1000$$

TABLE I
Effect of Time on R_h and Graft Parameters

Time (s)	$R_h \times 10^6$ (mol 1^{-1} s^{-1})	$R_g \times 10^7$ mol 1^{-1} sec^{-1}	% Grafting	% Grafting efficiency
900	21.3	5.28	0.75	4.76
1800	15.1	3.69	1.05	6.67
3600	12.8	2.81	1.60	10.1
5400	8.65	2.28	1.94	12.3
7200	5.91	2.06	2.34	14.9

[4VP] = 0.07 mol 1^{-1}; [PMS] = 0.005 mol 1^{-1}; [TGA] = 0.005 mol 1^{-1}; weight of nylon 6 = 0.20 g; temperature = 45°C.

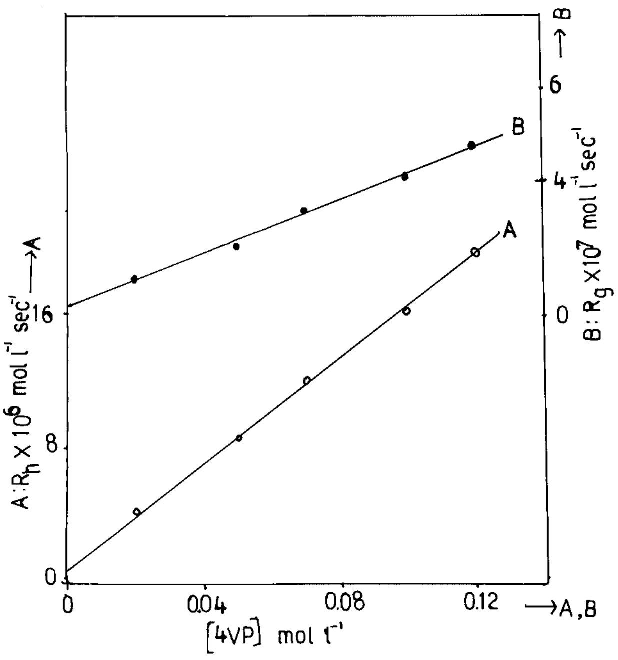

Figure 1 (A) Effect of [4VP] on R_h. (B) Effect of [4VP] on R_g. [PMS] = 0.005 mol 1^{-1}, [TGA] = 0.005 mol 1^{-1}, weight of nylon 6 = 0.20 g, temperature = 45°C.

$$R_h = \frac{(W_2 - W_3)}{VtM} \times 1000$$

where V is total volume of the reaction mixture, t is reaction time in seconds, and M is molecular weight of the monomer.

FTIR spectroscopy

The FTIR spectra of the grafted fiber were taken by the KBr pelletization method by using a Bruker Equinox55 model FTIR spectrophotometer.

Water retention capacity

Water retention capacities (WRC) of both ungrafted and grafted nylon 6 fibers were determined. One gram of fiber (grafted nylon 6 or pure nylon 6, without any physical deposition of homopolymer) was immersed in 100 mL doubly distilled water. After a particular retention time (12 h), the contents were then filtered with a sintered glass filter and sucked out at 700 mmHg pressure during which the grafted P4VP chains from nylon 6 backbone were not removed. The volume of the filtrate was measured and the water retention which is equal to the amount of water absorbed was calculated as grams of water per gram of dry nylon 6 fiber. The measurement was repeated by drying the samples in a hot air oven at 60°C to constant weight.

TABLE II
Effect of [4VP], [PMS], [TGA], and (amount of nylon 6 fiber) on % Grafting and % Grafting Efficiency

[4VP][a] (mol 1^{-1})	% Grafting	% Grafting efficiency	Section
0.02	0.45	8.57	
0.05	0.85	8.10	
0.07	1.31	8.25	II A
0.10	1.75	8.33	
0.12	2.14	8.17	

$[PMS]^{1/2} \times 10^{2}$[b] ($mol^{1/2}\ 1^{-1/2}$)	% Grafting	% Grafting efficiency	Section
3.16	0.60	3.81	
5.48	0.85	5.40	
7.07	1.05	6.67	II B
7.75	1.20	7.62	
8.94	1.35	8.57	

