

Photo-Induced Graft Copolymerization XI. Graft Copolymerization of Methyl Methacrylate onto Silk Using Isoquinoline-Sulphur Dioxide Charge-Transfer Complex as the Initiator

INTRODUCTION

Recently, Nayak and coworkers have reported a number of initiating systems for photo-graft copolymerization of vinyl monomer onto cellulose,¹ nylon,^{2,3} and PET⁴ fibers. Horio and coworkers⁵ have reported riboflavin-sensitized photo-grafting of acrylamide onto wool. Charge-transfer complexes of weak bases, such as pyridine, picolines, and isoquinoline, with acceptors, such as SO₂, Cl₂, and Br₂, are reported^{3,6,7} as efficient photoinitiators for initiating vinyl polymerization and graft copolymerization. This communication presents the photo-graft copolymerization of methyl methacrylate onto silk using an isoquinoline-SO₂ (IQ-SO₂) charge-transfer complex as the photo initiator.

EXPERIMENTAL

The isoquinoline-SO₂ charge-transfer complex was prepared by a method similar to that given by Eisch.⁸ The purification of silk and monomer and the details of the experimental procedure were reported in our previous communication.⁷

RESULTS AND DISCUSSION

Monomer and Initiator

The extent of grafting R_p was investigated by varying the monomer and the initiator in the concentration ranges of 0.2347–1.1735 mol/L and 1.2257 – 6.1287×10^{-3} mol/L, respectively. The graft yield becomes maximum at 0.9388 mol/L of the monomer and 4.903×10^{-3} mol/L of the initiator, beyond which a decreasing trend was observed. Formation of homopolymer and enhanced rate of termination are probable causes of decreased graft yield at higher concentration of monomer and initiator. The plots of R_p versus [MMA] and [IQ-SO₂] are linear (Fig. 1).

The charge-transfer complexes of isoquinoline with SO₂, Cl₂, and Br₂ were prepared, and their reactivity for grafting MMA onto silk fibers was compared. The IQ-SO₂ complex was found to be the most suitable initiator, the order of reactivity being IQ-SO₂ > IQ-Br₂ > IQ-Cl₂. This trend suggests the ease of formation of SO₂ radical over that of Br[•] and Cl[•].

Activation Energy

The graft copolymerization was carried out at four temperatures ranging from 35 to 50°C. The graft yield increases significantly with increase in temperature. This can be ascribed to the greater swellability of silk and the solubility and enhanced rate of diffusion of monomer. From the Arrhenius plot of log R_p versus $1/T$ (Fig. 2), the overall energy of activation was computed to be 37.5 kJ/mol.

Chain-Transfer Constant C_s and k_p^2/k_t Value

The chain-transfer constant for such solvents as dioxane and CCl₄ was evaluated employing Mayo's equation.

$$\frac{1}{P_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_s \frac{[S]}{[M]} + C_1 \frac{[I]}{[M]}$$

