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Photoinduced Graft Copolymerization. V. Graft Copolymerization of Methyl Methacrylate onto Cellulose in the Presence of N-Bromosuccinimide as Initiator

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ABSTRACT

The photoinduced graft copolymerization of methyl methacrylate onto cellulose was studied using N-bromosuccinimide as the photoinitiator. The formation of graft copolymer increases with an increasing amount of cellulose. The graft copolymerization increases with increasing initiator concentration up to 1.25×10^{-2} M and thereafter it decreases. The percentage of graft increases with increasing monomer concentration up to 46.9×10^{-2} M and thereafter it decreases. The percentage graft-on increases with increasing temperature. The overall activation energy was computed to be 8.40 kcal/mol. The percentage graft was investigated using different water-miscible organic solvents. The graft copolymerization was also investigated using differently modified cellulose. A possible mechanism for the photograft copolymerization onto cellulose is suggested.

INTRODUCTION

N-Bromosuccinimide (NBS) is a very good brominating agent for a number of olefinic aromatic, heterocyclic, and alicyclic compounds [1-8]. Bromination with NBS is highly selective. This compound has received wide attention for its capacity to introduce bromine into an allylic position. In 1955, Bloomfield [5] and Hey [6] suggested that NBS reacts via a radical chain mechanism. The rate of radical chain reaction was found to be enhanced by benzoyl peroxide and many other radical sources [8]. Walling [1] predicted that NBS is very prone to photolysis on irradiation by visible light. NBS has been used as a photoinitiator for the polymerization of vinyl monomers.

We have reported the graft copolymerization of vinyl monomers onto some natural and synthetic fibers using thermal and photochemical methods [9-13].

This communication presents the results of the photograft copolymerization of methyl methacrylate onto cellulose using NBS as photoinitiator.

EXPERIMENTAL

The purification of the monomer and cellulose fibers was carried out according to our previous procedure [9-13]. 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 cool, dry place. The methods of graft copolymerization and extraction of homopolymer etc. are similar to our previous procedure [9-13].

RESULTS AND DISCUSSION

The results of graft copolymerization on various amounts of cellulose are shown in Fig. 1. The formation of graft copolymer increases with an increase of the amount of cellulose and thereafter it decreases. These results seem to indicate that cellulose participates directly in the initiation of graft copolymerization. With an increase of the amount of cellulose, homopolymerization is facilitated, thereby decreasing the graft yield.

The photograft copolymerization of methyl methacrylate onto cellulose was investigated using NBS as the photoinitiator. The graft percentage increases with time (Fig. 2).

The effect of initiator concentration on graft yield was investigated by changing the initiator concentration up to 3×10^{-2} $\underline{M}$ (Fig. 3). The rate of grafting increases up to 1.25×10^{-2} $\underline{M}$ and thereafter it decreases. NBS initiated photopolymerization of MMA exhibited a

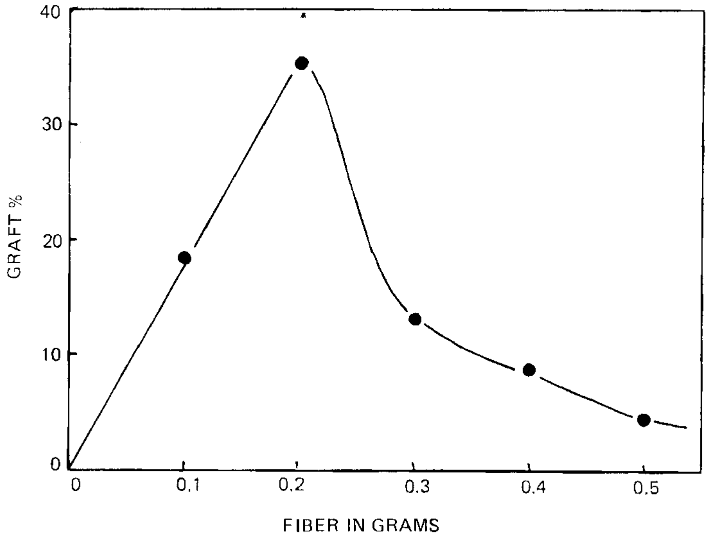


FIG. 1. Effect of fiber. [NBS] = 1.25×10^{-2} $\underline{M}$, [MMA] = 46.94×10^{-2} $\underline{M}$, time = 8 h, temperature = 35°C.

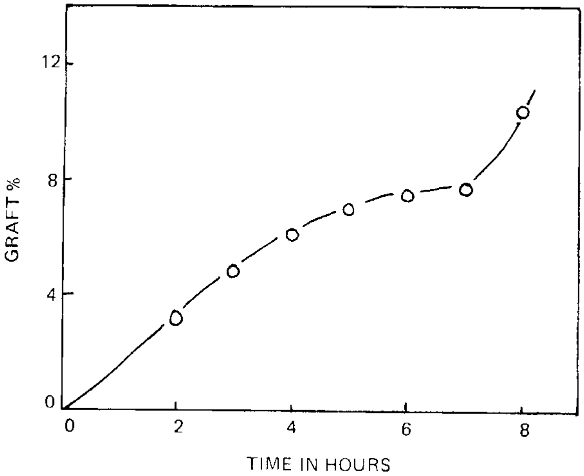


FIG. 2. Variation with time. [NBS] = 1×10^{-2} $\underline{M}$, [MMA] = 46.94×10^{-2} $\underline{M}$, M:L = 1:100, temperature = 35°C.

