Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Using Thallium(III) Ions as Initiator

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ABSTRACT

Graft copolymerization of methyl methacrylate onto nylon 6 was investigated in aqueous perchloric acid medium using thallium(III) ions as initiator. The rate of grafting was evaluated by varying the concentrations of monomer, initiator, acid, and temperature. The rate of grafting was found to increase with an increase of both monomer and initiator concentrations. The graft yield was found to increase with an increase in the acid concentration up to 0.49 mL^{-1}, and beyond this concentration of perchloric acid the graft yield was found to decrease. It also increased with an increase of temperature. From the Arrhenius plot the overall activation energy was found to be 3.9 kcal/mol. The effects of inhibitors, various solvents, inorganic salts, and swelling agents on graft yield were studied. A suitable kinetic scheme has been proposed and a rate equation has been derived.

INTRODUCTION

The versatility of nylon as a synthetic fiber and its utility in various fields such as textiles, oceanography, and industry are unchallenged. Substantial improvement in the physicochemical properties

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of the fiber is necessary to better its 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 to obtain a modified end product having improved
water absorption, better adherence to dyes, higher resistance to
climatic conditions [2], heat resistance, and antistatic properties
[3]. The graft copolymerization can be carried out by free radical
initiation achieved by activation of nylon 6 by powerful oxidants
[1, 4, 5]. In recent years much attention has been paid to the graft
copolymerization of nylon 6 by chemical initiation involving man-
ganese(III) [5] and cerium(IV) [6, 7] ions. The use of thallium(III)
salts as catalysts for vinyl polymerization has been scant [8].
Recently we have carried out detailed studies using thallium(III)
perchlorate as an initiator for the homopolymerization of vinyl mono-
mer. Work has also been carried out on graft copolymerization of
methyl methacrylate onto silk using thallium(III) ions as the initiator
[9]. So far no studies have been made on grafting vinyl monomers
onto synthetic fibers using the same initiator. This communication
presents the results of studies on the grafting of methyl methacrylate
onto nylon 6 using thallium(III) ions as the initiator.

EXPERIMENTAL

Nylon-6 fibers were supplied by J. K. Synthetics (Kota, Rajasthan,
India). They were swollen in formic acid for 30 min and neutralized
with dilute ammonium hydroxide, then washed with water, and dried
in air before grafting. Identical experimental procedures as de-
scribed in our earlier communication [9] were followed for the prepa-
ration and estimation of thallium(III) perchlorate solution, purification
of the monomer and chemicals, and for graft copolymerization re-
actions.

RESULTS AND DISCUSSION

The factors affecting the graft copolymerization of methyl meth-
acrylate onto nylon-6 fibers initiated by thallium(III) perchlorate were
investigated. Variables studied included monomer concentrations,
initiator concentrations, acid concentrations, and temperature.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was investigated
by changing the monomer concentration in the range 28.16 to 103.26
$\times 10^{-2}$ mL^{-1} at fixed concentrations of all other reagents. The rate
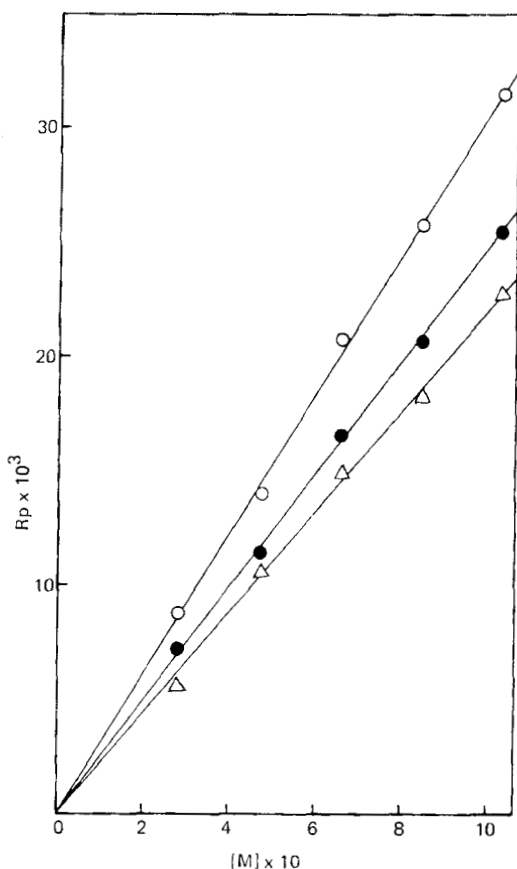of grafting was found to increase with an increase in the monomer