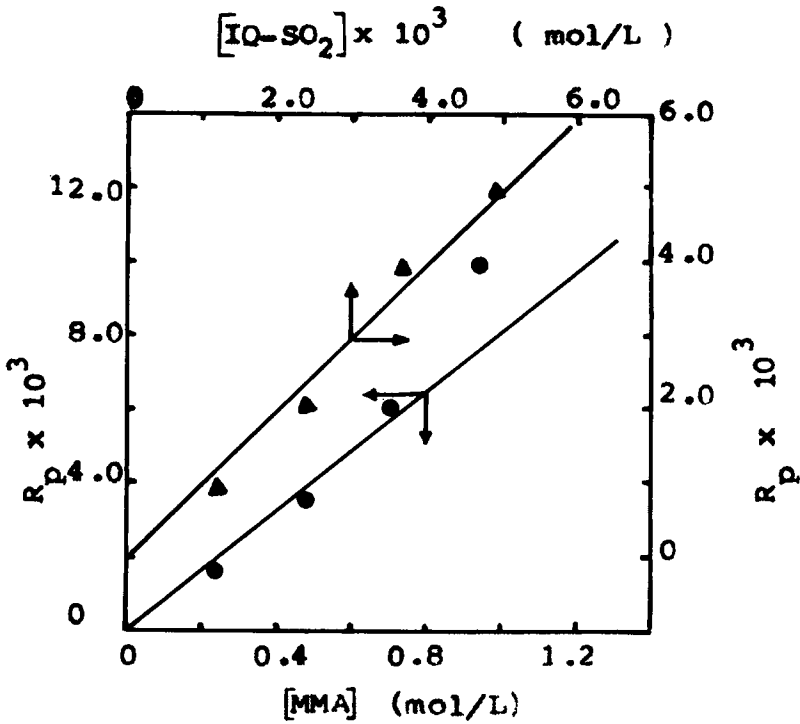


Fig. 1. Plot of R_p versus $[MMA]$ and $[IQ-SO_2]$. (●) Effect of monomer: $[IQ-SO_2] = 3.6772 \times 10^{-3}$ mol/L; $[dioxane] = 0.5878$ mol/L. (▲) Effect of initiator: $[MMA] = 0.4694$ mol/L; $[methanol] = 6.211$ mol/L. Temperature = $40^\circ C$; Time = 4 h; $M_1/L = 1:100$.

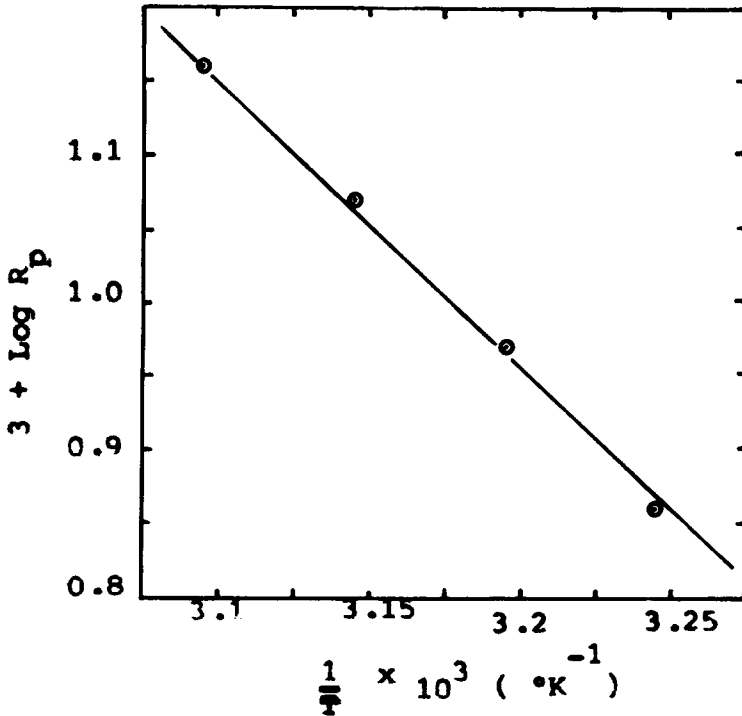


Fig. 2. Arrhenius plot of $\log R_p$ versus $1/T$. $[IQ-SO_2] = 4.2901 \times 10^{-3}$ mol/L; $[MMA] = 1.1735$ mol/L. Time = 4 h; $M:L = 1:100$.

