

## Grafting Vinyl Monomers onto Nylon 6. IV. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using the $V^{5+}$ -Thiourea Redox System

Nylon, essentially a polyamide, has been known for over 40 years for its large-scale utility in textile, household, and industrial applications. In recent years, chemical modification of nylon through graft copolymerization has received considerable interest by several group of workers.<sup>1-3</sup> A variety of property changes could be imparted to nylon through grafting without affecting its basic properties. Several methods have been used for grafting vinyl monomers onto nylon. Of all methods, the redox-initiated system has been proved to be the most effective, since it minimizes the degradation of the base polymer.

Thiourea coupled with a suitable metal ion acts as the most efficient initiator for both vinyl polymerization<sup>4-7</sup> and grafting.<sup>8-12</sup> This note presents the results of graft copolymerization of methyl methacrylate onto nylon 6 using the  $V^{5+}$ -thiourea redox system.

### EXPERIMENTAL

The experimental procedure for the grafting reaction and the methods of purification of chemicals used are the same as in our previous communication.<sup>12</sup> The moisture regain percentage was calculated according to the standard procedure.

### RESULTS AND DISCUSSION

The rate of grafting was found to increase with increase in monomer concentration<sup>12</sup> from  $4.69 \times 10^{-2}M$  to  $70.41 \times 10^{-2}M$  (Fig. 1). The initiator concentration was varied from  $0.49 \times 10^{-3}M$  to  $4.9 \times 10^{-3}M$ . The graft yield increases with increase in initiator concentration up to  $2.45 \times 10^{-3}M$  and then decreases [Fig. 2(b)]. The increase in the graft yield with increase in  $V^{5+}$  concentration might be due to the increase in the number of free radicals which initiates grafting. Beyond  $2.45 \times 10^{-3}M$  of  $V^{5+}$  concentration, the decrease in graft yield might be due to (1) oxidation of free radicals produced on the backbone of the polyamide to give oxidation products, (2) termination of graft macroradicals by the metal ions at higher concentration of initiator.

Thiourea concentration was varied from 0.5 to  $5 \times 10^{-3}M$  [Fig. 2(a)]. There is a significant increase in graft yield up to  $1.5 \times 10^{-3}M$  of thiourea concentration and a decrease thereafter. The acid concentration was varied from 1.5 to  $15 \times 10^{-2}M$ . The graft yield was found to increase up to 7.5

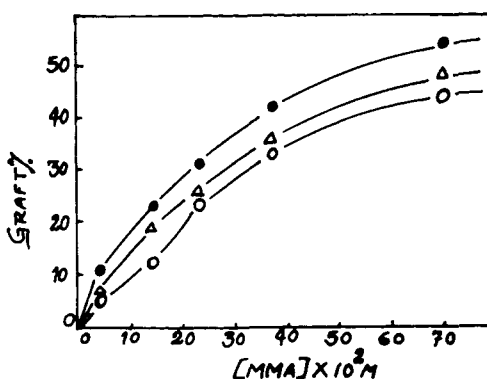


Fig. 1. Effect of [MMA] on graft yield: [TU] =  $1.5 \times 10^{-3}M$ ; [H<sup>+</sup>] =  $4.5 \times 10^{-2}M$ ; temp. = 50°C; time = 6 hr; (●) [V<sup>5+</sup>] =  $1.96 \times 10^{-3}M$ ; (Δ) [V<sup>5+</sup>] =  $2.94 \times 10^{-3}M$ ; (○) [V<sup>5+</sup>] =  $3.92 \times 10^{-3}M$ .