FIG. 1. Effect of monomer concentration on rate of grafting: $[HClO_4]$ = 4.75 × 10^{-1} mL^{-1}, [ether] = 2.5% v/v, time = 6 h, tempera-ture = 70°C, M:L = 1:100. (△) | Tl^{3+}] = 4.08 × 10^{-3} mL^{-1}. (●) $[Tl^{3+}]$ = 8.16 × 10^{-3} mL^{-1}. (○)$[Tl^{3+}]$ = 12.24 × 10^{-3} mL^{-1}.

concentration (Fig. 1). Several explanations can be offered to account for the higher rate of grafting observed upon increasing the monomer concentration. First, complexation of nylon 6 with monomer would be favored at higher monomer concentrations. Second, the gel effect [10] would be more pronounced at high monomer concentrations. This causes hindrance in termination, particularly by coupling of the growing polymer chains. The gel effect also causes swelling of nylon 6, thus facilitating diffusion of the monomer to growing chains and active sites on the nylon-6 skeleton, therby enhancing grafting. Lastly, some species which are either present or generated during the

polymerization reaction act as efficient radical scavengers. Competition between this and the monomer in capturing the free nylon-6 radical plays the key role in the amount of graft formation. It is likely that capture of nylon-6 radicals by monomer predominates at higher monomer concentrations.

Effect of Initiator Concentration

The effect of thallium(III) concentration on grafting was investigated by changing the thallium(III) concentration within the range 4.08 to 20.40×10^{-3} mL^{-1} at fixed concentrations of all other reagents. The data indicate that an increase of Tl^{3+} concentration is accompanied by a significant increase in the rate of grafting (Fig. 2). This is explained by assuming that as the concentration of the initiator continues to increase, more free radicals are formed, thus increasing the rate of grafting.

Effect of Acid Concentration

Acid is essential when thallium(III) is used as an initiator because, in the absence of acid, thallium(III) perchlorate is hydrolyzed and subsequently converted to black thallic oxide. It was therefore of interest to study the effect of acid concentration on graft yield. The graft copolymerization reaction was carried out in aqueous perchloric acid medium, and the acid concentration was varied from 0.19 to 0.69 mL^{-1} at fixed concentration of all other reagents. The graft yield was found to increase with an increase in the acid concentration up to 0.49 mL^{-1}, and beyond this concentration of perchloric acid the graft yield was found to decrease (Fig. 3). The enhancement of the rate of grafting observed upon increasing the concentration of perchloric acid may be due to the increased activity of thallium(III) perchlorate at high perchloric acid concentrations. The subsequent decrease in the percentage of grafting may be due to the recombination and disproportionation of the graft macroradicals.