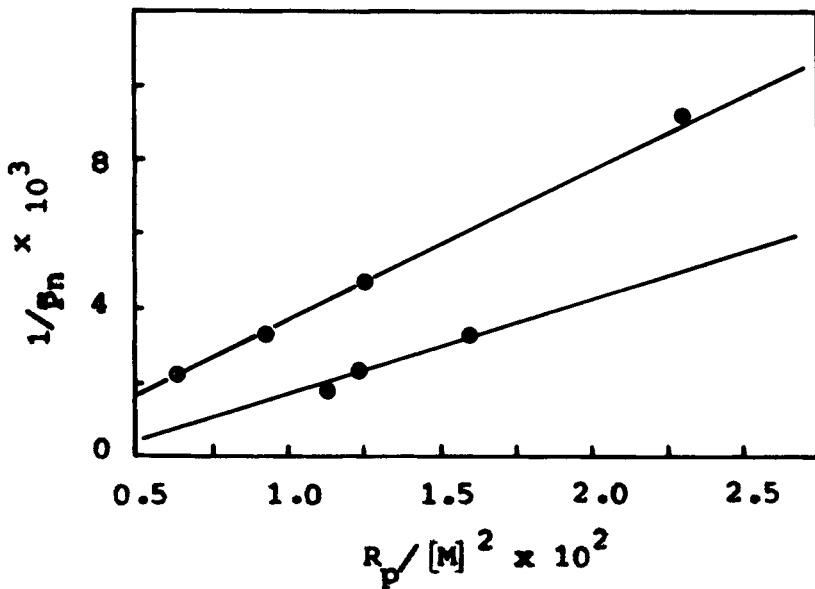


Fig. 3. Plot of $1/P_n$ versus $R_p/[M]^2$. (○) CCl_4 ; (●) dioxane.

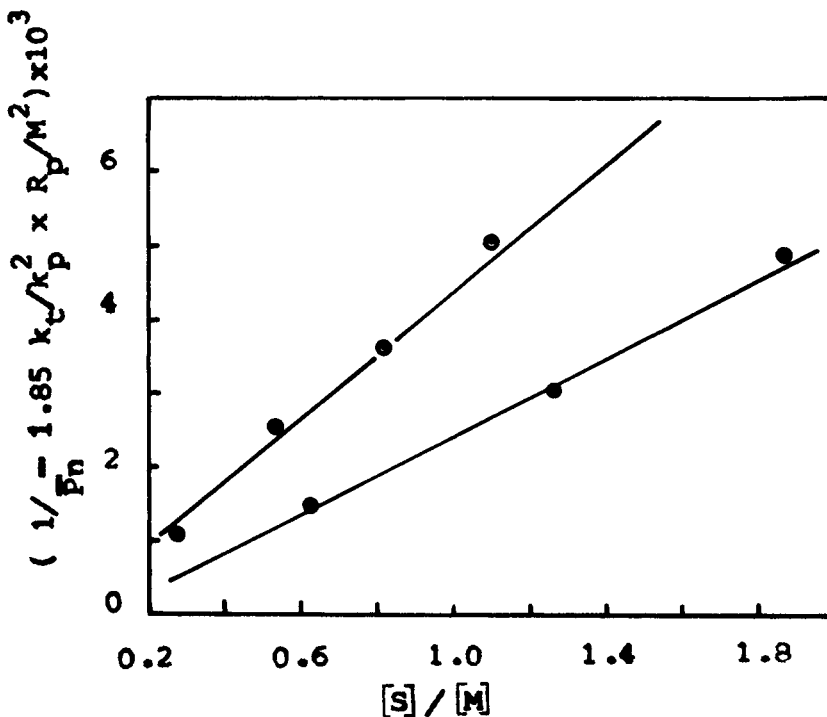


Fig. 4. Plot of $1/P_n - 1.85(k_t/k_p^2)(R_p/[M]^2)$ versus $[S]/[M]$. (○) CCl_4 ; (●) dioxane.

where P_n = degree of polymerization of grafted poly(methyl methacrylate) regenerated by a two-stage HCl digestion technique and all other terms have their usual significance.

At low initiator concentrations and at a fixed solvent concentration, this equation can be condensed to the form⁹

$$\frac{1}{P_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + \sum \frac{R_{tr}}{R_p}$$

where the last term on the right-hand side was included to account for chain-transfer effects, assuming that this would not affect the slope of the plot for low initiator concentration.

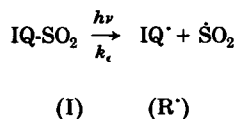
From the slope of the plot of $1/P_n$ versus $R_p/[M]^2$ (Fig. 3), the k_p^2/k_t value was evaluated. At 40°C, the calculated k_p^2/k_t values for CCl_4 and dioxane are 4.528 and 7.255 L/mol s⁻¹, respectively.

