

# Photo-Induced Graft Copolymerization: XVI: Graft Copolymerization of Methyl Methacrylate onto Nylon-6 Using Isoquinoline-Sulfur Dioxide and $\alpha$ -Picoline-Sulphur Dioxide Charge-transfer Complexes as Photoinitiators

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## Synopsis

The photo-induced graft copolymerization of methyl methacrylate onto nylon-6 fiber was investigated using isoquinoline-sulfur dioxide and  $\alpha$ -picoline-sulfur dioxide charge-transfer complexes as the photoinitiators. The graft copolymerization was carried out within the temperature range of 35–50°C and from the corresponding Arrhenius plot, the energy of activation has been evaluated. The effect of monomer, initiators, inhibitor, etc. on the graft yield has been investigated. The effect of solvent on the rate of grafting has also been investigated from which the chain-transfer constant ( $C_s$ ) of the solvent has been evaluated. The kinetic data and other evidence indicate that the overall polymerization takes place by a radical mechanism. The suitable mechanism has been suggested and the kinetic rate expression has been derived.

## INTRODUCTION

Most of the photopolymerization reactions proceed by free radical mechanism.<sup>1</sup> Monomers such as methyl methacrylate, styrene, and acrylonitrile undergo slow polymerization when exposed to ultraviolet (UV) light. The use of ultraviolet light for initiation of graft copolymerization is well known and numerous studies<sup>5–13</sup> have been carried out on this subject using various polymers as the base material. Ogiwara and Kubota have reported that the ultraviolet light has a high accelerating effect on graft copolymerization of methyl methacrylate (MMA) onto cellulose initiated by hydrogen peroxide<sup>2</sup> or ceric ion.<sup>3,4</sup> Nayak and co-workers have reported a number of initiating systems for photograft copolymerization of vinyl monomers onto cellulose,<sup>5</sup> nylon-6,<sup>6,7</sup> wool,<sup>8</sup> and silk<sup>9</sup> fibers. Recently, Lenka and Mohanty have reported the photograft copolymerization of methyl methacrylate onto nylon-6 using acryflavin<sup>10</sup> and erythrosin<sup>11</sup> as the photoinitiators. Ishibashi and co-workers<sup>12</sup> reported the photo-induced graft copolymerization of styrene onto nylon-6 without any specific photosensitizer.

Charge-transfer complexes of weak bases such as pyridine, picoline, isoquinoline, etc. with acceptors like SO<sub>2</sub>, Cl<sub>2</sub>, and Br<sub>2</sub>, are reported<sup>6,8,13</sup> as efficient photoinitiators for initiating vinyl polymerization and graft copolymerization. This communication presents the results of photograft copo-

lymerization of methyl methacrylate onto nylon-6 using isoquinoline-sulfur dioxide and  $\alpha$ -picoline-sulfur dioxide charge-transfer complexes as the photo-initiators.

### EXPERIMENTAL

Nylon-6 fiber was supplied by J.K. Synthetics, Kota, Rajsthan (India) as a gift sample. The purification of nylon-6 and monomer was done according to our previous procedure.<sup>11</sup> Isoquinoline and  $\alpha$ -picoline (SISCO, India) were dried over sodium hydroxide pellets and were distilled under vacuum. All solvents used were of reagent grade and were distilled before use. The charge-transfer complexes of isoquinoline-sulfur dioxide and  $\alpha$ -picoline-sulfur dioxide were prepared by the method given by Eisch.<sup>14</sup>

Graft copolymerization was carried out by adding a required amount of monomer containing a known amount of initiator, nylon-6, and other additives, flushed with purified nitrogen, stoppered, and placed in a thermostat at required temperature. The reaction vessel was illuminated by a monochromatic light of 440 nm wavelength by placing a corning filter in front of a 125 W high-pressure mercury lamp (Philips India Ltd.). The grafted sample was taken out at required intervals, and washed repeatedly with water. Finally, the grafted nylon-6 fiber was extracted with benzene in a soxhlet apparatus for 48 h until all the homopolymer was completely removed. Then the fiber was dried in a vacuum to constant weight. The percentage of grafting was calculated from the increase in weight of nylon-6 after grafting in the following manner:

$$\%G = \frac{W_1}{W_0} \times 100$$

where  $W_0$  and  $W_1$  are, respectively, the weights of nylon-6 and grafted nylon-6 after benzene extraction.