Effect of Temperature

The effect of temperature on the graft copolymerization reaction was studied in the temperature range 40 to $70°C$. It was observed that the graft percentage increases with an increase in temperature (Fig. 4). The increase in graft percentage can be ascribed to the increased activity of Tl^{3+} at elevated temperatures. This increase may also be due to greater activation energy, increased swellability of the fiber, greater solubility of the monomer, and a higher rate of diffusion of the monomer.
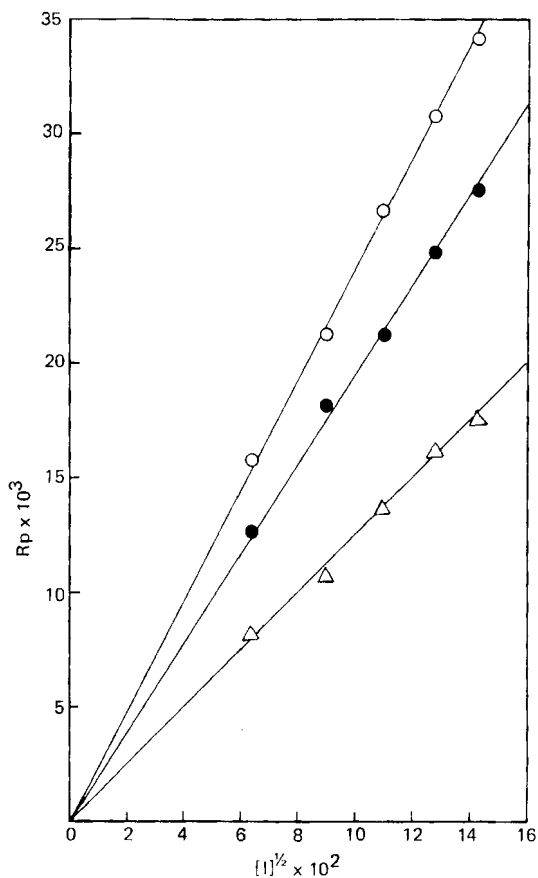
FIG. 2. Effect of initiator concentration on rate of grafting: [HClO$_4$] = 1.2 mL^{-1}, [ether] = 2.5% v/v, time = 6 h, temperature = 70°C, M:L = 1:100. (△): [MMA] = 4.694 × 10^{-1} mL^{-1}. (●): [MMA] = 7.041 × 10^{-1} mL^{-1}. (○) [MMA] = 9.388 × 10^{-1} mL^{-1}.
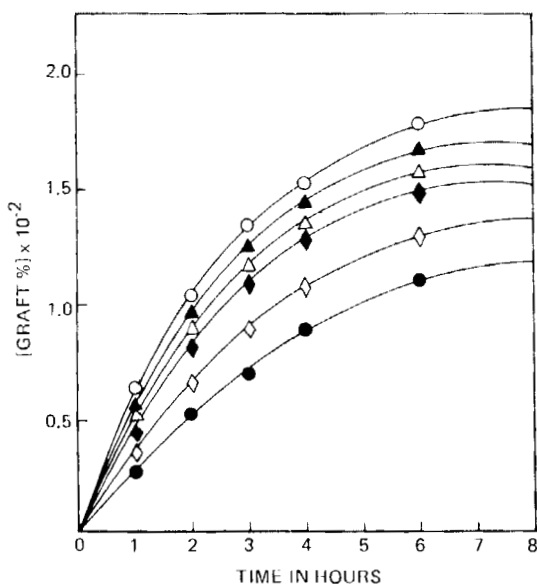
FIG. 3. Effect of acid concentration on graft yield: $[MMA]$ = 4.694×10^{-1} mL^{-1}, $[Tl^{3+}]$ = 3.26×10^{-3} mL^{-1}, $[ether]$ = 2.5% v/v, temperature = $70°C$, M:L = 1:100. (•) $[HClO_4]$ = 1.90×10^{-1} mL^{-1}. (◇) $[HClO_4]$ = 2.90×10^{-1} mL^{-1}. (♦) $[HClO_4]$ = 3.90×10^{-1} mL^{-1}. (○): $[HClO_4]$ = 4.90×10^{-1} mL^{-1}. (▲) $[HClO_4]$ = 5.90×10^{-1} mL^{-1}. (△): $[HClO_4]$ = 6.90×10^{-1} mL^{-1}.

From the Arrhenius plot of log R_p versus $1/T$ (Fig. 5), the overall activation energy was calculated to be 3.9 kcal/mol.

Effect of Polymerization Medium

The reaction medium plays an important role in grafting vinyl monomers onto nylon 6. The effect of different types of solvents, such as alcoholic solvents and chain transfer solvents, on graft yield was investigated. With alcoholic solvents (Fig. 6) the order of graft yield is methanol > ethanol > amyl alcohol. With chain transfer solvents (Fig. 6) the order is chloroform > carbon tetrachloride.

