

Grafting Vinyl Monomers into Nylon-6. II. Graft Copolymerization of Methyl Methacrylate onto Nylon-6 by Hexavalent Chromium Ion

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Synopsis

The feasibility of chromium(VI) to induce graft copolymerization of methyl methacrylate onto nylon-6 was investigated in the presence of nitrogen. The rate of grafting was determined by varying monomer concentration, chromium(VI) concentration, temperature, acidity of the medium, solvents, inorganic salts, and redox system. The graft yield increases significantly by increasing the monomer concentration. The graft yield increases with increase of [Cr(VI)] up to 0.025 mole/liter. With further increase of [Cr(VI)], the graft yield decreases. The increase of acid concentration up to 0.395 mole/liter results the increase in graft yield. Beyond this concentration the graft yield decreases. The graft yield increases with increase in temperature up to 55°C and thereafter it decreases. The graft yield is medium dependent. The graft yield increases with increasing thiourea concentration upto 0.0025 mole/liter but beyond this concentration, the percentage graft yield decreases. A suitable kinetic scheme has been proposed and the rate equation has been evaluated.

INTRODUCTION

Nylon is one of the most versatile synthetic fibers which has unchallenged utility in textiles, household, and industrial applications. Substantial improvement in the physicochemical properties of the fiber is necessary for its better commercial value. Attempts have been made by several workers to modify the properties of nylon through graft copolymerization.¹ Grafting promises to be a suitable method resulting in a modified end product having improved dyeability, higher resistance to weathering,² improved water absorbancy, heat resistance, antistatic properties,³⁻⁶ etc.

The graft copolymerization can be carried out by ionic and free radical initiation methods. The latter could be achieved by the physical activation of nylon-6 by (i) radiation process,⁷⁻¹³ (ii) chain transfer,¹⁴ (iii) activation by different powerful oxidants, i.e., chemical initiation.^{1,15,16} In recent years, much attention has been focussed on vinyl graft copolymerization of nylon-6 through chemical initiation using ceric ion,^{17,18} manganese(IV),¹⁶ manganese(III),¹⁹ dimethyl aniline coupled with benzyl chloride,²⁰ azobisisobutyronitrile,¹⁴ and thiourea-potassium bromate redox systems.²¹

In recent years, metal ions in their higher valence states have been extensively used for polymerization of a number of vinyl monomers.²²⁻²⁹ Chromium(VI) has been used by Nayak and co-workers^{25,28,29} as a redox initiator for homopolymerization of vinyl monomers and as an initiator for graft copolymerization onto wool³⁰ and silk³¹ fibers.

This communication presents the results of studies of grafting methyl methacrylate onto nylon-6 using hexavalent chromium ion.

EXPERIMENTAL

Nylon-6 was supplied by J. K. Synthetics, Kota, Rajsthan (India) as a gift sample. It was swollen in formic acid for 30 min and neutralized with dilute ammonium hydroxide, then washed with water, and dried in air before grafting. Potassium dichromate (AR Sarabhai, M. Chemicals) and perchloric acid (GR, E. Merck, 60%) were used. Cr(VI) concentration was estimated by titrimetry. The graft copolymerization was carried out according to our previous procedure³¹ using Cr(VI) (0.005 to 0.035 mole/liter) in HClO₄ (0.093 to 0.698 mole/liter) at the temperature from 45 to 65°C. The graft yield was calculated as the percentage increase in weight over the original weight of the polymer. The homopolymer formed during the process of grafting was removed by repeated extraction of the grafted fibers using benzene as the solvent.