The molecular weight of the grafted poly(methyl)methacrylate (PMMA) was determined viscometrically in benzene by using the purified water-insoluble acid hydrolyzate of the graft. A single-point method<sup>15</sup> was employed for calculating intrinsic viscosity. The average molecular weight was determined using the following relationship.<sup>16</sup>

$$[\eta] = 9.6 \times 10^{-5} \times M_v^{0.69}$$

### RESULTS AND DISCUSSION

The photograft copolymerization of methyl methacrylate onto nylon-6 fibers was investigated using isoquinoline-sulfur dioxide and  $\alpha$ -picoline-sulfur dioxide charge-transfer complexes as photoinitiators. Figure 1 represents the time conversion curve at  $1 \times 10^{-3}$  m.l<sup>-1</sup> initiator concentrations for both the initiators at  $45 \pm 0.05^\circ\text{C}$ . It was observed that for both the initiators, the graft yield increases up to 5 hours, beyond which a sharp decrease is noticed. It was also observed that IQ-SO<sub>2</sub> is much more reactive than  $\alpha$ -pi-SO<sub>2</sub>.

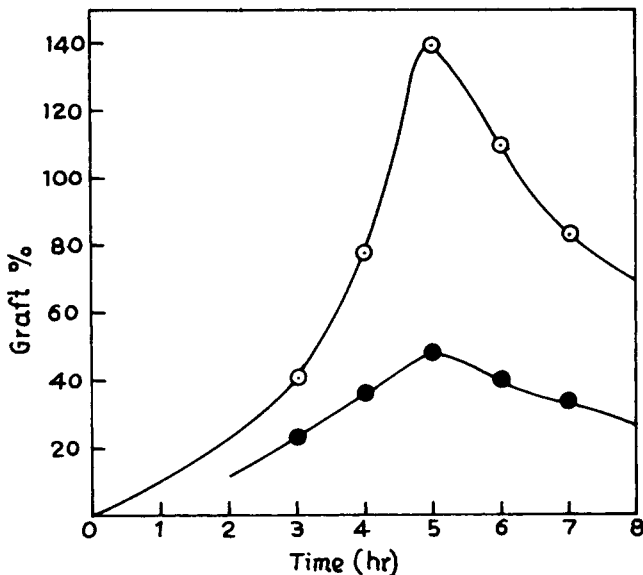


Fig. 1. Time conversion curve:  $[MMA] = 0.9388 \text{ m.l}^{-1}$ ; (O):  $[IQ-SO_2] = 1 \times 10^{-3} \text{ m.l}^{-1}$ ; (●):  $[\alpha\text{-pi-SO}_2] = 1 \times 10^{-3} \text{ m.l}^{-1}$ . Temp. =  $45^\circ\text{C}$ ; M:L = 1:100.

**Effect of Monomer Concentration.** The effect of monomer concentration on the graft yield was studied by varying the monomer within the concentration range of  $0.2347\text{--}1.1735 \text{ m.l}^{-1}$  for a polymerization time of 5 hours. It was observed that, the graft yield increases steadily with increase in the monomer concentration for both the initiators. The possible reasons for the increasing trend in the graft yield might be due to (i) complexation of nylon-6 fibers with

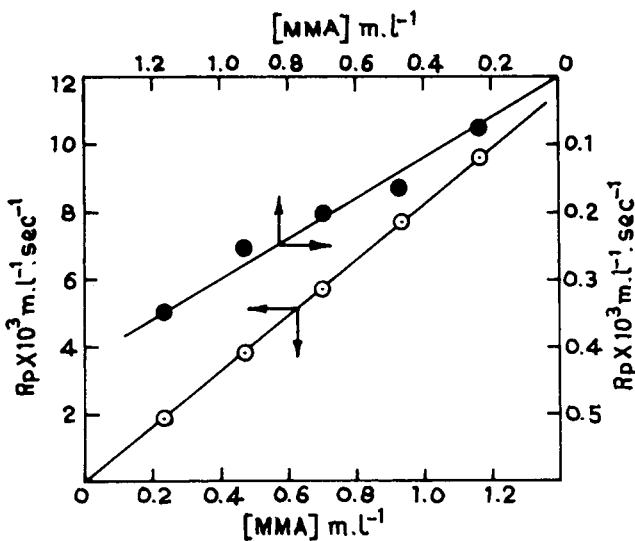


Fig. 2. Plot of  $R_p$  versus  $[MMA]$ : (O):  $[IQ-SO_2] = 1 \times 10^{-3} \text{ m.l}^{-1}$ ; (●):  $[\alpha\text{-pi-SO}_2] = 1 \times 10^{-3} \text{ m.l}^{-1}$ ; Time = 4 h; Temp. =  $45^\circ\text{C}$ ; M:L = 1:100.