The dependence of grafting upon the nature of the solvent suggests that the solvents examined differ considerably in their (1) capability of swelling nylon 6, (2) miscibility with monomer, (3) formation of solvent radicals from the primary radical species of the initiating system, (4) contribution of the solvent radical in the activation of
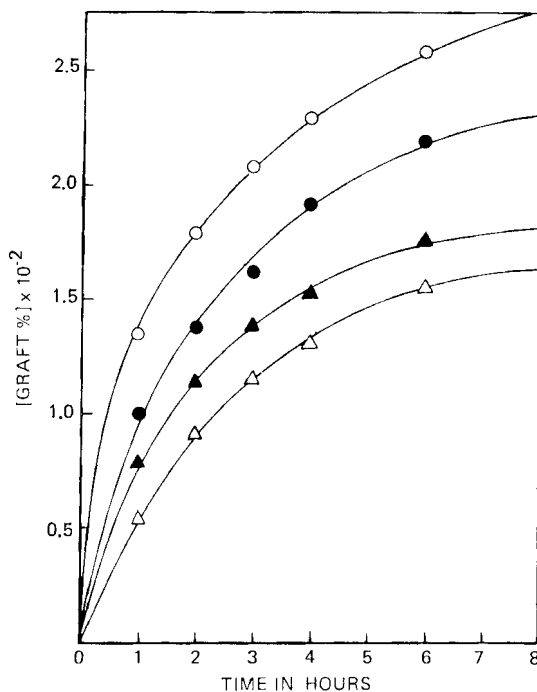
FIG. 4. Effect of temperature on graft yield: $[MMA]$ = 4.694 × 10^{-1} mL^{-1}, $[Tl^{3+}]$ = 8.16 × 10^{-3} mL^{-1}, $[HClO_4]$ = 4.75 × 10^{-1} mL^{-1}, $[ether]$ = 2.5% v/v, M:L = 1:100. (△): Temperature = 40°C. (●): Temperature = 60°C. (▲): Temperature = 50°C. (○): Temperature = 70°C.
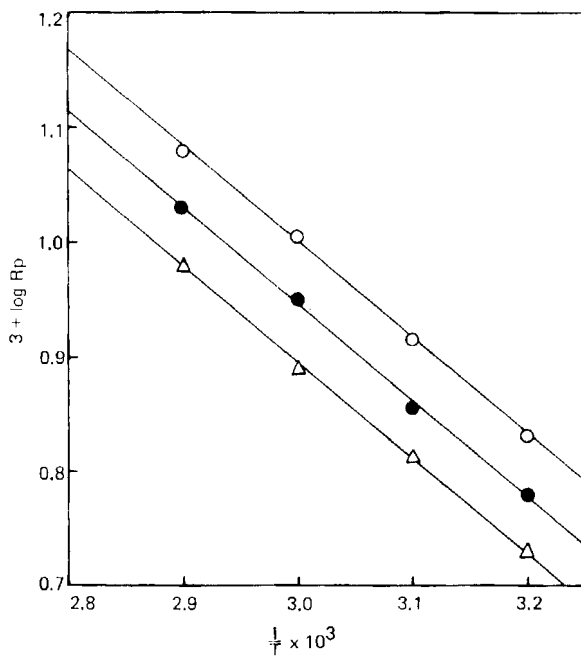
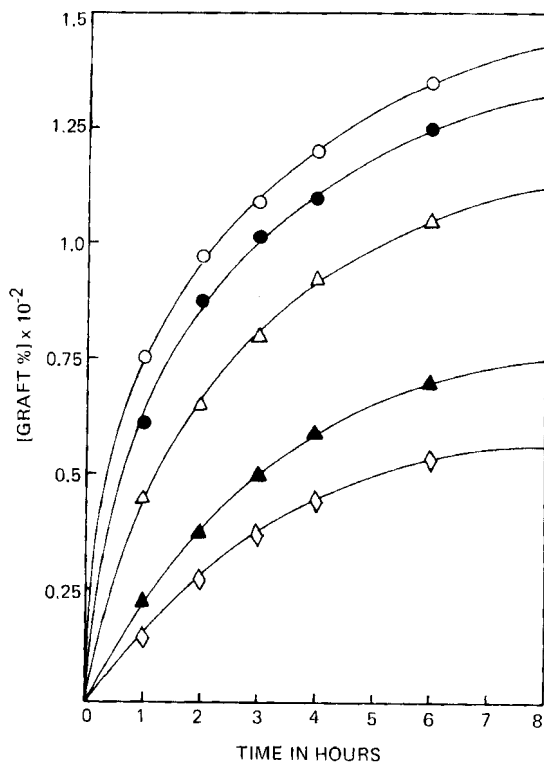FIG. 5. Arrhenius plot of log R_p versus $1/T$. ($\triangle$): 3 h. ($\circ$): 6 h. ($\bullet$): 4 h.