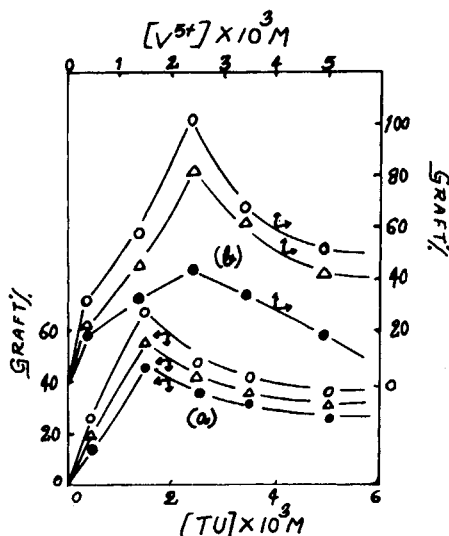


Fig. 2. (a) Effect of  $[TU]$  on graft yield:  $[H^+] = 6.00 \times 10^{-2}M$ ;  $[V^{5+}] = 1.96 \times 10^{-3}M$ ; temp. =  $50^\circ C$ ; time = 6 hr; (●)  $[MMA] = 23.47 \times 10^{-2}M$ ; (Δ)  $[MMA] = 46.94 \times 10^{-2}M$ ; (○)  $[MMA] = 70.41 \times 10^{-2}M$ . (b) Effect of  $[V^{5+}]$  on graft yield:  $[H^+] = 7.5 \times 10^{-2}M$ ;  $[TU] = 2.0 \times 10^{-3}M$ ; temp. =  $50^\circ C$ ; time = 6 hr; (●)  $[MMA] = 28.164 \times 10^{-2}M$ ; (Δ)  $[MMA] = 46.94 \times 10^{-2}M$ ; (○)  $[MMA] = 65.72 \times 10^{-2}M$ .

$\times 10^{-2}M$  and to decrease thereafter [Fig. 3(a)]. The rate of grafting also increased by increasing the temperature [Fig. 3(b)]. From the Arrhenius plot of  $\log R_p$  vs.  $1/T$ , the overall activation energy was computed to be 11.00 kcal/mole (Fig. 4). Using the values of  $E_p - \frac{1}{2}E_t = 4-5$  kcal/mole given by Tobolsky,<sup>13</sup>  $E_d$  was found to be 13.00 kcal/mole. The percentage of moisture regain increases from 26 to 100% of grafting [Fig. 5(a)]. The effect of certain solvents was studied, from which HCOOH was proved to be the most effective. The grafted polymers were isolated by the HCl digestion technique.<sup>14</sup> The molecular weights of the isolated polymers were determined using the following equation<sup>15</sup>:

$$[\eta] = 5.5 \times 10^{-5} \times M^{0.75}$$

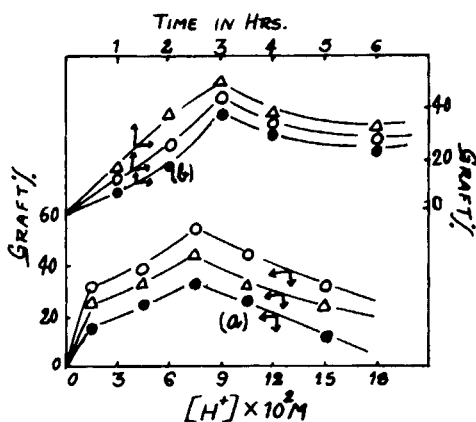


Fig. 3. (a) Effect of  $[H^+]$  on graft yield:  $[V^{5+}] = 2.45 \times 10^{-3}M$ ;  $[TU] = 2.5 \times 10^{-3}M$ ; temp. =  $50^\circ C$ ; time = 6 hr; (●)  $[MMA] = 18.776 \times 10^{-2}M$ ; (Δ)  $[MMA] = 32.85 \times 10^{-2}M$ ; (○)  $[MMA] = 46.94 \times 10^{-2}M$ . (b) Effect of temperature on graft yield:  $[V^{5+}] = 2.45 \times 10^{-3}M$ ;  $[TU] = 1.0 \times 10^{-3}M$ ;  $[H_2SO_4] = 4.5 \times 10^{-2}M$ ;  $[MMA] = 23.47 \times 10^{-2}M$ ; (●) temp. =  $40^\circ C$ ; (○) temp. =  $50^\circ C$ ; (Δ) temp. =  $60^\circ C$ .