$[TGA]^{1/2} \times 10^{2}$[c] ($mol^{1/2}\ 1^{-1/2}$)	% Grafting	% Grafting efficiency	Section
3.16	0.45	2.86	
5.48	0.65	4.13	
7.07	0.80	5.05	III A
7.75	0.95	6.03	
8.94	1.05	6.67	

(Wt. of nylon 6 fiber)$^{1/2}$[d] (g)$^{1/2}$	% Grafting	% Grafting efficiency	Section
0.32	0.80	5.08	
0.39	1.00	6.35	
0.50	1.30	8.25	III B
0.55	1.45	9.21	
0.59	1.55	9.84	

[a] [PMS] = 0.005 mol 1^{-1}; [TGA] = 0.005 mol 1^{-1}; weight of nylon 6 fiber = 0.20 g; temperature = 45°C.

[b] [4VP] = 0.07 mol 1^{-1}; [TGA] = 0.005 mol 1^{-1}; weight of nylon 6 fiber = 0.20 g; temperature = 45°C.

[c] [4VP] = 0.07 mol 1^{-1}; [PMS] = 0.005 mol 1^{-1}; weight of nylon 6 fiber = 0.20 g; temperature = 45°C.

[d] [4VP] = 0.07 mol 1^{-1}; [PMS] = 0.005 mol 1^{-1}; [TGA] = 0.005 mol 1^{-1}; temperature = 45°C.

RESULTS AND DISCUSSION

Effect of time on R_h and graft parameters

R_h and graft parameters were determined at various time intervals while keeping other experimental conditions as given in Table I. Both R_h and R_g decreased with an increase of time. To follow the kinetics of graft copolymerization in a smooth fashion, a reaction time of about 2700 s was selected for the present study based on trial experiments. Up to 3600 s, both R_h and R_g increase; thereafter, homopolymer formation was found to be far higher than graft copolymer formation. To avoid the homopolymer formation in larger amounts, the average reaction time of 2700 s was selected from Table I. The % grafting and % grafting efficiency were observed to increase with an increase in time up to 2 h (Table I).

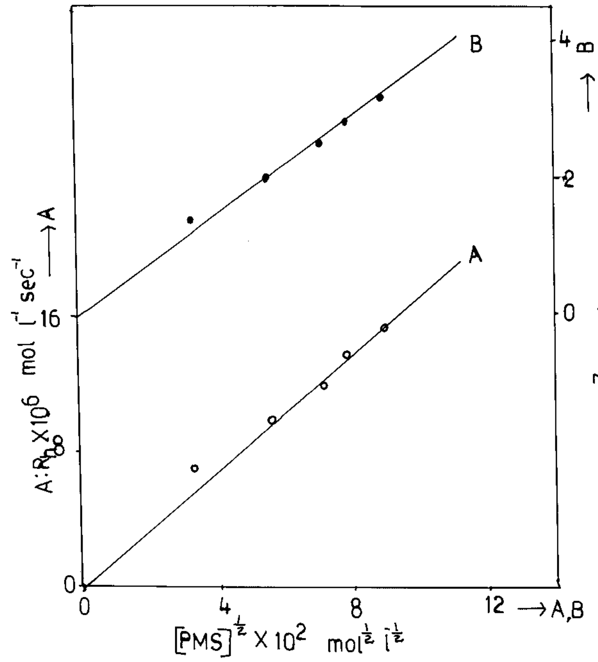

Figure 2 (A) Effect of [PMS] on R_h. (B) Effect of [PMS] on R_g. [4VP] = 0.07 mol l^{-1}, [TGA] = 0.005 mol l^{-1}, weight of nylon 6 = 0.20 g, temperature = 45°C.

Effect of [4VP] on R_h and graft parameters

Experimental results were obtained by changing [4VP] in the range of 0.02 to 0.12 mol l^{-1}, while keeping other experimental conditions constant. It is interesting to note that both R_h and R_g increase with an

