

Photoinduced Graft Copolymerization. II. Graft Copolymerization of Methyl Methacrylate onto Nylon-6 in Presence of γ -Picoline-Bromine Charge Transfer Complex

During the last decade several methods have been used for modifying the properties of natural and synthetic fibers through graft copolymerization.¹⁻⁶ Nayak and co-workers⁷⁻¹⁷ have used a multitude of metal and nonmetal ions for initiating grafting onto some natural and synthetic fibers. Ultraviolet light has been used for the initiation of graft copolymerization by a number of workers. The use of photosensitizers such as anthraquinone¹⁸ and riboflavine¹⁹ enhance the percentage of grafting. When a polymer is irradiated, it absorbs energy which may lead to the formation of macroradical. For low energy radiation, the absorbed energy is usually dissipated without formation of free radical sites. If a photosensitizer which decomposes into active radicals or transfers its energy to the substrate is included in the system, it gives rise to sites for polymerization.¹

Horio and co-workers²⁰ have reported riboflavine-sensitized photopolymerization of acrylamide onto wool. Ogiwara and Kubota have reported that the ultraviolet light has high accelerating effect on graft copolymerization of methyl methacrylate onto cellulose initiated by hydrogen peroxide² or ceric ion.²¹⁻²³ Ishibashi and co-workers²⁴⁻²⁶ reported the photoinduced grafting of styrene onto nylon-6 without any specific photosensitizer. Ogiwara and co-workers reported that cellulose radical formed by photoirradiation can easily initiate graft copolymerization which is sharply affected by the wavelength of light,²⁷ solvent,²⁸ and the kind of sensitizers^{29,30} employed. The use of charge transfer complexes for photopolymerization of vinyl monomers has attracted the attention in recent years.^{31,32}

This communication presents the photoinduced graft copolymerization of methyl methacrylate onto nylon-6 using γ -picoline-bromine charge-transfer complex as the photoinitiator.

EXPERIMENTAL

Nylon-6 was supplied by J.K. Synthetics, Kota, Rajsthan (India) as a gift sample. γ -picoline (4-methyl pyridine) was dried over sodium hydroxide pellets and was distilled under vacuum. Bromine was E. Merck analytical grade material and was used as such. All solvents used were reagent grade and were distilled before use. The charge-transfer complex of γ -picoline-bromine was prepared by a method similar to that given by Eisch.³³

The polymerization was carried out by our previous procedure.⁷⁻¹⁰ 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.

RESULTS AND DISCUSSION

The photograft copolymerization of methyl methacrylate onto nylon-6 was investigated using γ -picoline-bromine as photoinitiator. The percentage graft increases up to 4 h and remains almost constant thereafter (Fig. 1). The initiation of graft copolymerization does not take place in the absence of a sensitizer.

Effect of Monomer

Figure 2 shows the dependence of percentage of graft yield on the concentration of monomer. The percentage of graft yield increases as the monomer concentration increases up to 0.4694M, and with further increase of monomer concentration the percentage of graft yield decreases. A similar trend has also been noted by us for the photograft copolymerization of methyl methacrylate onto silk using lutidine-bromine charge transfer complex.³⁴ The plot of R_p vs. monomer concentration is linear (Fig. 3).

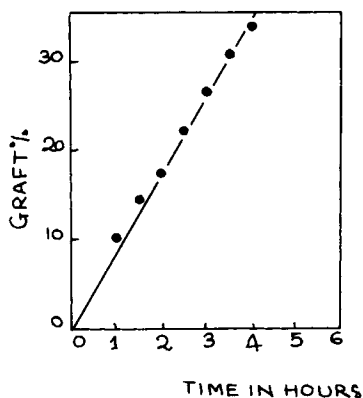


Fig. 1. Effect of reaction time on graft yield: $[\text{Pi}-\text{Br}_2] = 2.5 \times 10^{-3}M$; $[\text{MMA}] = 0.4694M$; temp = 35°C ; M:L = 1:100.

Effect of Initiator Concentration

Figure 4 shows the effect of initiator concentration on graft yield. The concentration of complex was varied from 0.25×10^{-3} to $5.0 \times 10^{-3}M$, keeping the concentration of all other reagents constant. The percentage graft yield increases steadily with increase of initiator concentration up to $1 \times 10^{-3}M$ and then decreases with further increase of the complex concentration. At higher complex concentration there is abundance of free radicals which favors the formation of homopoly(methyl methacrylate), thereby decreasing the graft yield. The R_p values were computed from the percentage graft values. The plot of R_p vs. square root of the complex concentration is linear, indicating 0.5 order with respect to the complex (Fig. 5).

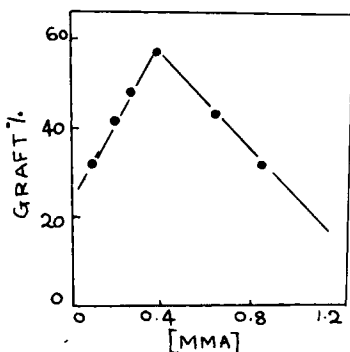


Fig. 2. Effect of monomer on graft yield: $[\text{Pi}-\text{Br}_2] = 1.0 \times 10^{-3}M$; time = 4 h; temp = 35°C ; M:L = 1:100.