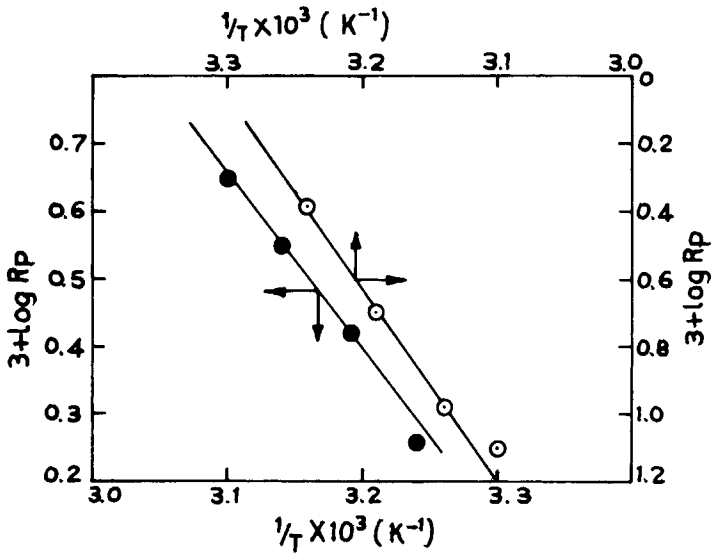


Fig. 3. Plot of  $R_p$  versus  $[I\text{-SO}_2]^{1/2}$  (O). Plot of  $R_p$  versus  $[\alpha\text{-pi-SO}_2]^{1/2}$  (●);  $[\text{MMA}] = 1.1735 \text{ m.l}^{-1}$ . Time = 5 h; Temp. =  $45^\circ\text{C}$ ; M:L = 1:100.

the monomer which enhances monomer activity, (ii) gel effect, and (iii) swelling of fibers by monomer.

The plot of  $R_p$  versus  $[\text{MMA}]$  is found to be linear (Fig. 2) for both the initiating systems, indicating the termination to be of mutual type.

**Effect of Initiator Concentration.** The effect of initiator concentration on the graft yield was investigated by changing the initiator concentration from  $2.5 \times 10^{-4} - 10 \times 10^{-4} \text{ m.l}^{-1}$  for a polymerization time of 5 hours. It was

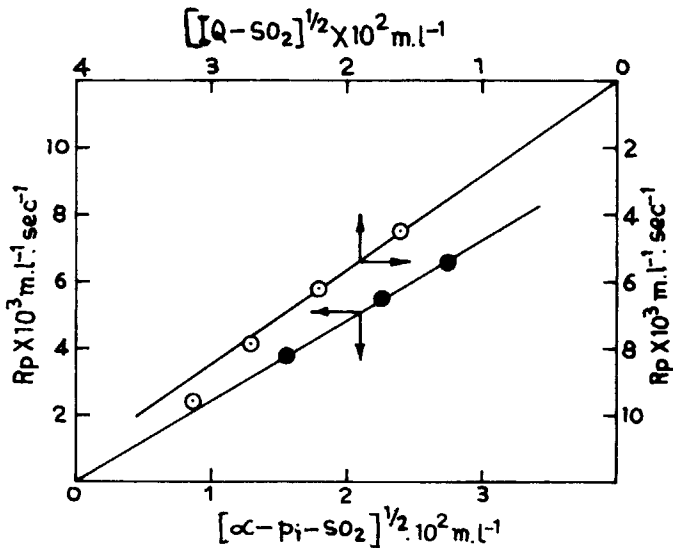


Fig. 4. Arrhenius plot of  $\log R_p$  versus  $\frac{1}{T}$ .

