Graft Copolymerization of Acrylamide onto Nylon 6 Using Quinquevalent Vanadium Ion

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Synopsis

Nylon 6 has been graft copolymerized with acrylamide using a quinquevalent vanadium ion as an initiator in aqueous media under a variety of conditions. Effects of initiator concentration, monomer concentration, acid concentration, $CuSO_4$ concentration, temperature, and chain transfer solvents have been studied. The graft yield shows a maxima at 0.005 mole/liter of initiator concentration. Similarly, the graft yield maxima with respect to acid concentration is 0.45 mole/liter. The graft yield increases within the range of the monomer concentration studied. The graft yield is temperature dependent. In addition, the reactions involved in initiation of grafting are elucidated. The work was also extended to study the moisture regain of grafted samples.

INTRODUCTION

Recently, most of the advances in research made in textile fibers have been aimed at giving fibers some desirable properties, and a lot of it has been done via graft copolymerization of vinyl monomers onto nylon.[1-11]

The graft copolymerization can be carried out by ionic and free radical initiation. In recent years much attention has been focused on the vinyl graft copolymerization of nylon-6 through chemical initiation. Several methods have been used for grafting vinyl monomers onto nylon which include: ceric ion,[10,11] manganese (IV),[12] manganese (III),[13] chromium (VI),[14] Cu (II),[15] dimethyl aniline coupled with benzyl chloride,[16] Thiourea–potassium bromate[17] redox system, and azobisisobutyronitrile.[18] Recently, we have reported graft copolymerization of methyl methacrylate onto cellulose using a vanadium (V)[19] ion as the initiator.

In this article, we have studied the detailed kinetic investigations of the graft copolymerization of acrylamide onto nylon-6 initiated by a quinquevalent vanadium ion.

EXPERIMENTAL

The nylon 6 fibers were swollen in formic acid for 30 min and neutralized with dilute ammonia, then washed with water and air dried before grafting.

Ammonium metavanadate (AR BDH), sulfuric acid (18M, AR BDH), acrylamide (E. Merck) were used. Double distilled, deionized water was used to prepare all solutions.

The reaction was carried out in Pyrex vessels having inlet and outlet tubes. Nitrogen used to deaerate the experimental systems was freed from oxygen by being passed through Fieser's solution. 2-Ethoxy ethanol was used as the monomer solubilizer.

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The moisture regain of grafted and parent nylon was determined by vacuum desiccator as described by Urqurt and Williams.[20] Phosphorus pentoxide was used as a dehydrating agent.

Graft Polymerization Procedure

The graft polymerization reaction was carried out as follows: nylon 6 samples (0.2 g) were steeped in 20 ml of a solution containing known concentration of V^{5+}, Am, and H^+. They were kept in a thermostatted water bath. During the reaction, the fibers were kept well immersed in the solution. After the desired reaction time, the contents of the flask were filtered on a sintered glass crucible and repeatedly washed with water, dried in an oven, cooled to room temperature, and weighed. The percentage of graft uptake was calculated as follows.
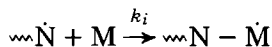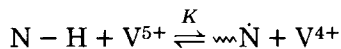
$$\% \text{ graft uptake} = \frac{\text{dry wt of grafted sample} - \text{dry wt of original sample}}{\text{dry wt of original sample}} \times 100$$
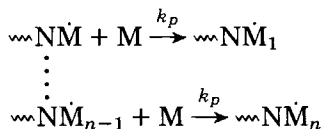
RESULTS AND DISCUSSION

Nylon 6 is essentially a polyamide which has an amino group at one end and a carboxyl acid group at the other end. The free radical is generated by the abstraction of hydrogen atoms from the amino and/or —CONH— group in the polyamide chain.