RESULTS AND DISCUSSION

Effect of Chromium(VI) Concentration

The effect of chromium(VI) concentration on the grafting of methyl methacrylate onto nylon-6 is shown in Figure 1. With an increase of the chromium(VI) concentration up to 0.005 mole/liter, the graft yield increases and thereafter decreases. This finding could be explained as follows: In the initial stages with increasing Cr(VI) concentration, more nylon macroradicals are formed and hence the rate of grafting increases. At higher concentration of Cr(VI), the free radicals produced on the backbone of the nylon-6 might be oxidized to give rise to the oxidation products and hence the percentage of graft-on decreases. Further, graft formation and homopolymerization depend on the direct attack of Cr(VI) ion on nylon-6 and the monomer. At higher concentrations of Cr(VI), the metal ions might interact with the monomer to produce homopolymer thereby decreasing grafting.

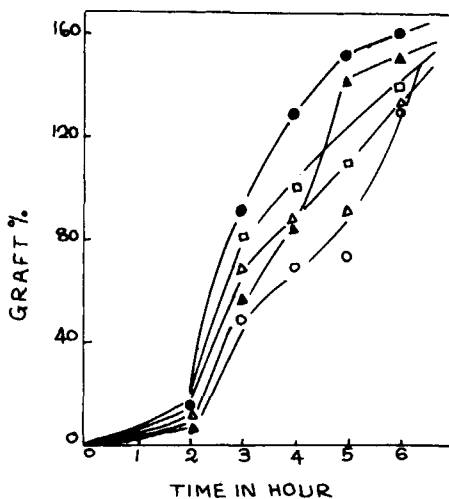


Fig. 1. Effect of [Cr(VI)] on graft yield: [HClO₄] = 0.395 mole/liter; [MMA] = 0.4694 mole/liter; temperature = 55 °C; *M:L* = 1:100; (○) [Cr(VI)] = 0.005 mole/liter; (Δ) [Cr(VI)] = 0.01 mole/liter; (□) [Cr(VI)] = 0.015 mole/liter; (●) [Cr(VI)] = 0.025 mole/liter; (▲) [Cr(VI)] = 0.035 mole/liter.

Effect of [MMA] on Graft Yield

The effect of monomer concentration on grafting was investigated by varying the monomer concentration from 27.98×10^{-2} to 103.27×10^{-2} mole/liter (Fig. 2). A perusal of the result indicates that with increasing monomer concentration there is a significant increase in graft yield. The higher rate of grafting observed could be attributed to a variety of reasons: (i) increase in rate of swelling of the polyamide; (ii) complexation of polyamide with monomer; (iii) gel effect,³² i.e., increase in viscosity of the medium due to the solubility of poly(methyl methacrylate) in its own monomer; (iv) some species, which are either present or generated during the copolymerization reaction, act as an efficient radical scavenger. Competition between this and the monomer in capturing the free nylon radical would play the key role in the amount of graft formation. It is likely that capturing of nylon radicals by monomer predominates at higher monomer concentration.

Effect of Acid Concentration on Graft Yield

Acid is essential when Cr(VI) is used as an initiator. It is therefore interesting to study the effect of acid concentration on graft yield. The grafting reaction was studied by varying acid concentrations from 0.093 to 0.698 mole/liter (Fig. 3). It has been observed that percentage of grafting increases with increasing acid concentration upto 0.395 mole/liter and then decreases. Similar observation has been noted by us while grafting MMA onto silk³¹ using Cr(VI) as the initiator. With increasing acid concentrations, the acid anions probably complex with monochromate ion, thus reducing the oxidizing power of the latter, as pointed out by Stewart and Lee,³³ and hence the graft yield decreases.