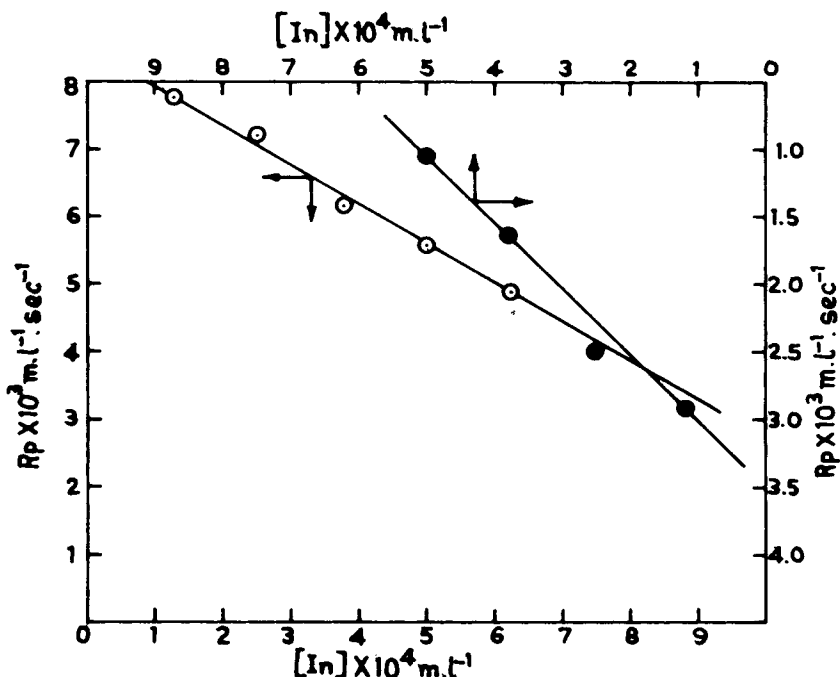


Fig. 5. Plot of  $R_p$  versus  $[I_n]$ :  $[MMA] = 1.1735 \text{ m.l.}^{-1}$ ;  $[IQ-SO_2] = 1 \times 10^{-3} \text{ m.l.}^{-1}$  (○);  $[\alpha\text{-pi-SO}_2] = 1 \times 10^{-3} \text{ m.l.}^{-1}$  (●). Time = 5 h; Temp. = 45°C; M:L = 1:100

noticed that the extent of grafting ( $R_p$ ) increases with increased concentration of initiators. Possibly this increasing trend in the extent of grafting might be due to the fact that in the initial stages of reaction, a greater number of  $R\cdot$  is formed, which enhances the extent of grafting. The plots of  $R_p$  versus  $[IQ-SO_2]^{1/2}$  and  $[\alpha\text{-pi-SO}_2]^{1/2}$  are linear (Fig. 3).

The charge-transfer complexes of isoquinoline with  $SO_2$ ,  $Cl_2$ , and  $Br_2$  are prepared and their reactivity for grafting MMA onto nylon-6 fibers is compared. Among them  $IQ-SO_2$  complex is found to be the most suitable initiator, the order of reactivity being  $IQ-SO_2 > IQ-Br_2 > IQ-Cl_2$ . This trend suggests the ease of formation of  $SO_2$  radical over that of  $Br\cdot$  and  $Cl\cdot$ .

**Effect of Temperature.** The graft copolymerization was carried out at four different temperatures ranging from 35 to 50°C, keeping the concentration of all other reagents constant. It is observed that for both the initiating systems, the graft yield increases significantly with the increase of temperature. From the Arrhenius plot of  $\log R_p$  versus  $\frac{1}{T}$  (Fig. 4), the overall energy of activation was computed to be 25.5 kcal/mole and 11.5 kcal/mol for  $IQ-SO_2$  and  $\alpha\text{-pi-SO}_2$ , charge transfer complexes, respectively.

**Effect of Inhibitor Concentration.** The effects of inhibitor concentration on the extent of grafting was investigated for both initiating systems. It was observed that the extent of grafting decreases with increasing inhibitor concentration from  $1.25 \times 10^{-4} - 6.25 \times 10^{-4} \text{ m.l.}^{-1}$  (Fig. 5).