In a system consisting of V^{5+} ion sulfuric acid, Am, and nylon, an intermediate complex of V^{5+} nylon might be forming. This complex may dissociate giving rise to nylon macroradicals. The macroradicals react with the vinyl monomer to cause the formation of the graft copolymer on the backbone of the fiber.
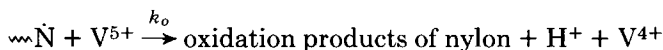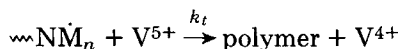Initiation:

$$N - H + V^{5+} \underset{K}{\rightleftharpoons} \text{\tiny{$\sim\sim$}}\dot{N} + V^{4+}$$

$$\text{\tiny{$\sim\sim$}}\dot{N} + M \xrightarrow{k_i} \text{\tiny{$\sim\sim$}}N - \dot{M}$$

Propagation:

$$\text{\tiny{$\sim\sim$}}N\dot{M} + M \xrightarrow{k_p} \text{\tiny{$\sim\sim$}}N\dot{M}_1$$
$$\vdots$$
$$\text{\tiny{$\sim\sim$}}N\dot{M}_{n-1} + M \xrightarrow{k_p} \text{\tiny{$\sim\sim$}}N\dot{M}_n$$

Termination:

$$\text{\tiny{$\sim\sim$}}N\dot{M}_n + V^{5+} \xrightarrow{k_t} \text{polymer} + V^{4+}$$

$$\text{\tiny{$\sim\sim$}}\dot{N} + V^{5+} \xrightarrow{k_o} \text{oxidation products of nylon} + H^+ + V^{4+}$$

where $N - H$ is nylon 6; M is a monomer; K is equilibrium constant; and k_i, k_p, k_t, and k_o are rate constants.

Dependence of Graft Uptake on V^{5+} Concentration

The plots of the percentage of graft uptake and the V^{5+} concentration are shown in Figure 1. Here, the concentration of Am and acid was kept constant at 60°C. As can be seen, the percentage graft uptake increases from 0.00125 to 0.005 mole/liter, and thereafter decreases, i.e., to 0.015 mole/liter within the range studied. A possible explanation for these observations might be as follows. At higher concentrations of V^{5+}, the free radical produced on the backbone of the nylon might be oxidized to give rise to the oxidation product, and hence, the percentage graft-on decreases. At higher concentrations of V^{5+}, the metal ions might interact with the monomer to give rise to a higher amount of homopolymer, thereby decreasing grafting. Similar observation have been noted by us in the V^{5+} initiated graft polymerization of MMA onto cellulose.[19]

Dependence of Graft Uptake on Am Concentration

The effect of an Am concentration on the extent of grafting is illustrated in Figure 2, where monomer concentrations ranging from 0.2 to 1.2 mole/liter are plotted against the graft uptake. The percentage graft uptake increases with the increasing monomer concentration. This means that the monomer participates in the grafting process. We have also noted this trend.[14,19,21]

Dependence of Graft Uptake on H^+ Concentration

Figure 3 shows the graft percentage as a function of H^+ concentration on grafting Am onto nylon 6. The grafting reaction has been carried out by varying the acid concentrations from 0.3 to 0.9 mole/liter. A perusal of the results indicates that the percentage graft-on increases with increasing acid concentration, from 0.3 to 0.45 mole/liter, then decreases with further increase in the acid concentration.

VO_2^+ and $VO(OH)^{2+}$ are the active species of quinquevalent vanadium ion as suggested by Jones and Waters.[22] These species are in equilibrium with each other as shown below.
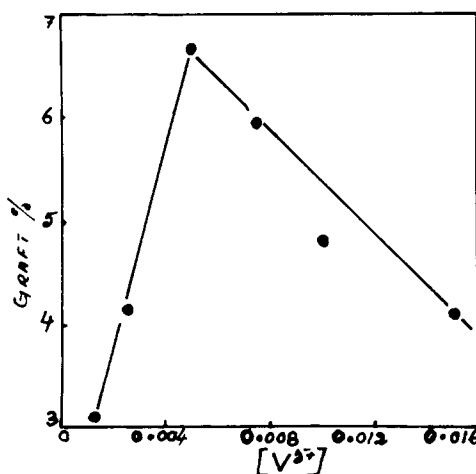

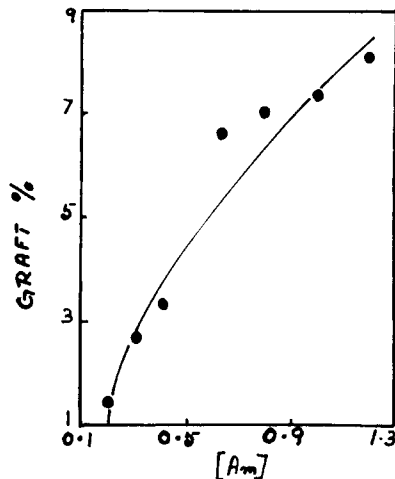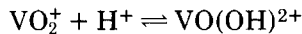Fig. 1. $[H^+]$ = 0.45 mole/liter; [Am] = 0.625 mole/liter; temp. = 60°C; time = 6 hr; $M:L$ = 1:100.