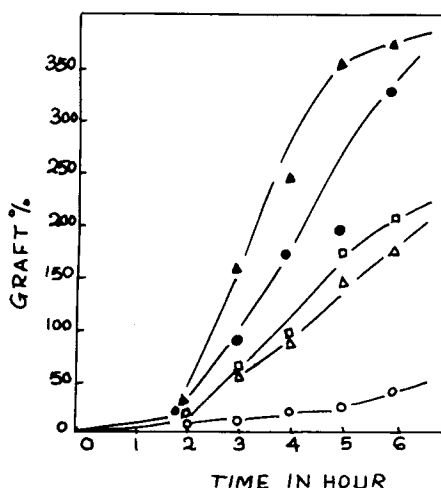


Fig. 2. Effect of [MMA] on graft yield: [Cr(VI)] = 0.025 mole/liter; [HClO₄] = 0.395 mole/liter; temperature = 55°C; M:L = 1:100; (○) [MMA] = 27.95×10^{-2} mole/liter; (Δ) [MMA] = 46.94×10^{-2} mole/liter; (□) [MMA] = 65.72×10^{-2} mole/liter; (●) [MMA] = 84.50×10^{-2} mole/liter; (▲) [MMA] = 103.27×10^{-2} mole/liter.

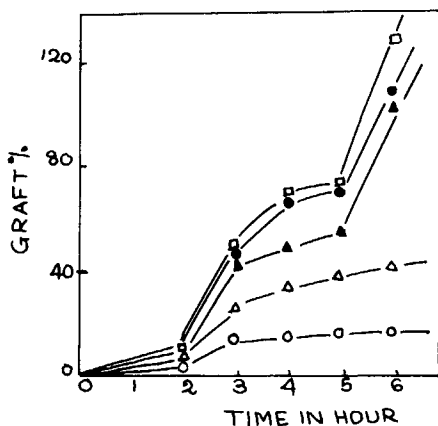


Fig. 3. Effect of $[\text{HClO}_4]$ on graft yield: $[\text{Cr(VI)}] = 0.005$ mole/liter; $[\text{MMA}] = 0.4694$ mole/liter; temperature = 55°C ; $M:L = 1:100$; (O) $[\text{HClO}_4] = 0.093$ mole/liter; (Δ) $[\text{HClO}_4] = 0.232$ mole/liter; (\square) $[\text{HClO}_4] = 0.395$ mole/liter; (\bullet) $[\text{HClO}_4] = 0.465$ mole/liter; (\blacktriangle) $[\text{HClO}_4] = 0.698$ mole/liter.

Effect of Temperature on Graft Yield

The graft copolymerization was carried out at different temperatures ranging from 45 to 65°C (Fig. 4). The data indicate that the graft-on percentage increases with increase of temperature upto 55°C and thereafter decreases. The increase in graft-on percentage could be ascribed to the greater activation energy, swellability of fiber, higher solubility of monomer, and its diffusion rate. Beyond 55°C , the decrease in graft-on percentage could be explained taking into account of higher combination of monomer. A similar observation was also noted by Nayak and co-workers while grafting MMA onto wool³⁴ and silk³¹ using V^{5+} -thiourea redox system and Cr(VI) , respectively. From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy was found to be 12.8 kcal/mole (Fig. 5). Using the value of $E_p - \frac{1}{2} E_t = 4-5$ kcal/mole given by Tobolsky,³⁵ where E_p and E_t are energies of propagation and termination, respectively; the activation energy of initiation E_d can be calculated from the equation $E_d = 2 E_a - (2 E_p - E_t)$, where E_a is the overall activation energy. The value of E_d was calculated to be 16.6 kcal/mole.

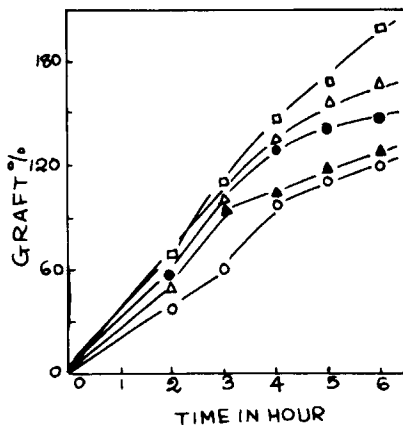


Fig. 4. Effect of temperature on graft yield: $[\text{Cr(VI)}] = 0.005$ mole/liter; $[\text{HClO}_4] = 0.395$ mole/liter; $[\text{MMA}] = 0.4694$ mole/liter; $M:L = 1:100$; (O) temperature = 45°C ; (Δ) temperature = 50°C ; (\square) temperature = 55°C ; (\bullet) temperature = 60°C ; (\blacktriangle) temperature = 65°C .