FIG. 6. Effect of solvents on graft yield: $[MMA] = 4.694 \times 10^{-1}$ mL^{-1}, $[Tl^{3+}] = 8.16 \times 10^{-3}$ mL^{-1}, $[HClO_4] = 1.2$ mL^{-1}, $[ether] = 2.5\%$ v/v, $[solvent] = 25\%$ v/v, temperature $= 70°C$, M:L = 1:100. (○): Methanol. (▲): Chloroform. (●) Ethanol. (◊): Carbon tetrachloride. (△): Amyl alcohol.
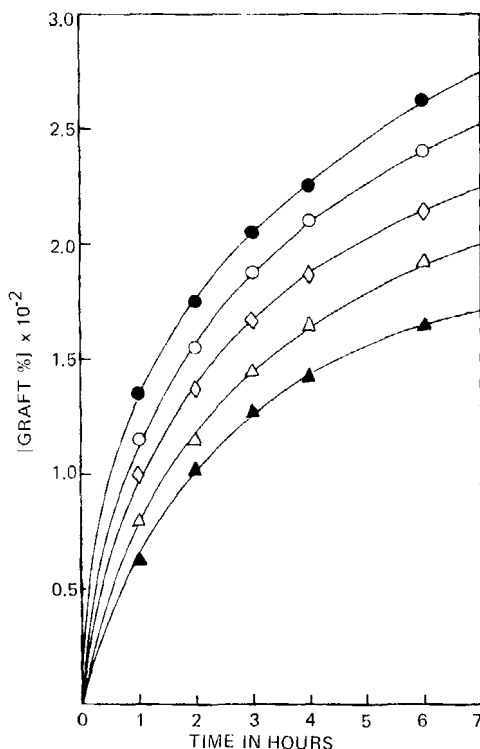
FIG. 7. Effect of inorganic salts on graft yield: $[HClO_4] = 0.525$ mL^{-1}, $[Tl^{3+}] = 8.16 \times 10^{-3}$ mL^{-1}, $[MMA] = 4.694 \times 10^{-1}$ mL^{-1}, [ether] = 2.5% v/v, [salt] = 0.01 mL^{-1}, temperature = 70°C, M:L = 1:100, (●): Copper sulfate. (○): Magnesium sulfate. (◇) Lithium nitrate. (ᐱ): Sodium fluoride. (▲): Manganese sulfate.

nylon 6, and (5) termination of the graft chain radical via chain transfer. While the first four factors favor grafting, the last factor adversely affects grafting.

Effect of Swelling Agents

The percentage of graft yield has been calculated in the presence of various swelling agents, and they were found to be in the following order: phenol > benzyl alcohol > without any swelling agent > m-cresol.
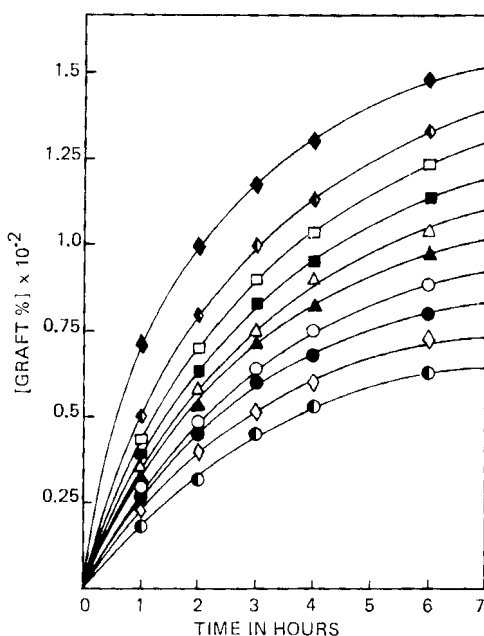
FIG. 8. Effect of inhibitors on graft yield: $[MMA]$ = 4.694×10^{-1} mL^{-1}, $[Tl^{3+}]$ = 3.26×10^{-3} mL^{-1}, $[HClO_4]$ = 1.9×10^{-1} mL^{-1}, $[ether]$ = 2.5% v/v, temperature = $70°C$, M:L = 1:100. ($\blacklozenge$): [Hydroquinone] = 5×10^{-5} mL^{-1}. ($\square$): [Hydroquinone] = 10×10^{-5} mL^{-1}. ($\triangle$): [Hydroquinone] = 15×10^{-5} mL^{-1}. ($\circ$): [Hydroquinone] = 20×10^{-5} mL^{-1}. ($\diamond$): [Hydroquinone] = 25×10^{-5} mL^{-1}. ($\blacklozenge$): [Picryl chloride] = 5×10^{-5} mL^{-1}. ($\blacksquare$): [Picryl chloride] = 10 $\times 10^{-5}$ mL^{-1}. ($\blacktriangle$): [Picryl chloride] = 15×10^{-5} mL^{-1}. ($\bullet$): [Picryl chloride] = 20×10^{-5} mL^{-1}. ($\circleddash$): [Picryl chloride] = 25 $\times 10^{-5}$ mL^{-1}.