Fig. 2. [H⁺] = 0.45 mole/liter; [V⁵⁺] = 0.005 mole/liter; temp. = 60°C; time = 6 hr; $M:L$ = 1:100.

$$VO_2^+ + H^+ \rightleftharpoons VO(OH)^{2+}$$

Of these two active species, $VO(OH)^{2+}$ is a stronger oxidizing agent than VO_2^+.[23] As the concentration of acid increases beyond 0.45 mole/liter, the formation of most active species might be more, which could interact with the radicals on the nylon backbone producing oxidation products and thereby decreasing grafting.

Dependence of Graft Uptake on Reaction Temperature

Figure 4 shows the effect of temperature on grafting and follows the order 70°C > 65°C > 60°C > 55°C. The dependence of the rate of grafting on the increase in temperature could be ascribed to the greater activation energy. The swellability of nylon and monomer diffusion rates are enhanced by increasing the re-
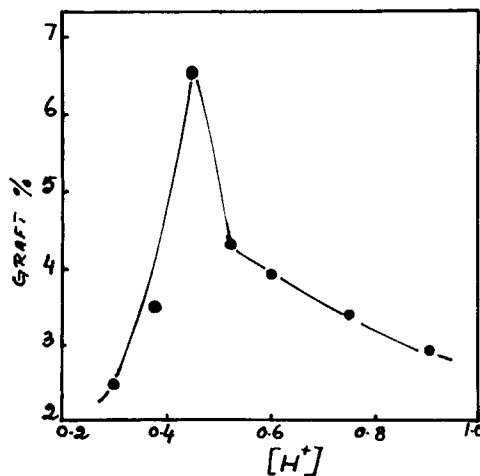

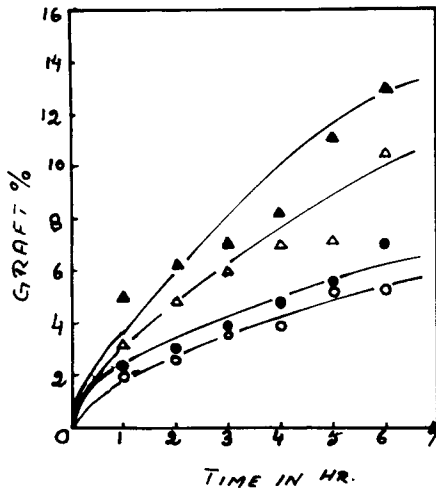Fig. 3. [V⁵⁺] = 0.005 mole/liter; [Am] = 0.625 mole/liter; temp. = 60°C; time = 6 hr; $M:L$ = 1:100.

Fig. 4. [H$^+$] = 0.45 mole/liter; [V^{5+}] = 0.005 mole/liter; [Am] = 0.625 mole/liter; $M:L$ = 1:100. O, temp. = 55°C; ●, temp. = 60°C; △, temp. = 65°C; ▲, temp. = 70°C.

action temperature. Similar observation have been described by us in our previous articles.[19,21]

From the Arrhenius plot of log R_p vs. (1/T) (Fig. 5), the overall activation energy was found to be 16.1 kcal/mole. Using the value of $E_p - \frac{1}{2}E_t = 4 \sim 5$ kcal/mole given by Tobolsky,[24] where E_p and E_t are energies of propagation and termination, respectively. The activation energy of initiation E_d can be calculated from these values as follows.

$$E_d = 2E_a - (2E_p - E_t)$$

where, E_a is the overall activation energy, and E_d = 23.2 kcal/mole for the total conversion reaction of Am to P Am.