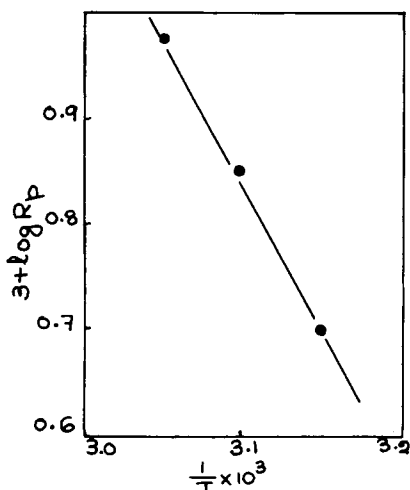


Fig. 5. Arrhenius plot of $\log R_p$ vs. $1/T$.

Effect of Inorganic Salts on Graft Yield

The graft copolymerization onto nylon-6 has been carried out by adding some salts like LiNO_3 , NaF , MnSO_4 , etc. (Fig. 6). The graft yield follows the order: $\text{LiNO}_3 > \text{NaF} > \text{MnSO}_4$, depending on the ability of these salts to catalyze the propagation step. The graft copolymerization has been studied using CuSO_4 from 0.002 to 0.03 mole/liter (Fig. 7). The graft yield increases up to 0.015 mole/liter and then decreases. In the initial stages there is the formation of a lot of free radicals like SO_4^- , OH^- by the interaction of the nylon macroradical with SO_4^{2-} which might enhance the graft-on percentage. Furthermore there is easy involvement of Cu^{2+} in the nylon-6-monomer complex which might facilitate the rate of grafting. Also the creation of free radical species under the influence of Cu^{2+} ion would be in the proximity of nylon thus assisting formation of nylon macroradicals. The sharp drop in the graft yield with higher concentration of cupric sulphate could be attributed to a variety of reasons: (i) Cu^{2+}

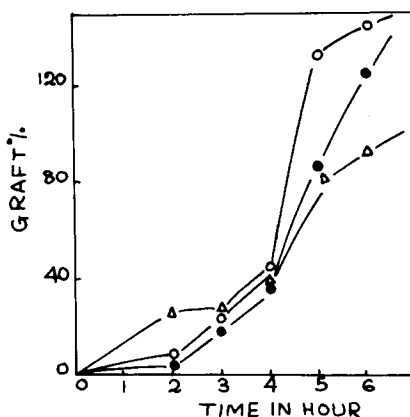


Fig. 6. Effect of salts on graft yield: $[\text{Cr(VI)}] = 0.025$ mole/liter; $[\text{HClO}_4] = 0.395$ mole/liter; $[\text{MMA}] = 0.4694$ mole/liter; temperature = 55°C ; $M:L = 1:100$; (O) LiNO_3 ; (●) NaF ; (Δ) MnSO_4 .

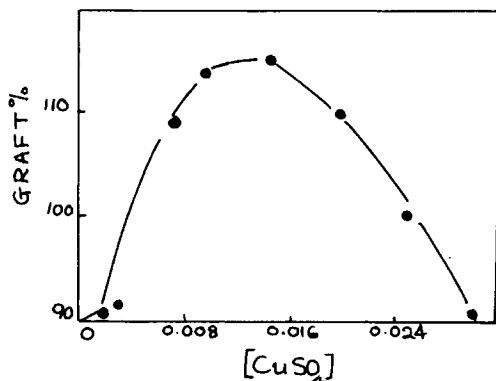


Fig. 7. Effect of $[\text{CuSO}_4]$ on graft yield: $[\text{Cr(VI)}] = 0.025$ mole/liter; $[\text{HClO}_4] = 0.395$ mole/liter; $[\text{MMA}] = 0.4694$ mole/liter; temperature = 55°C ; $M:L = 1:100$; time = 6 hr.

ions seem to act as radical traps, (ii) a particular concentration of Cu^{2+} favors complexation of monomer with nylon and that beyond this concentration the Cu^{2+} ions perturb such complexation.