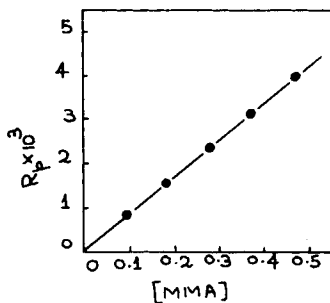


Fig. 3. Plot of R_p vs. $[\text{MMA}]$.

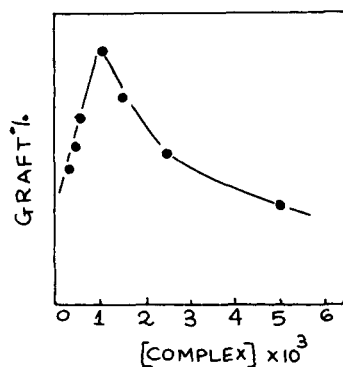


Fig. 4. Effect of initiator on graft yield: $[MMA] = 0.4694M$; time = 4 h; temp = $35^{\circ}C$.

Effect of Temperature

The graft copolymerization was carried out at three different temperatures ranging from $30^{\circ}C$ to $40^{\circ}C$ keeping the concentrations of all other reagents constant (Fig. 6). The data so obtained indicate that with increasing temperature the graft yield increases significantly. From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy and energy of initiation were found to be 5.6 kcal/mol and 2.2 kcal/mol, respectively (Fig. 7).

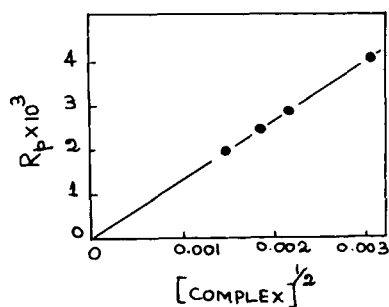


Fig. 5. Plot of R_p vs. $[Pi-Br_2]^{1/2}$.

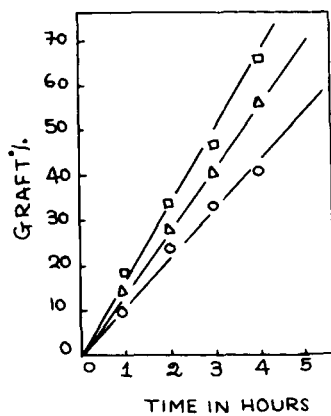
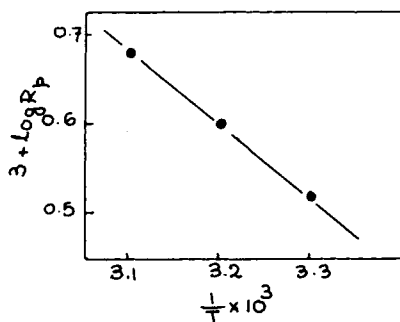
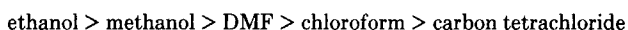


Fig. 6. Effect of temperature on graft yield: $[Pi-Br_2] = 1.0 \times 10^{-3}M$; $[MMA] = 0.4694M$; M:L = 1:100; temp ($^{\circ}C$): (O) 30; (Δ) 35; (\square) 40.

Fig. 7. Arrhenius plot of $\log R_p$ vs. $1/T$.

Effect of Solvent

The effect of solvent on graft copolymerization has been investigated by using various protic, dipolar aprotic, and nonpolar solvents. The reactivity of various solvents in terms of percentage of grafting follows the order:

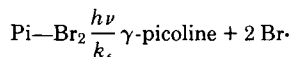


MECHANISM

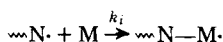
According to the views of Eisch and Jaselskis,³⁵ the charge transfer complexes of the type involving nitrogen heterocyclic compounds and bromine are of n -donor type compounds. The complex is believed to decompose slowly, liberating bromine radical in presence of light.

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 through mutual mechanism.

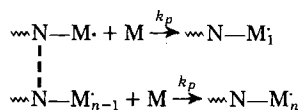
Decomposition of the complex:



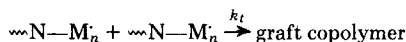
Initiation:



Propagation:



Termination:



Here M represents the monomer $\sim\text{N}-\text{M}$, $\sim\text{N}\cdot$ are the growing fiber radical, Pi is γ -picoline.

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

$$R_p = k_p [\text{NM}_n] [\text{M}] = (k_i/k_t)^{1/2} [\text{Pi}-\text{Br}_2]^{1/2} [\text{M}]$$

The dependence of R_p on $[\text{M}]$ and $[\text{Pi}-\text{Br}_2]^{1/2}$ favors the above reaction scheme.

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