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Adwait K. Pradhan[a]; Nrusingha C. Pati[a]; Padma L. Nayak[a]
[a] Laboratory of Polymers and Fibers Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

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Grafting Vinyl Monomers onto Cellulose. VIII. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using H_2O_2-Cysteine Redox System

ADWAIT K. PRADHAN, NRUSINGHA C. PATI, and PADMA L. NAYAK

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

ABSTRACT

The application of the H_2O_2-cysteine redox system to induce graft copolymerization of methyl methacrylate onto cellulose was investigated under various conditions. The rate of grafting was determined by varying the concentrations of monomer, initiator, cysteine, acid, and temperature. The effect of some solvents was studied and a suitable reaction mechanism has been proposed.

INTRODUCTION

Literature survey reveals that graft copolymerization onto cellulose has been extensively studied by several group of workers [1-22], but there is no report regarding the use of the hydrogen peroxide-cysteine redox system for grafting vinyl monomers onto cellulose. Nayak and co-workers [23, 24] have reported the use of hydrogen peroxide-thiourea and hydrogen peroxide-sodium thiosulfate redox systems as initiators for graft copolymerization onto silk fibers.

In the present investigation the authors report the use of the hydrogen peroxide-cysteine redox system as initiator for graft copolymerization of methyl methacrylate onto cellulose.

EXPERIMENTAL

Egyptian cotton slivers were purified by a mild alkaline scouring (2% Na_2CO_3, 1.0% Na_3PO_4 and 0.2% wetting agent on weight of the material) for 5 h at 110°C.

Methyl methacrylate was washed with 5% NaOH solution, dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Hydrogen peroxide (30% w/v, BDH) and cysteine hydrochloride (Eastman Kodak), H_2SO_4 (~18 M, AR, BDH) were used. Water distilled twice over alkaline permanganate and deionized by passing through a Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. A stock solution of hydrogen peroxide (0.08 M) in distilled water was used throughout the experiment. The concentration of H_2O_2 in the experimental system was determined by titration with permanganate.

The reaction was carried out according to our previous methods [17].

RESULTS AND DISCUSSION

Figure 1 shows the effect of different monomer concentrations on the rate of grafting. The percentage of graft yield increases steadily with the increase of monomer concentration from (14.694 to 70.41) $\times 10^{-2}$ M. Similar results have been reported by Nayak and coworkers [17] in the case of grafting methyl methacrylate onto cellulose using quinquevalent vanadium ion as the initiator.

Figure 2 describes the effect of different initiator concentrations on graft yield. The percentage of grafting increases from (3.95 to 11.85) $\times 10^{-2}$ M after which it decreases. A probable explanation for these observations could be as follows.

In a system consisting of hydrogen peroxide, cysteine, sulfuric acid, monomer, and cellulose, the free radical formation might take place as represented below.

Haber and Weiss [25] have reported that hydrogen peroxide could be activated by the presence of reducing agents. Thus the formation of OH is facilitated by the presence of cysteine owing to one electron transfer with concomitant cleavage of the O–O bond.

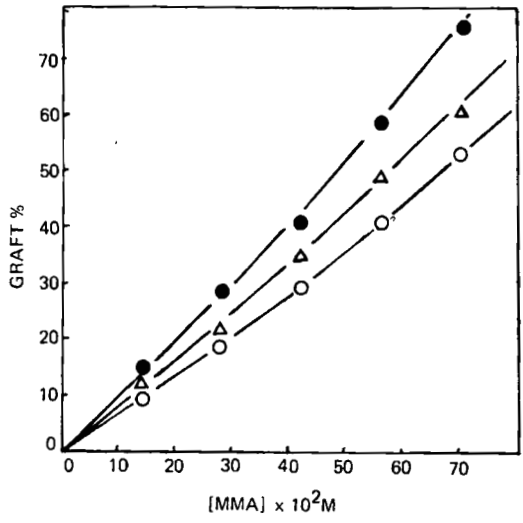


FIG. 1. Effect of monomer concentration on graft yield: [Cy] = 2.5×10^{-3} M; [H_2SO_4] = 3.0×10^{-2} M. Temperature = 50°C, time = 3 h, M:L = 1:100. (●) [H_2O_2] = 7.9×10^{-2} M. (△) [H_2O_2] = 15.8×10^{-2} M. (○) [H_2O_2] = 23.7×10^{-2} M.