Dependence of Graft Uptake on CuSO$_4$ Concentration

The effect of the CuSO$_4$ concentration on grafting is quite interesting (Fig. 6). The graft copolymerization that has been studied has the concentration range of 0.0025 to 0.015 mole/liter. The graft yield first increases up to 0.005 mole/liter,
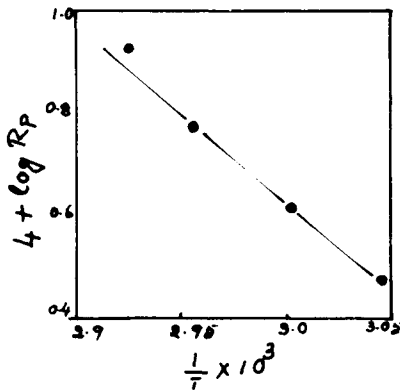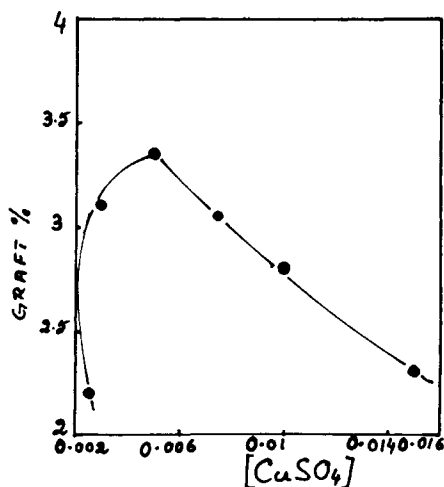

Fig. 5. Plot of log R_p vs. 1/T.

Fig. 6. [H+] = 0.045 mole/liter; [V5+] = 0.005 mole/liter; [Am] = 0.625 mole/liter; temp. = 60°C; time = 6 hr; $M:L$ = 1:100.

then decreases. The initial increase in graft yield might be due to the presence of Cu^{2+} ions in the vicinity of nylon, which certainly favors grafting since the involvement of Cu^{2+} ion in a nylon–monomer complex would be easier. For the decrease in graft yield beyond 0.005 mole/liter, the Cu^{2+} might act as a radical trap. It also might be that a particular concentration of Cu^{2+} favors complexation of monomer with nylon and, beyond this, concentration of Cu^{2+} ions perturb such complexation.[19,25]

Dependence of Graft Uptake on Presence of Solvents

Grafting experiments have been carried out in the presence of conventional chain transfer agents like CCl_4 and $CHCl_3$. It was observed that all the chain transfer agents, e.g., CCl_4 and $CHCl_3$, reduce the percentage of grafting. Similar results have been noted by Mishra, Jassal, and Pande,[26] while grafting onto cellulose using a benzoylperoxide–azobisisobutyronitrile initiated system. The results are as shown in Table I.

TABLE I
Results of Grafting onto Nylon 6 using Quinquevalent Vanadium Ion Initiated System[a]

CCl_4 in cc	graft, %	$CHCl_3$ in cc	graft, %
1	3.25	1	3.95
2	3.00	2	1.9
3	2.9	3	1.25

[a] [H+] = 0.45 mole/liter; [V5+] = 0.005 mole/liter; [Am] = 0.625 mole/liter; Temp. = 60°C; time = 6 hr; $M:L$ = 1:100
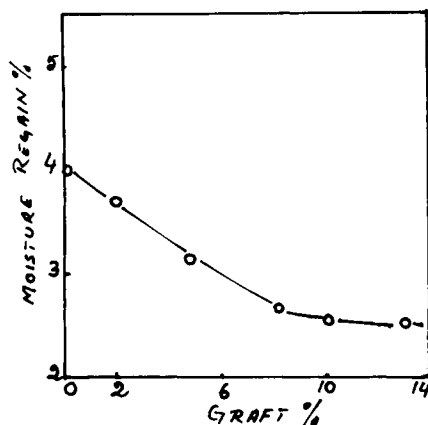
Fig. 7. Plot of % moisture regain vs. % graft.

Moisture Regain of Grafted Samples

The percentage moisture regain versus the percentage graft are plotted in Figure 7. From the figure, it is shown that as the percentage graft-on increases, the moisture regain decreases.

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