The k_t/k_p^2 value was employed in the expanded form of the Mayo equation. The concentration of the solvent was varied at a fixed concentration of the initiator and the monomer. At low initiator concentrations and over a narrow range of monomer concentration, $[I]/[M]$ can be expected not to affect the slope of the plot of $1/P_n - 1.85(k_t/k_p^2)(R_p/[M]^2)$ versus $[S]/[M]$ (Fig. 4). The chain-transfer constant for dioxane and CCl_4 was evaluated from the slope of this plot and found to be 2.6315×10^{-3} and 4.2307×10^{-3} , respectively.

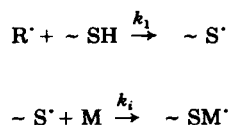
Mechanism and Rate Equation

Eisch⁸ reported that the charge-transfer complexes of nitrogen heterocyclic compounds and SO_2 are of n -donor type of compounds. In the presence of light, the complex slowly decomposes, liberating sulfur dioxide radical. Since, in the present case, R_p varies linearly with $[IQ-SO_2]$, it is suggested that the termination step is predominantly by solvent.

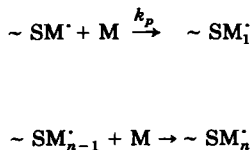
Decomposition of the complex:



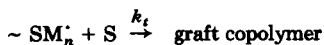
Initiation:



Propagation:



Termination:



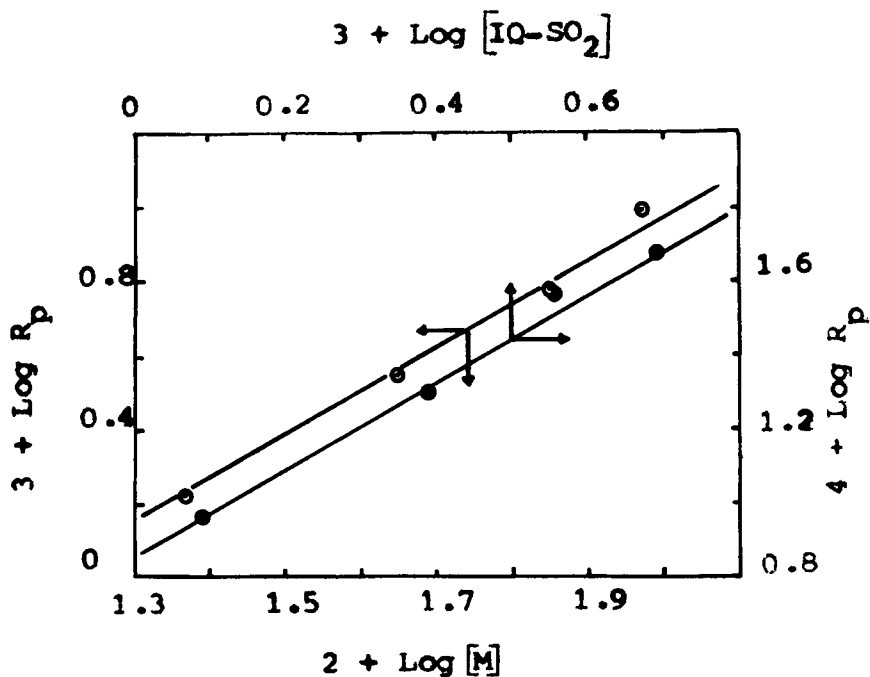


Fig. 5. Plot of $4 + \log R_p$ versus $2 + \log [M]$ and $3 + \log R_p$ versus $3 + \log [IQ-SO_2]$.

Here $\sim SH$ represents the reactive group in the silk backbone, $\sim S'$ and $\sim SM'$ the growing radicals, and S the solvent.

Applying a steady-state assumption, the rate of graft copolymerization is derived to be

$$R_p = \frac{k_p k_i h \nu [M][I]}{k_t [S]}$$

At a fixed solvent concentration, this equation predicts linear plots of R_p versus $[M]$ and R_p versus $[I]$, i.e., unity exponents for monomer and initiator, which has been experimentally observed (Fig. 5).

S. Samal thanks U.G.C., New Delhi, for financial assistance.

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Received July 22, 1985
Accepted May 8, 1986