Photo-Induced Graft Copolymerization. IV. Graft Copolymerization of Methyl Methacrylate onto Nylon-6 Using N-Bromosuccinamide as Photoinitiator

INTRODUCTION

N-bromosuccinamide (NBS) has been extensively used for brominating a number of simple or conjugated olefines, aromatic or heterocyclic nuclei and other organic compounds.[1-8] The bromination with NBS as the brominating reagent is highly selective. NBS received wide attention for its capacity to introduce bromine into an allylic position. Bloomfield[5] and Hey[6] in 1955 suggested that NBS reacts via a radical chain mechanism. The radical mechanism is generally accepted for reactions in nonhydroxylic solvents, but in polar media, such as in water, NBS reacts by a polar mechanism behaving as a carrier for electrophilic halogen.[2,7] Rate of radical chain reaction was found to be accelerated by benzoylperoxide and many other radical sources.[8] NBS is also very prone to photolysis on irradiation by visible light.[1] NBS has been used as a photoinitiator for the polymerization of methyl methacrylate.

We have reported the graft copolymerization of vinyl monomers onto some natural[9-11] and synthetic fibers[12-14] using thermal and photochemical methods. This note presents the result of the photo graft copolymerization of methyl methacrylate onto nylon-6 using NBS as photoinitiator.

EXPERIMENTAL

The purification of the monomer and nylon-6 fibers were carried out according to our previous procedure.[12,14] BDH analytical grade NBS was used without further purification as the photoinitiator. Since NBS is very prone to photolytic decomposition, it was stored in a container covered with a black paper and kept in a cooled and dry place. The method of graft copolymerization and extraction of homopolymer, etc. are similar to our previous procedure.[10-14]

RESULTS AND DISCUSSION

The photograft copolymerization of methyl methacrylate onto nylon-6 was investigated using NBS as photoinitiator. The percentage graft increases with time (Fig. 1). The rate of grafting was investigated by changing the monomer concentration from 0.1877 to 1.032 mol/L for a polymerization time of 6 h. The percentage of graft increases with increasing monomer concentration up to 0.75 mol/L and thereafter it decreases[9,10] (Fig. 2). The effect of initiator concentration on graft yield was investigated by changing initiator concentration (NBS) from 1×10^{-3} to 17×10^{-3} mol/L. The percentage graft increases with increasing initiator concentration up to 12.5×10^{-3} mol/L, and
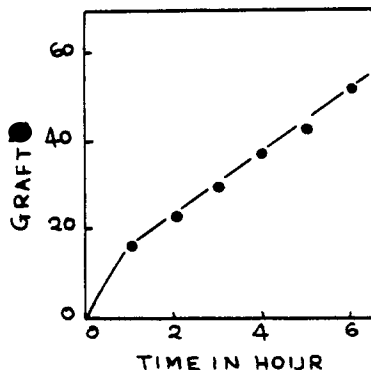

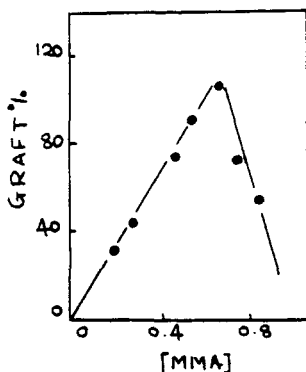Fig. 1. Time conversion: [NBS] = $5.0 \times 10^{-3}M$; [MMA] = $46.94 \times 10^{-2}M$; temp = 35°C; M:L = 1:100.

Fig. 2. Effect of [monomer] on graft %:   [NBS] = 12.50 × 10⁻³M; time = 6 h; temp = 35°C; M:L = 1:100.

thereafter it decreases[11] (Fig. 3).   The graft copolymerization was carried out at three different temperature ranging from 30°C to 40°C, keeping the concentrations of all other reagents constant. The perusal of the results indicate that the graft yield increases significantly with increase of temperature (Fig. 4).   From the Arrhenius plot (Fig. 5) the overall activation energy was computed to be 6.50 kcal/mol.   The values of R_p used in Figures 5 and 6 have been computed from Figures 2 and 3 below the monomer and initiator concentrations whose the drop in yields take place.   The poly-
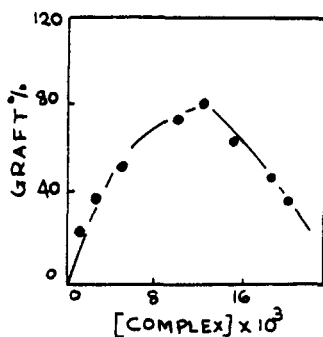

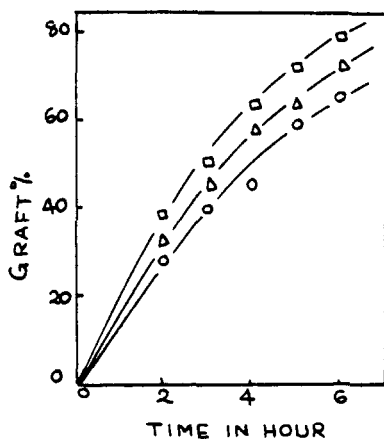Fig. 3. Effect of [NBS] on graft %:   [MMA] = 46.94 × 10⁻²M; time = 6 hr; temp = 35°C; M:L = 1:100.

