

Photoinduced Graft Copolymerization. IX. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 in the Presence of Pyridine–Bromine Charge–Transfer Complex as Photoinitiator

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Synopsis

Photoinduced graft copolymerization of methyl methacrylate onto nylon 6 was investigated by using pyridine–bromine (Py–Br₂) charge–transfer complex as initiator. The graft yield increased with increasing monomer and initiator concentration at the initial stages, and therefore it decreased. The initiator exponent was computed to be 0.5. The reaction was carried out at three different temperatures, and the overall activation energy was computed. A suitable mechanism has been suggested.

INTRODUCTION

The effectiveness of bromine as a photoinitiator in the photopolymerization of methyl methacrylate (MMA) and some other vinyl monomers has been studied recently.^{1,2} It is of considerable interest to note that the rate of bromine-initiated photopolymerization of MMA was significantly enhanced by the presence of basic solvents like pyridine and quinoline.² Ghosh and Mitra have reported the photopolymerization of vinyl monomers by the use of pyridine–bromine³ and quinoline bromine⁴ charge–transfer complex as photoinitiators.

Ishibashi and co-workers^{5–7} reported the photoinduced grafting of styrene onto nylon 6 without any specific photosensitizer. Ogiwara and co-workers have reported that cellulose radicals formed by photoirradiation can easily initiate graft copolymerization, which is sharply affected by the wavelength of light,⁸ the solvent,⁹ and the kind of sensitizers^{10,11} employed.

In the present investigation, the photoinduced graft copolymerization of methyl methacrylate onto nylon 6 has been studied using pyridine–bromine charge–transfer complex as the photoinitiator.

EXPERIMENTAL

The purification of nylon 6 and monomer were done according to our previous procedure.^{12–14} Pyridine was dried over sodium hydroxide pellets and was distilled under vacuum. Bromine (E. Merck) was of analytical grade and was used without further purification. All solvents used were reagent grade and were distilled before use. The charge–transfer complex of pyridine–bromine was prepared by a method similar to that given by Eisch.¹⁵

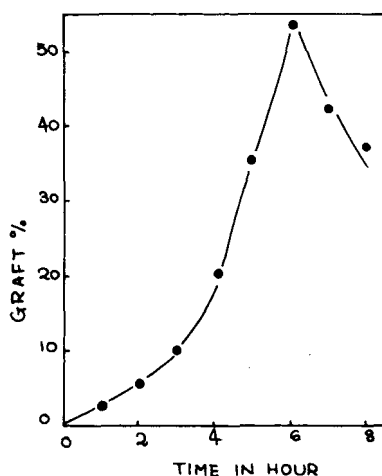


Fig. 1. Effect of reaction time on graft yield: $[\text{Py-Br}_2] = 1.72 \times 10^{-4}$ mol/L; $[\text{MMA}] = 9.384 \times 10^{-3}$ mol/L; temp = 35°C ; M:L = 1:100.

The graft copolymerization was carried out by adding a required amount of monomer containing known amount of initiator, nylon, and other additives, flushed with purified nitrogen, stoppered, and placed in a thermostat at the 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, washed repeatedly with water, soxhlet-extracted with benzene, and dried in vacuum to constant weight.

DISCUSSION

The photo graft copolymerization of methyl methacrylate onto nylon 6 fibres was investigated using pyridine-bromine as photoinitiator. The graft yield increases up to 6 h. and decreases thereafter (Fig. 1). The initiation of graft copolymerization does not take place in the absence of sensitizer.

Effect of Monomer. The rate of grafting was investigated by changing the monomer concentration from 0.375×10^{-3} to 16.88×10^{-3} mol/L for a polymerization time of 6 h. The graft yield increases with increasing monomer concentration up to 13.13×10^{-3} mol/L and thereafter it decreases (Fig. 2). At higher monomer concentration, the reactions that are competitive with the grafting probably take place in the solution, i.e., combination and disproportionation of PMMA macroradicals. When the concentration of PMMA macroradicals increases, the rate of their combination and disproportionation increases faster than the rate of their combination with nylon molecules. On the other hand, the rate of monomer diffusion is found to be progressively affected by the polymer deposit formed, which, of course, grows most rapidly when high concentrations of monomer are used. The plot of R_p vs. monomer concentration (Fig. 3) is linear.

Effect of Initiator Concentration. The effect of initiator concentration on graft yield was investigated by changing the initiator concentrations from 0.43

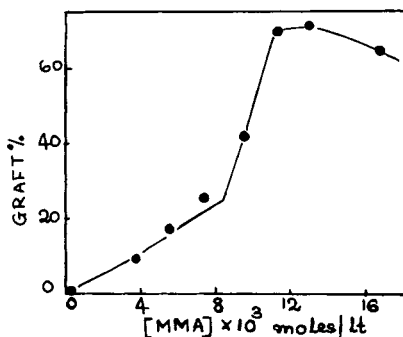


Fig. 2. Effect of monomer concentration on graft yield: [Py-Br₂] = 2.58 × 10⁻⁴ mol/L; temp = 35°C; time = 6 h; M:L = 1:100.