Effect of Solvents on Graft Yield

The reaction medium plays an important role on grafting vinyl monomers onto nylon-6. The graft yield follows the order methanol > ethanol > propanol > butanol > pentanol. The decrease in graft yield from methanol to pentanol is due to the decrease in the ability of swelling of polyamide, and the difference in capability of these solvents as the terminator for the nylon-6 macroradical.

When grafting process was carried out using chain transfer reagents like CCl_4 and CHCl_3 it was found that graft-on percentage decreases. Similar observation was also noted by Mishra et al.³⁶ while grafting cellulose using a benzoylperoxide-azobisisobutyronitrile initiated system.

Effect of Redox System

Thiourea coupled with some metal and nonmetal ions have been used extensively for homopolymerization^{22-24,27-29} as well as graft copolymerization onto wool^{34,37} and silk.³⁸ Hebeish et al.²¹ reported the redox initiated graft copolymerization of methyl methacrylate and methacrylic acid onto nylon-6 using potassium bromate-thiourea as cocatalyst.

The graft copolymerization of nylon-6 has been investigated by using Cr(VI)-thiourea redox system changing the thiourea concentration from 0.0005 to 0.0025 mole/liter. The graft yield increases up to 0.0025 mole/liter and then decreases (Fig. 8). Cr(VI) abstracts hydrogen from thiourea forming thiourea radicals which then abstract hydrogen from the nylon backbone forming nylon macroradicals which initiate graft copolymerization. In the initial stages with increasing thiourea concentration more nylon macroradicals are formed which increase the graft percentage. However, at very high concentration of thiourea, the decrease in graft yield might be due to (i) faster rate of termination probably owing to the abundance of free radical species in polymerization system, (ii) the increased amount of free radical inhibitor in thiourea that is always present in

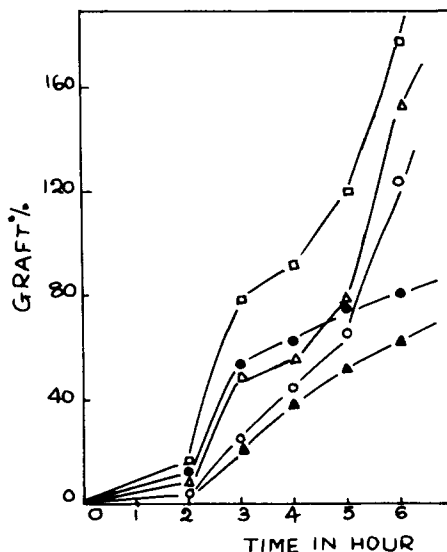


Fig. 8. Effect of [thiourea] on graft yield: $[\text{Cr(VI)}] = 0.025$ mole/liter; $[\text{HClO}_4] = 0.395$ mole/liter; $[\text{MMA}] = 0.4694$ mole/liter; temperature = 55°C ; $M:L = 1:100$; (○) [thiourea] = 0.005 mole/liter; (Δ) [thiourea] = 0.0015 mole/liter; (□) [thiourea] = 0.0025 mole/liter; (●) [thiourea] = 0.0035 mole/liter; (▲) [thiourea] = 0.0005 mole/liter.

it, (iii) fixed amount of thiourea being converted to isothiurea which is required for producing initiating species, (iv) at the higher concentration of thiourea some species might be generated which might act as radical scavenger, and (v) formation of homopolymer.

Mechanism

Nylon-6 is essentially a polyamide having an amino group at one end and a carboxylic acid group at the other end. The free radical is generated by the abstraction of hydrogen atom from the carboxyl or amino group.