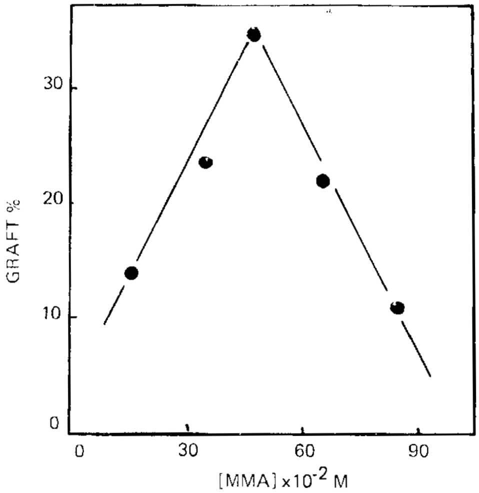


FIG. 3. Effect of monomer concentration. [NBS] = 1.25 × 10^{-2} M, time = 8 h, temperature = 35°C, M:L = 1:100.

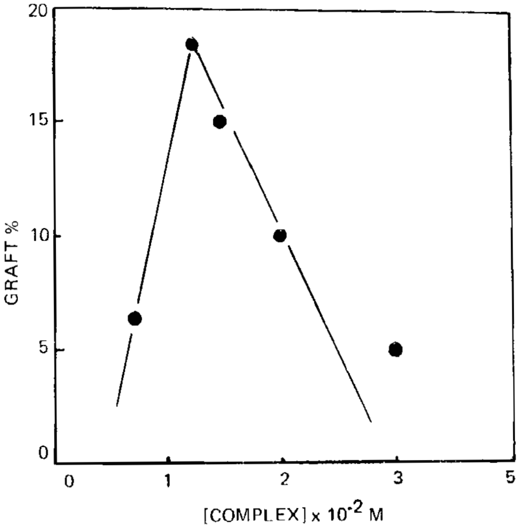


FIG. 4. Effect of initiator concentration. [MMA] = 46.94 × 10^{-2} M, time = 8 h, temperature = 35°C, M:L = 1:100.

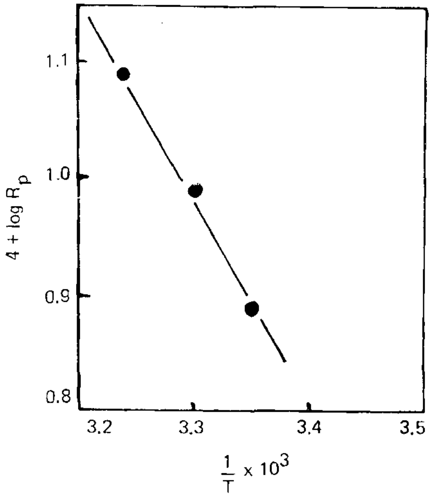


FIG. 5. Arrhenius plot of log R_p versus 1/T.

strong inhibition in the presence of a free radical inhibitor (hydroquinone), NBS is a well-known brominating agent, and bromination takes place via a radical chain mechanism. The rate of chain reaction is enhanced under photosensitized conditions. With an increase of NBS concentration, larger amounts of free radicals are formed, and this encourages homopolymer formation, thereby decreasing the graft yield.

The rate of grafting was investigated by changing the monomer concentration from 23.50 to 1.40 × 10^{-2} M (Fig. 4). The percentage of graft increases with increasing monomer concentration up to 46.9 × 10^{-2} M and thereafter it decreases. The decrease in graft yield at higher monomer concentrations can be explained by considering the fact that there is competition between combination and disproportionation of PMMA macroradicals in solution. When the concentration of PMMA macroradicals increases, the rate of their combination and disproportionation increases faster than their combination with cellulose molecule. On the other hand, the rate of monomer diffusion is progressively affected by the polymer deposit formed, which, of course, grows most rapidly when high concentrations of monomer are used. Similar observations have been noted by Haworth and Holker [14].

The graft copolymerization was carried out at three different temperatures ranging from 25 to 35°C, keeping the concentrations of all other reagents constant. Perusal of the results indicates that the graft yield increases significantly with an increase of temperature. From the Arrhenius plot of log R_p versus 1/T (Fig. 5), the overall activation energy was computed to be 8.40 kcal/mol.

TABLE 1. Variation of Percentage of Grafting with Different Solvents[a]

Solvents	Graft percentage
Control	18.5
Formic acid	31.3
Acetic acid	26.5
Methanol	26
DMF	46.5

[a] [NBS] = 1.25×10^{-2} M, [MMA] = 46.94×10^{-2} M, time = 8 h, temperature = 35°C, [solvent] = 50×10^{-2} M.