**Determination of Chain-Transfer Constant ( $C_s$ ).** Employing nylon-6 fibers as the substrate, the chain-transfer constant for the solvent,  $CHCl_3$  was

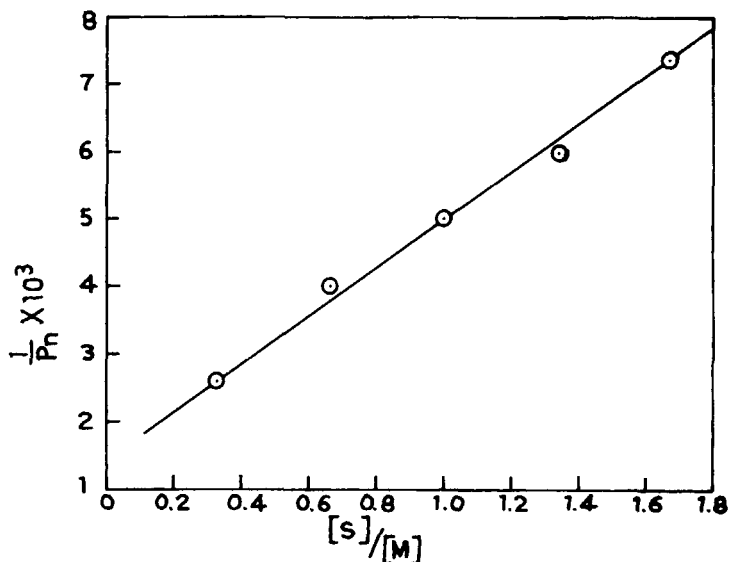


Fig. 6. Plot of  $\frac{[S]}{[M]}$  versus  $\frac{1}{\bar{P}_n}$ .

evaluated by employing the relationship,

$$\frac{1}{\bar{P}_n} = \left[ \frac{1}{\bar{P}_n} \right]_0 + C_s \frac{[S]}{[M]}$$

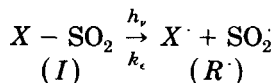
where,  $\bar{P}_n$  = degree of polymerization of grafted poly(methyl methacrylate)

The plot of  $\frac{1}{\bar{P}_n}$  versus  $\frac{[S]}{[M]}$  (Fig. 6) is linear. The slope of the plot gives the  $C_s$  value of the solvent as 2.8.

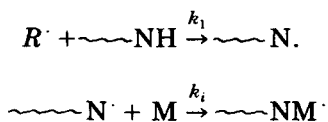
**Reaction Scheme and Rate Expressions.** Eisch<sup>14</sup> reported that the charge-transfer complexes of the type involving nitrogen heterocyclic compounds and sulfur dioxide are of the n-donor-type compounds. In the presence of light, the complex slowly decomposes, liberating sulfur dioxide radical.

From the proportionalities obtained between the measurable parameters and the variables, the following reaction scheme initiated by a radical pair and terminated by a mutual mechanism is suggested.

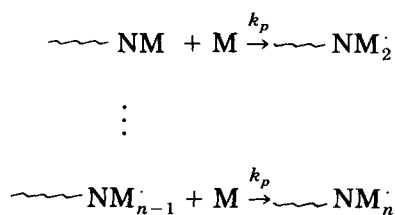
Decomposition of the complex:



Here,  $X$  represents both for isoquinoline and  $\alpha$ -picoline  
Initiation:



Propagation:



Termination:



Here, M represents the monomer (methyl methacrylate), NH, the reactive group in the nylon-6 backbone,  $\text{NM}^\cdot$  and  $\text{N}^\cdot$ , the corresponding growing radicals.

Applying steady-state assumptions, the following rate equation is derived.

$$d\frac{[R^\cdot]}{dt} = k_i[I] - k_i[R^\cdot][\text{NH}] = 0$$

or,

$$[R^\cdot] = \frac{k_i[I]}{k_i[\text{NH}]}$$

$$d\frac{[\text{NM}_n^\cdot]}{dt} = k_i[R^\cdot][\text{NH}] - k_t[\text{NM}_n^\cdot]^2 = 0 \quad (1)$$

or,

$$[\text{NM}_n^\cdot] = \left\{ \frac{k_i[R^\cdot][\text{NH}]}{k_t} \right\}^{1/2} \quad (2)$$

Putting the value of  $[R^\cdot]$  in the above equation,

$$\begin{aligned} [\text{NM}_n^\cdot] &= \left( \frac{k_i}{k_t} \right)^{1/2} \cdot [I]^{1/2} \\ R_p &= k_p[\text{NM}_n^\cdot][\text{M}] \end{aligned} \quad (3)$$

or,

$$R_p = k_p \left( \frac{k_i}{k_t} \right)^{1/2} \cdot [I]^{1/2} \cdot [\text{M}] \quad (4)$$

The dependence of  $R_p$  on  $[I]^{1/2}$  and  $[\text{M}]$  for both the systems favors the above reaction scheme.

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