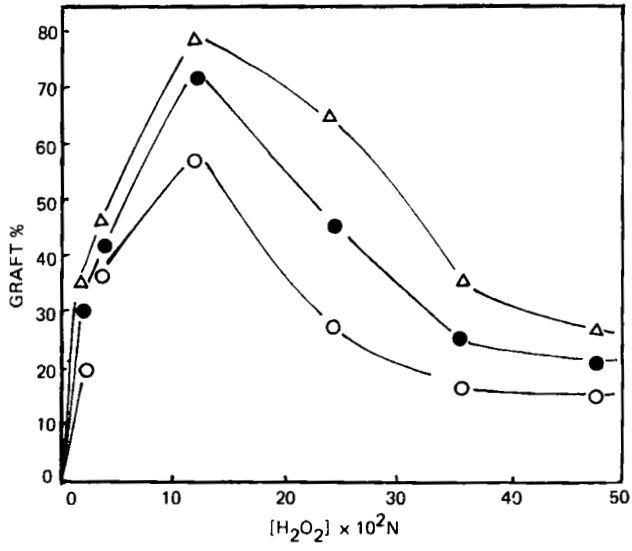
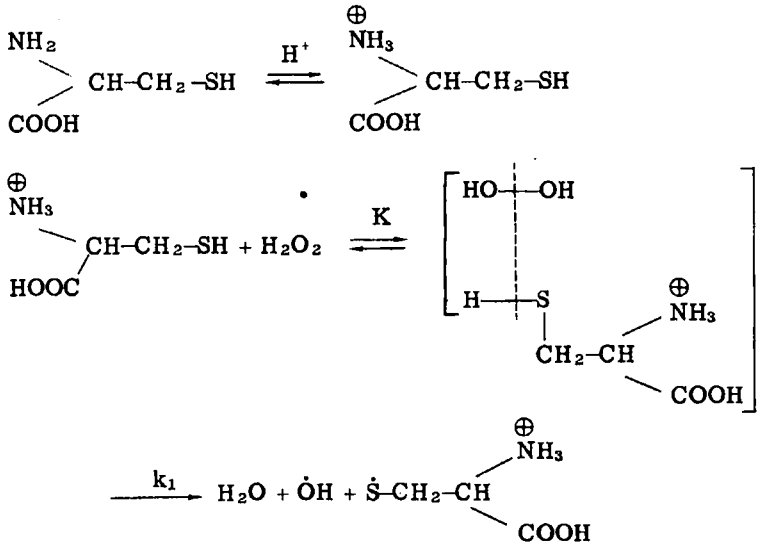


FIG. 2. Effect of [H_2O_2] on graft yield: [Cy] = 2.5×10^{-3} M; [H_2SO_4] = 3.0×10^{-2} M. Temperature = 50°C, time = 3 h, M:L = 1:100. (○) [MMA] = 46.94×10^{-2} M. (●) [MMA] = 70.41×10^{-2} M. (△) [MMA] = 93.88×10^{-2} M.



The above free radicals (ȮH or Ṡ–CH_2–CH(⊕NH_3)COOH = R·) interact with the cellulose molecule to produce cellulose macroradicals (Cell·) which initiate the graft copolymerization reaction:

$$\text{Cell—H} + \text{R}^{\cdot} \xrightarrow{k_d} \text{Cell}^{\cdot} + \text{RH}$$

Initiation:

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

Propagation:

$$\text{Cell—M}^{\cdot} + \text{M} \xrightarrow{k_p} \text{Cell—M}_2^{\cdot}$$

$$\vdots$$

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

Termination:

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

Applying the steady-state assumptions to $[R^{\bullet}]$, $[Cell^{\bullet}]$, and $[Cell\text{–}M_n^{\bullet}]$, the following expressions could be derived:

$$\frac{d[R^{\bullet}]}{dt} = Kk_1[Cy][H_2O_2] - k_d[Cell\text{–}H][R^{\bullet}] = 0$$

$$[R^{\bullet}] = \frac{Kk_1[Cy][H_2O_2]}{k_d[Cell\text{–}H]}$$

$$\frac{d[Cell\text{–}M_n^{\bullet}]}{dt} = k_1[Cell^{\bullet}][M] - k_t[Cell\text{–}M_n]^2 = 0$$

$$[Cell\text{–}M_n^{\bullet}] = \left\{\frac{k_i[Cell^{\bullet}][M]}{k_t}\right\}^{1/2}$$

Again

$$\frac{d[Cell^{\bullet}]}{dt} = k_d[Cell\text{–}H][R^{\bullet}] - k_i[Cell^{\bullet}][M] = 0$$

Therefore

$$[Cell^{\bullet}] = \frac{k_d[Cell\text{–}H][R^{\bullet}]}{k_i[M]}$$

Substituting the value of $[R^{\bullet}]$ in the above equation, we get

$$[Cell^{\bullet}] = \frac{Kk_1[Cy][H_2O_2]}{k_i[M]}$$

$$[Cell\text{–}M_n^{\bullet}] = \left\{\frac{Kk_1}{k_t}[Cy][H_2O_2]\right\}^{1/2}$$

$$R_p = k_p[\text{Cell-}M_n^{\cdot}][M]$$

$$= \frac{k_p K^{1/2} k_1^{1/2}}{k_t^{1/2}} [Cy]^{1/2}[H_2O_2]^{1/2}[M]$$

Thus the plots of R_p versus $[M]$ (Fig. 3) and R_p versus $[H_2O_2]^{1/2}$ (Fig. 4) favor the above reaction scheme.

The initial increase in graft yield with the increase of hydrogen peroxide concentration might be due to the formation of a large number of free radicals ($R^{\cdot}$) which initiate grafting.