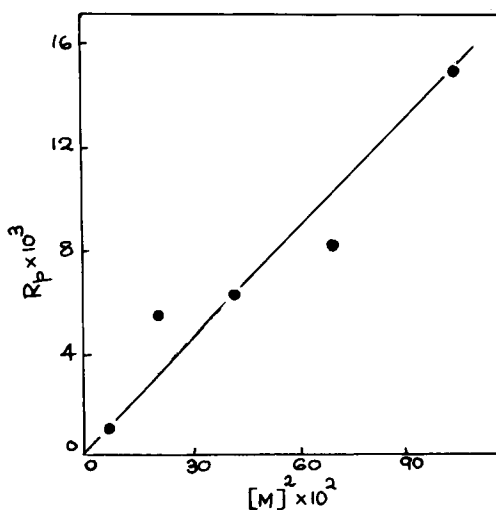
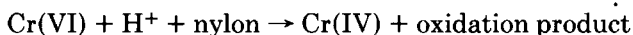
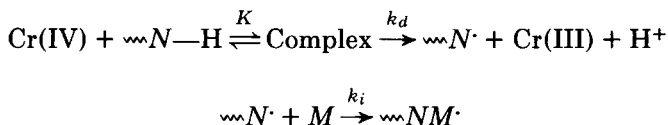


Fig. 9. Plot of R_p vs. $[M]^2$.

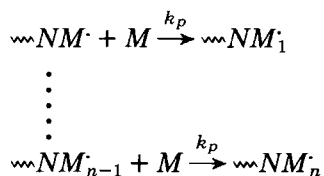
In a system consisting of Cr(VI), nylon-6, MMA, and acid, Cr(VI) is reduced to unstable Cr(IV) which is further reduced to a stable oxidation state of Cr(III). In tetravalent state chromium forms a complex with nylon-6 which breaks down to form nylon-6 macroradical. The proposed mechanism is given:



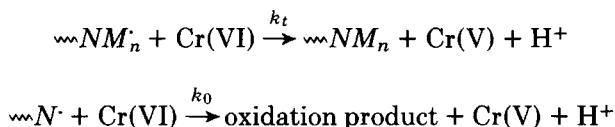
Initiation:



Propagation:



Termination:



where nylon-H is nylon-6, nylon \cdot is the nylon-6 macroradical, M is a monomer, K is the equilibrium constant, and k_i , k_p , k_t , k_0 are rate constants. Applying the steady state assumption, we get

$$\frac{d[\text{N}\cdot]}{dt} = Kk_d[\text{Cr(IV)}][\text{N-H}] - k_i[\text{N}\cdot][M] - k_0[\text{N}\cdot][\text{Cr(VI)}] = 0$$

or

$$[\text{N}\cdot] = \frac{Kk_d[\text{Cr(IV)}][\text{N-H}]}{k_i[M] + k_0[\text{Cr(VI)}]}$$

Again

$$\frac{d[\text{N-M}\cdot]}{dt} = k_i[\text{N}\cdot][M] - k_t[\text{N-M}\cdot][\text{Cr(VI)}] = 0$$

or

$$[\text{N-M}\cdot] = \frac{k_i[\text{N}\cdot][M]}{k_t[\text{Cr(VI)}]}$$

Inserting the value $[\text{N}\cdot]$ in the above expression, we get

$$\begin{aligned} [\text{N-M}\cdot] &= \frac{Kk_d[\text{N-H}][M]}{k_t\{[M] + (k_0/k_i)[\text{Cr(VI)}]\}} \\ R_p &= k_p[\text{N-M}\cdot][M] \end{aligned}$$

Inserting the value of $[N-M^*]$ gives

$$R_p = \frac{k_p}{k_t} [M]^2 \left(\frac{Kk_d [N-H]}{[M] + (k_0/k_i)[Cr(VI)]} \right)$$

The plot of R_p vs. $[M]^2$ is a straight line passing through the origin (Fig. 9). The above mechanism also supports the idea that with an increase of the Cr(VI) concentration, the graft yield decreases.

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