Fig. 4. Effect of temperature on graft %:   [NBS] = 12.50 × 10⁻³M; [MMA] = 46.94 × 10⁻²M; M:L = 1:100; temp (°C):   (O) 30; (△) 35; (□) 40.
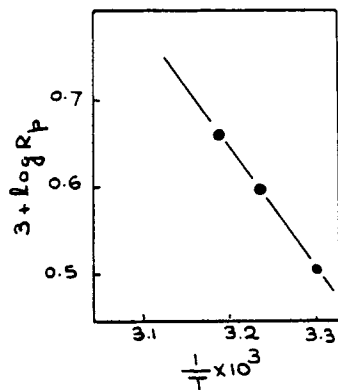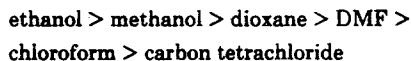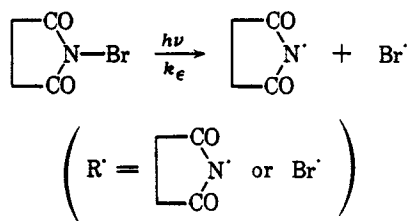
Fig. 5. Arrhenius plot.

merization reaction was also carried out in different solvent medium. The percentage graft follows the order:

ethanol > methanol > dioxane > DMF >
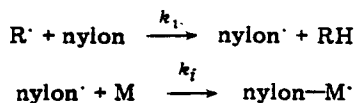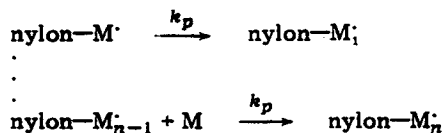
chloroform > carbon tetrachloride

MECHANISM

NBS is a well-known brominating agent for olefins, and, as has been discussed previously, the bromination takes via a radical chain mechanism and the rate of chain reaction is enhanced under-photosensitized conditions. The present study of the graft photo copolymerization of MMA with NBS initiation indicates a radical chain mechanism for graft copolymerization which is evident from kinetic data and from inhibition of polymerization by hydroquinone. Initiation of polymerization appears to take place by the mechanism outlined below:

Initiation:

$$R^{\cdot} + \text{nylon} \xrightarrow{k_1} \text{nylon}^{\cdot} + RH$$

$$\text{nylon}^{\cdot} + M \xrightarrow{k_i} \text{nylon—M}^{\cdot}$$

Propagation:

$$\text{nylon—M}^{\cdot} \xrightarrow{k_p} \text{nylon—M}_1^{\cdot}$$

$$\vdots$$

$$\text{nylon—M}_{n-1}^{\cdot} + M \xrightarrow{k_p} \text{nylon—M}_n^{\cdot}$$

Termination:

$$\text{nylon—M}_n^{\cdot} + \text{nylon—M}_m^{\cdot} \xrightarrow{k_t} \text{graft copolymer}$$

Here M represents the monomer. Applying steady state assumptions for the free radicals, the following rate expression could be derived for the rate of polymerization, R_p:
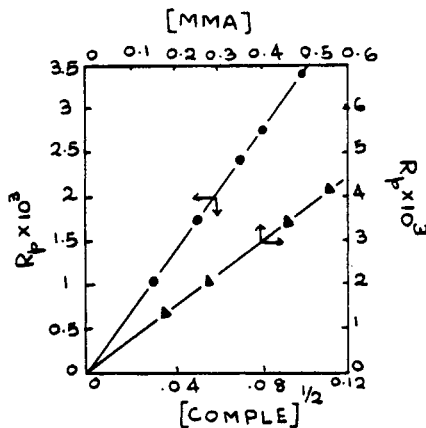
$$R_p = k_p (k_i/k_t)^{1/2} [\text{NBS}]^{1/2} [M]$$

Fig. 6. Plot of R_p vs. [MMA]. Plot of R_p vs. [NBS]$^{1/2}$.

The dependence of R_p on [M] and [NBS]$^{1/2}$ favors the above reaction scheme (Fig. 6).

The percentage of moisture regain was calculated. The perusal of the result indicates that with the increase of percentage of grafting the percentage of moisture regain decreases. The reduction in moisture regain after graft copolymerization suggests that the synthetic polymer chains act as diffusion barrier towards moisture penetration onto the nylon fibers.

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