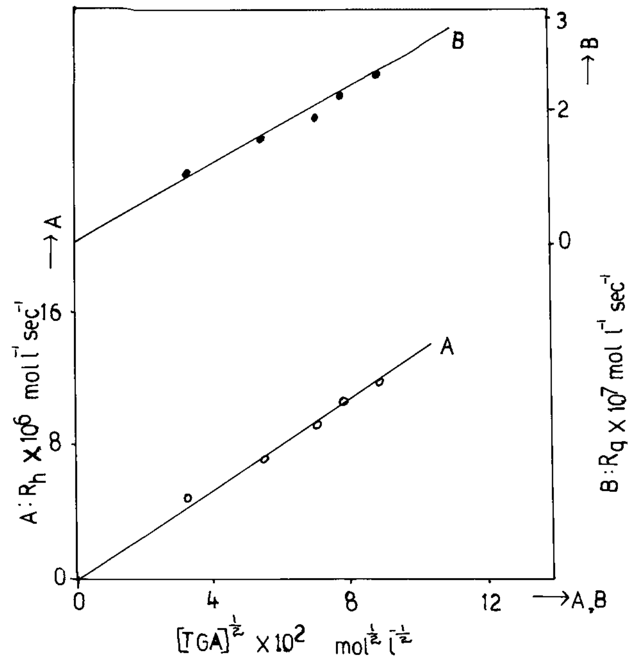

Figure 3 (A) Effect of [TGA] on R_h. (B) Effect of [TGA] on R_g. [4VP] = 0.07 mol l^{-1}, [PMS] = 0.005 mol l^{-1}, weight of nylon 6 = 0.20 g, temperature = 45°C.

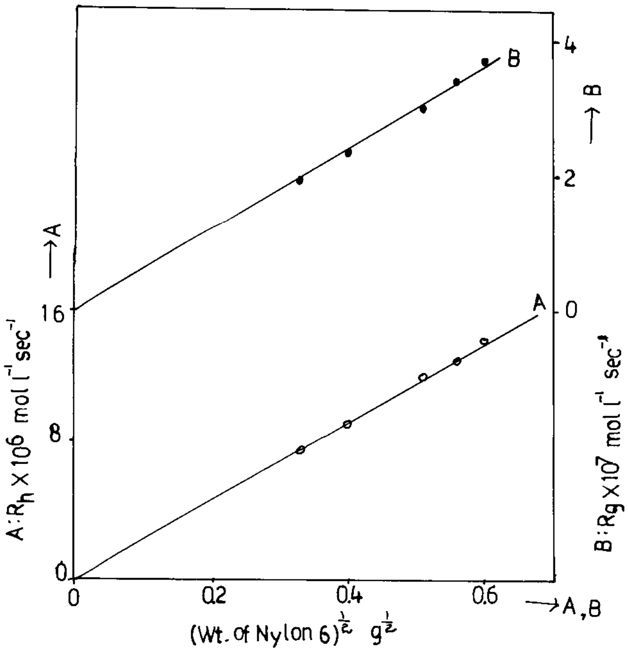

Figure 4 (A) Effect of (amount of nylon 6 fiber) on R_h. (B) Effect of (amount of nylon 6 fiber) on R_g. [4VP] = 0.07 mol l^{-1}, [PMS] = 0.005 mol l^{-1}, [TGA] = 0.005 mol l^{-1}, temperature = 45°C.

increase in [4VP] (Fig. 1). It was observed that the % grafting increased steadily with an increase in [4VP], but the % grafting efficiency remained unaffected for a change in [4VP] (Table II). To determine the order dependence of [4VP] on R_h and R_g, plots of R_h versus [4VP] [Fig. 1(A)] and R_g versus [4VP] [Fig. 1(B)] were drawn. These plots were found to be straight lines, indicating the first-order dependence of R_h and R_g on [4VP]. The increase in R_h and R_g may be due to an increase in monomer radicals.

Effect of [PMS] on R_h and graft parameters

The [PMS] varied between 0.001 and 0.008 mol l^{-1}, while other experimental conditions were kept constant. Here again, both R_h and R_g increased with an increase in [PMS]. The % grafting and % grafting efficiency are also increased with [PMS] as represented in Table II. The plots of R_h versus [PMS]$^{1/2}$ [Fig. 2(A)] and R_g versus [PMS]$^{1/2}$ [Fig. 2(B)] were drawn. The plots were found to be straight lines passing through the origin, indicating half-order dependence of both R_h and R_g on [PMS]. The increase in R_h and R_g may be due to an increase in initiator radicals.