× 10⁻³ to 3.5 × 10⁻³ mol/L. The graft yield increases steadily up to 2.58 × 10⁻³ mol/L of initiator concentration (Fig. 4) and thereafter it decreases. The *R_p* values were computed from the percentage of graft yield. The plot of *R_p* vs. square root of initiator concentration is linear indicating 0.5 order with respect to the initiator (Fig. 3).

Effect of Temperature. The graft copolymerization was carried out at three different temperatures ranging from 35° to 55° keeping the concentration of all other reagents constant. It is observed that the graft yield increases significantly with the increase of temperature. The dependence of the rate of grafting on the temperature could be ascribed to the greater activation energy, swellability of nylon, solubility, and enhancement of the rate of diffusion of monomer. From the plot of log *R_p* vs. 1/*T* (Fig. 5) the energy of activation was computed to be 11.3 kcal/mol.

Effect of the Amount of Fiber. Figure 6 shows the relationship between the percent of grafting and the quantity of nylon used for the copolymerization after a polymerization time of 6 h at a temperature of 35°C. It is found that the percent of grafting increases up to 0.1 g and then decreases exponentially with nylon quantity. This might be due to several factors such as: (1) with the increase of the quantity of the nylon the surface area will be increased and the fiber molecule might terminate the growing polymer chain; (2) the concentration of

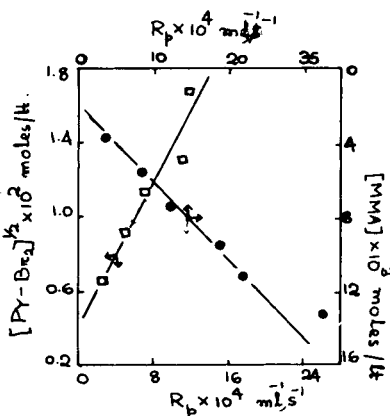


Fig. 3. Plot of *R_p* vs. [MMA] and [Py-Br₂]^{1/2}.

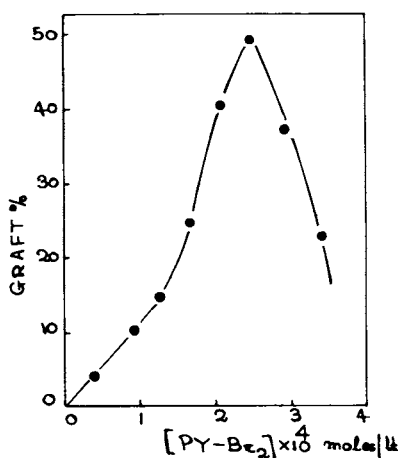
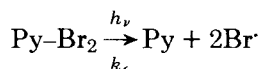


Fig. 4. Effect of [Py-Br₂] on graft yield: [MMA] = 9.38×10^{-3} mol/L; temp = 35°C; time = 6 h; M:L = 1:100.

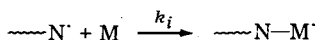
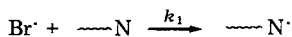
monomer decreases at the grafting sites because of its adsorption at a greater surface area.

Mechanism. According to the view of Eisch and Jaselskis,¹⁶ the charge-transfer complexes of the type involving nitrogen heterocyclic compounds and bromine are of the *n*-donor type compounds. The complex is believed to decompose slowly, liberating bromine radicals in the presence of light. From the proportionalities obtained between the measurable parameters and the variables, the following reaction scheme is suggested, involving initiation by bromine free radical and termination by a mutual mechanism:

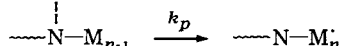
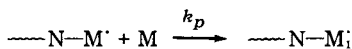
Decomposition of the complex:



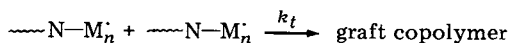
Initiation:



Propagation:



Termination:



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

Applying steady state assumption, the following expression could be derived for the rate of polymerization, R_p :

$$R_p = k_p \left(\frac{k_e k_i}{k_t} \right)^{1/2} [\text{Py-Br}_2]^{1/2} [\text{M}]$$

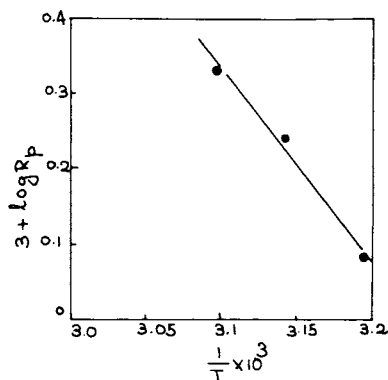
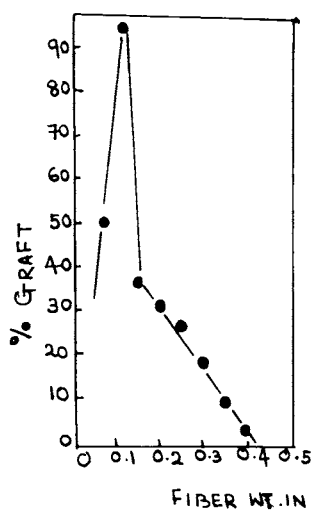
Fig. 5. Arrhenius plot of $\log R_p$ vs. $1/T$.

Fig. 6. Plot of graft % vs. amount of fiber.

The dependence of R_p on $[M]$ and $[Py-Br_2]^{1/2}$ favors the above reaction scheme.

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