Effect of Inorganic Salts

Graft copolymerization onto nylon 6 was carried out in the presence of different added salts. It was observed (Fig. 7) that the graft yield followed the order: copper sulfate > magnesium sulfate > lithium nitrate > sodium fluoride > manganese sulfate. The increase or decrease of the graft yield may be due to catalysis or inhibition, respectively, of the propagation step by the added salt.

The effect of copper sulfate on grafting is quite interesting. With an increase of copper sulfate concentration, the graft yield increased up to a concentration of 0.02 mL^{-1}. Beyond this concentration of copper sulfate a decrease in graft yield was observed. The initial

increase in graft yield may be due to the production of more free radical species under the influence of Cu^{2+} ions in the proximity of nylon 6. The subsequent drop in the graft yield might be due to the radical trap on nylon 6 by Cu^{2+} ions.

Effect of Inhibitors

The effect of different inhibitors such as picryl chloride and hydroquinone on the graft yield was studied (Fig. 8). It was observed that the graft percentage was greatly suppressed in the presence of either inhibitor. The inhibiting efficiency of picryl chloride was found to be more than that of hydroquinone. It was also observed that the extent of inhibition increases with an increase in the concentration of the inhibitor. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby reducing the molecular size of the graft and hence reducing the graft yield.
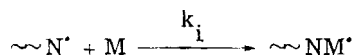
MECHANISM

The following mechanism has been suggested for the graft copolymerization of methyl methacrylate onto nylon 6 using thallium(III) ion as initiator.
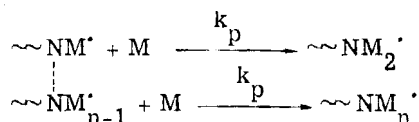
(i) Production of free radical on nylon-6:

$$\sim\!\!\sim N + Tl^{3+} \xrightarrow{\quad k_d \quad} \sim\!\!\sim N^{\bullet} + Tl^{2+}$$
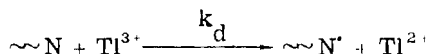
where N = nylon 6 and $N^{\bullet}$ = nylon-6 macroradical.

(ii) Initiation:

$$\sim\!\!\sim N^{\bullet} + M \xrightarrow{\quad k_i \quad} \sim\!\!\sim NM^{\bullet}$$

where M = monomer.

(iii) Propagation:

$$\sim\!\!\sim NM^{\bullet} + M \xrightarrow{\quad k_p \quad} \sim\!\!\sim NM_2^{\bullet}$$
$$\sim\!\!\sim NM_{n-1}^{\bullet} + M \xrightarrow{\quad k_p \quad} \sim\!\!\sim NM_n^{\bullet}$$

(iv) Termination:

$$\sim\!\!NM_n^{\,\bullet} + \,\sim\!\!NM_n^{\,\bullet} \xrightarrow{\ \ k_t\ \ } \text{graft copolymer}$$
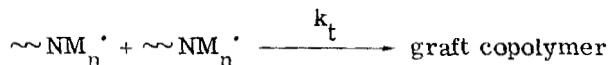
Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

$$-\frac{d[N^\bullet]}{dt} = k_d[Tl^{3+}][N] - k_i[N^\bullet][M] = 0$$

$$[N^\bullet] = \frac{k_d[Tl^{3+}][N]}{k_i[M]}$$

$$-\frac{d[NM_n^\bullet]}{dt} = k_i[N^\bullet][M] - k_t[NM_n^\bullet]^2 = 0$$

$$[NM_n^\bullet] = \left\{ \frac{k_i[N^\bullet][M]}{k_t} \right\}^{1/2}$$

Substituting the value of $[N^\bullet]$ in the above equation,

$$[NM_n^\bullet] = \left\{ \frac{k_d[Tl^{3+}][N]}{k_t} \right\}^{1/2}$$

Then

$$R_p = k_p[M][NM_n^\bullet]$$

or

$$R_p = k_p \left[\frac{k_d}{k_t}\right]^{1/2} [N]^{1/2} [Tl^{3+}]^{1/2} [M]$$

The plots of R_p versus $[M]$ (Fig. 1) and R_p versus $[\text{initiator}]^{1/2}$ (Fig. 2) are linear and pass through the origin, which confirms the validity of the above reaction scheme.

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