Effect of [TGA] on R_h and graft parameters

As represented in Table II, [TGA] varied between 0.001 to 0.008 mol l^{-1}, while keeping other experimental conditions constant. Both R_h and R_g steadily increased with [TGA]. It was found that the % grafting and % grafting efficiency were found to have increasing trends with [TGA] (Table II). To determine the order dependence, the plots of R_h versus [TGA]$^{1/2}$ [Fig. 3(A)] and R_g versus [TGA]$^{1/2}$ [Fig. 3(B)] were drawn and indicated a half-order dependence of both R_h and R_g on [TGA]. The reason for the increase in R_h and R_g may be due to an increase in initiator radicals.

Effect of (amount of nylon 6 fiber) on R_h and graft parameters

The weight of backbone material varied from 0.10 to 0.35 g, while keeping other experimental conditions constant. It was observed that both R_h and R_g values increased steadily with an increase in the weight of nylon 6 fiber. The % grafting and % grafting efficiency values obtained with the change in backbone weight are given in Table II. It is interesting to note that both % grafting and % grafting efficiency were found to increase linearly.

The plot of R_h versus (amount of nylon 6 fiber)$^{1/2}$ [Fig. 4(A)] and R_g versus (amount of nylon 6 fiber)$^{1/2}$ [Fig. 4(B)] were drawn and found to be 0.5 order dependent on both R_h and R_g on the amount of nylon 6 fiber. When the amount of nylon 6 fiber increased, the grafting site, surface effect, and macroradicals also increased.

Effect of temperature on R_h and graft parameters

The values of R_h and R_g obtained when changing the temperature from 32 to 60°C are given in Table III. Both R_h and R_g increase initially up to 50°C and then

TABLE III
Effect of Temperature on R_h and Graft Parameters

Temperature (°C)	$1/T \times 10^3$ (K^{-1})	$R_h \times 10^6$ (mol 1^{-1} s^{-1})	$R_g \times 10^7$ (mol 1^{-1} s^{-1})	% Grafting	% Grafting efficiency
32	3.28	5.86	1.53	0.65	4.13
40	3.19	9.18	2.58	1.10	6.98
50	3.09	12.2	3.17	1.35	8.57
55	3.05	10.6	2.46	1.05	6.67
60	3.00	7.22	1.99	0.85	5.40

[4VP] = 0.07 mol 1^{-1}; [PMS] = 0.005 mol 1^{-1}; [TGA] = 0.005 mol 1^{-1}; weight of nylon 6 fiber = 0.20 g.

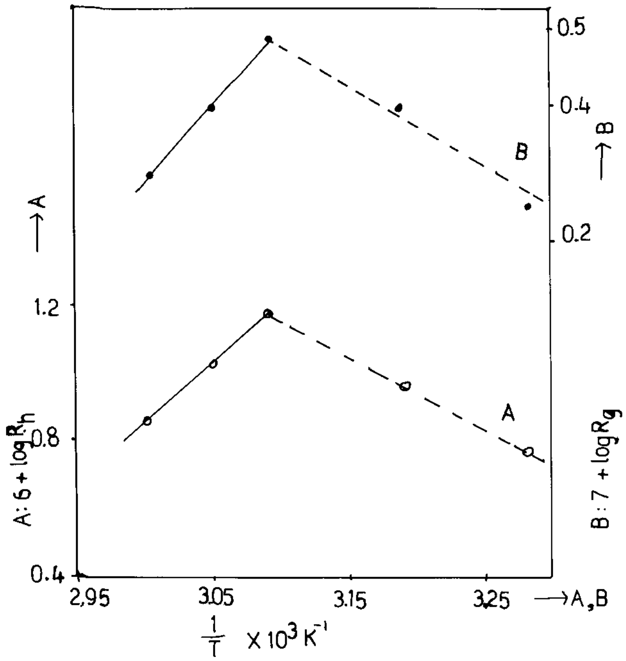

Figure 5 (A) Effect of temperature on R_h. (B) Effect of temperature on R_g.

fell (Table III). The % grafting and % grafting efficiency also follow the same trend. The decrease in R_h and graft parameters at higher temperatures is attributed to the depletion and evaporation of monomer.

The Arrhenius plots of log R_h versus $1/T$ [Fig. 5(A)] and log R_g versus $1/T$ [Fig. 5(B)] were drawn. Both these plots were found to show an initial increasing trend followed by a decreasing trend. The first linear portion (increasing trend) was taken into account with maximum log R_h and log R_g values of 1.08 and 0.50, respectively. The *Ea* values were determined for both R_h and R_g as 9.62 and 5.09 K cal/mol, respectively, for the above-mentioned linear region.