The results of photoinduced graft copolymerization of MMA on various cellulose samples are shown in Table 1. Though there were appreciable differences among polymerization characteristic of the samples, the percentage of grafting was increased markedly by the swelling of the samples in general. This tendency may be ascribed to the higher reactivity of the swollen samples because of the increased ease of diffusion of the monomer into the samples. A perusal of the results indicates that the percentage of graft copolymerization is almost doubled at 25 vol% of each organic solvent. Thus it is clear that the swelling of the sample contributes effectively to the graft copolymerization in cooperation with the organic solvent. Among the solvents studied, DMF was found to be the most effective solvent. Any one of the solvents studied made the initiation of polymerization impossible at 100% concentration, and this fact suggests that the organic solvents themselves inhibit the photoinduced reactions. Reine et al. [14] and Ogiwara et al. [15] have reported that cellulose radicals are captured by solvents when γ-irradiated celluloses are dipped in solvents such as MeOH, DMF, and acetone, and this tendency is related to the ability of these solvents to penetrate into fiber structures. All organic solvents used in the present investigation are capable of dissolving MMA. Therefore, it is reasonable to suppose that the increase in monomer solubility in the organic solvent-water solutions stimulates the monomer supply for the growing radicals and therefore increases the percentage of grafting.

The cellulose was subjected to different modifications prior to grafting. The percentage graft follows the order: NaOH-treated cell > native > cyanoethylated cell > cross-linked cell > oxidized cell.

The graft yield for sodium hydroxide cellulose is substantially higher than that for native cellulose. This is expected since sodium hydroxide cellulose has a greater accessibility than native cellulose.

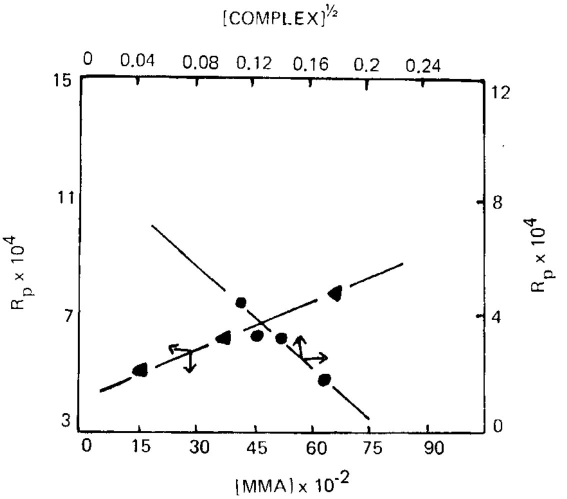


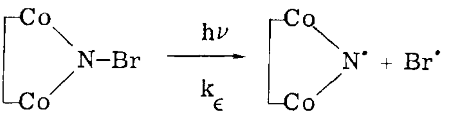
FIG. 6. Plot of R_p versus [M] and R_p versus [complex]$^{1/2}$

The percentage of graft yield is lower in cyanoethylated than in native cellulose.

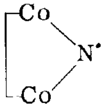
It is noteworthy to point out that cross-linking of cellulose decreases the extent of grafting. This is because cross-linking adversely affects diffusion of monomer and initiator, and it also reduces the number of the grafting sites on the cellulose backbone, thereby lowering the graft yield. When cellulose is oxidized, the oxidizing agent attacks the 1,2 glycol units, converting them to aldehyde groups. This destroys the grafting sites and consequently the graft yield decreases.

Mechanism

NBS is a well-known brominating agent for olefins. Bromination takes place via a radical chain mechanism. The rate of chain reaction is enhanced by photosensitizer conditions. The present study of the photoinduced graft copolymerization of MMA by NBS initiation indicates a radical chain mechanism for graft copolymerization which is evident from the kinetic data and from the inhibition of polymerization by hydroquinone. Initiation of polymerization appears to take place by the mechanism outlined below.



where

$R^{\bullet}$ =

or $Br^{\bullet}$

Initiation:

$$R^{\bullet} + \text{cellulose} \xrightarrow{k_1} \text{cellulose}^{\bullet}$$

$$\text{Cellulose}^{\bullet} + M \xrightarrow{k_i} \text{cellulose–}M^{\bullet}$$

Propagation:

$$\text{Cellulose–}M^{\bullet} + M \xrightarrow{k_p} \text{cellulose–}M_1{}^{\bullet}$$

$$\text{Cellulose–}M^{\bullet}_{n-1} + M \xrightarrow{k_p} \text{cellulose–}M_n{}^{\bullet}$$

Termination:

$$\text{Cellulose–}M_n{}^{\bullet} + \text{cellulose–}M_m{}^{\bullet} \xrightarrow{k_t} \text{graft copolymer}$$

$$R_p = k_p \left(\frac{k_{\epsilon}}{k_t}\right)^{1/2} [\text{NBS}]^{1/2}[M]$$

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

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