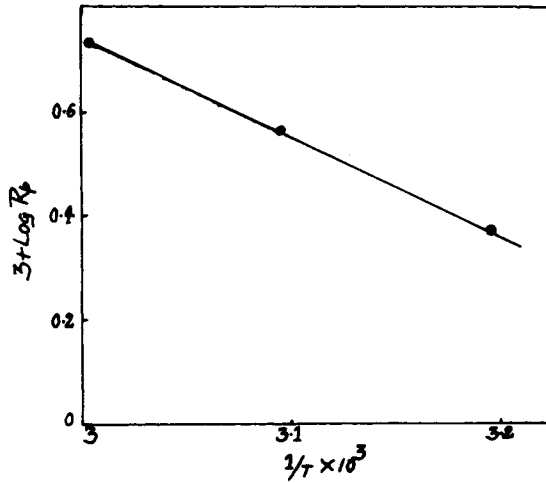
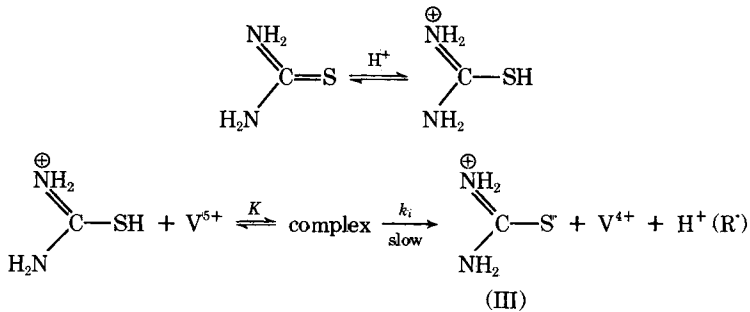


Fig. 4. Arrhenius plot.

The molecular weight ( $\bar{M}$ ) as well as the degree of polymerization were found to increase with increase in percentage of graft yield (Table I).

### MECHANISM

In an initiating system containing thiourea (I), the redox component is the isothiurea (II). In the presence of an initiator like  $V^{5+}$  and acid ( $H_2SO_4$ ), the isothiurea might first complex with  $V^{5+}$  which breaks down giving rise to amidinosulphenyl free radical (III) as shown below:



The isothiocarbamido radicals abstract hydrogen from the amino groups in nylon 6 to yield nylon 6 macroradicals ( $N^\cdot$ ), which interact with the monomer to initiate grafting as shown below:

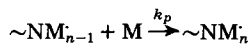


(1) Initiation:



where M is monomer,  $\sim\text{NM}^\cdot$  is nylon graft radical, and TU is thiourea.

(2) Propagation:



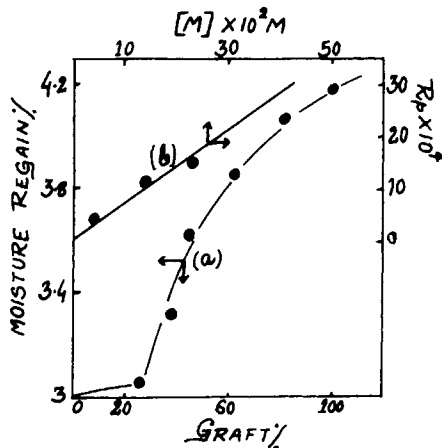
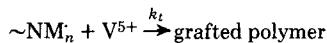
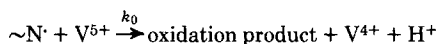


Fig. 5. (a) Plot of moisture regain % vs. graft %. (b) Plot of  $R_p$  vs.  $[M]$ .

(3) Termination:



(4) Oxidation:



Taking into account the above reaction scheme and applying steady-state assumption to both  $[\text{R}^\cdot]$  and  $[\text{NM}^\cdot]$  separately, the following expression have been derived:

$$\frac{d[\text{R}^\cdot]}{dt} = k_1 K [\text{TU}] [\text{V}^{5+}] - k_2 [\text{N}^\cdot] [\text{R}^\cdot] = 0$$

$$\frac{d[\text{NM}^\cdot]}{dt} = k_i [\text{N}^\cdot] [\text{M}] - k_t [\text{NM}^\cdot] [\text{V}^{5+}] = 0$$

$$\therefore [\text{N}^\cdot] = k_2 [\text{N}^\cdot] [\text{R}^\cdot] / k_i [\text{M}]$$

$$\therefore [\text{NM}^\cdot] = \frac{k_1 K [\text{TU}]}{k_t}$$

$$R_p = k_p [\text{NM}^\cdot] [\text{M}] = \left( \frac{k_i K k_p}{k_t} \right) [\text{TU}] [\text{M}]$$

The plot of  $R_p$  vs.  $[M]$  [Fig. 5(b)] is linear, which favors the above reaction scheme.

TABLE I  
Molecular Weight of the Grafted Polymer

Graft %	$\bar{M} \times 10^5$	$\overline{DP} \times 10^3$ <sup>a</sup>
40	6.053	6.053
60	6.683	6.683
81	7.112	7.112
67	7.554	7.554
100	8.433	8.433

<sup>a</sup>  $\overline{DP}$  = Degree of polymerization.

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