TABLE IV
Water Retention Capacity of Nylon 6 Fiber Before and After Grafting

Polymer	% Grafting	Water retention (g/g)
Nylon 6	—	1.1
Nylon 6-*g*-P(4VP)	1.31	3.8
	1.75	5.3
	2.14	7.9

FTIR spectroscopy

The FTIR spectrum of nylon 6-*g*-4VP [Fig. 6(A)] shows additional peaks at 1602 and 1551 cm^{-1} due to the presence of aromatic C—H stretching vibration. These were not found in pure nylon 6 fiber. The appearance of the above peaks indicate the chemical grafting of poly(4VP) onto nylon 6 fiber. For the sake of comparison, the FTIR spectrum of poly(4VP) [Fig. 6(B)] and pure nylon 6 fiber [Fig. 6(C)] are included.

Water retention capacity

The WRC of grafted and virgin nylon 6 fibers is given in Table IV. WRC increases with increase in % grafting. The plot of % grafting versus retention [Fig. 7] was made. The increase in retention capacity may be due to (1) the formation of hydrogen bonds between the nitrogen atom of vinyl pyridine ring and water

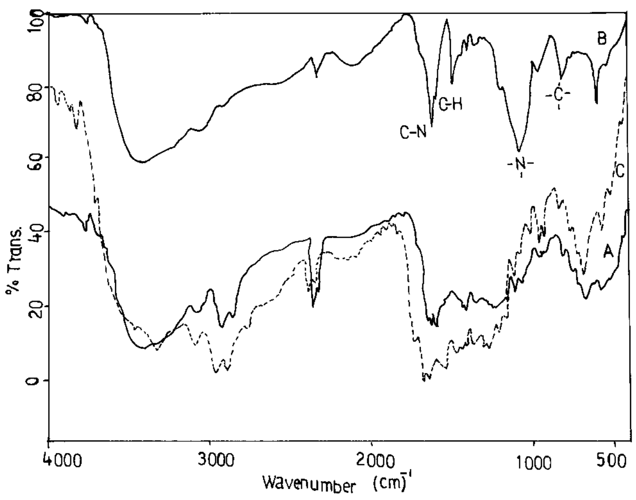

Figure 6 (A) FTIR spectrum of nylon 6-*g*-4VP. (B) FTIR spectrum of poly(4VP). (C) FTIR spectrum of pure nylon 6 fiber.

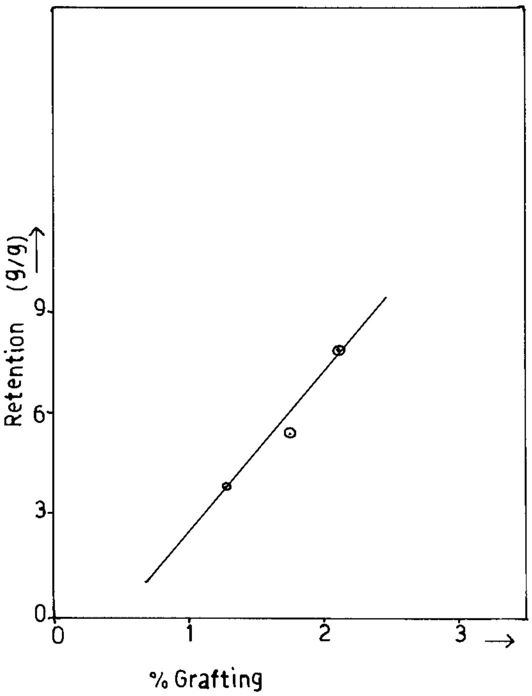

Figure 7 Water retention capacity.

molecules and (2) the fact that void formation is increased because of the increase in % grafting. This is in accordance with earlier reports.[17,18]

CONCLUSIONS

From the above kinetic study, the following conclusions can be made. (1) Graft copolymerization occurs with simultaneous homopolymerization. (2) Both R_h and R_g showed first-order dependence on [4VP], and half-order dependence on [PMS], [TGA], and (amount of nylon 6 fiber). (3) FTIR spectroscopy confirms the chemical grafting of poly(4-vinyl pyridine) onto nylon 6 fiber. (4) The water retention capacity of grafted fiber increased with an increase of % grafting.

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