However, the decrease in graft yield beyond 11.85×10^{-4} M of hydrogen peroxide concentration could be attributed to 1) the abundance of free radicals in the solution at higher initiator concentration which might terminate the growing chain, 2) the production of more homopolymer, and 3) the oxidation of free radicals produced at the backbone of the fiber at higher initiator concentration.

The graft copolymerization reaction has been carried out at different sulfuric acid concentrations from $(1.5 \text{ to } 15.5) \times 10^{-2}$ M. The result indicates that the graft yield increases from 1.5×10^{-2} to 7.5×10^{-2} M and then decreases (Fig. 5). The increase in the graft yield with acid concentration may be due to the increase in the oxidizing capacity of the initiator at higher acid concentration.

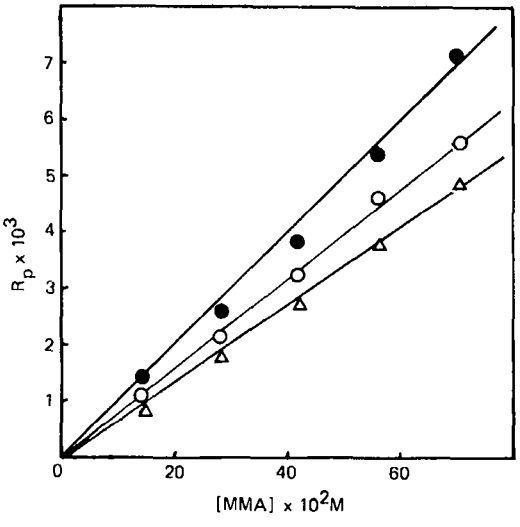


FIG. 3. Plot of R_p vs $[M]$.

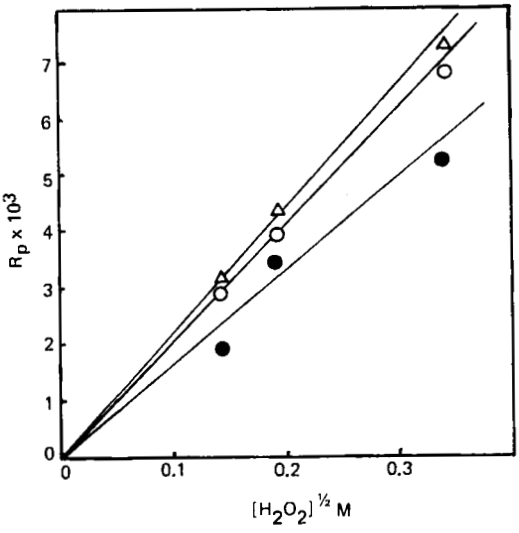


FIG. 4. Plot of R_p vs $[H_2O_2]^{1/2}$.

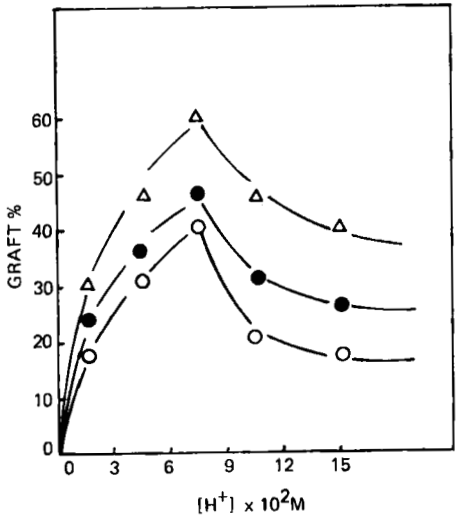


FIG. 5. Effect of acid concentration on graft yield: $[H_2O_2] = 19.7 \times 10^{-2}$ M; [Cy] = 2.5×10^{-3} M. Temperature 50°C, time = 3 h, M:L = 1:100. (○) [MMA] = 28.16×10^{-2} M. (●) [MMA] = 46.94×10^{-2} M. (△) [MMA] = 70.41×10^{-2} M.

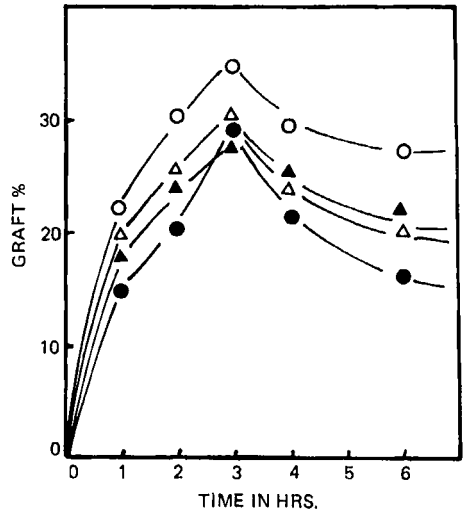


FIG. 6. Effect of temperature on graft yield: $[H_2O_2] = 19.7 \times 10^{-2}$ M; $[Cy] = 2.5 \times 10^{-3}$ M; $[H_2SO_4] = 3.0 \times 10^{-2}$ M; $[MMA] = 46.94 \times 10^{-2}$ M. M:L = 1:100. Temperatures: 40°C (●) 45°C (△), 50°C (○), 60°C (▲).

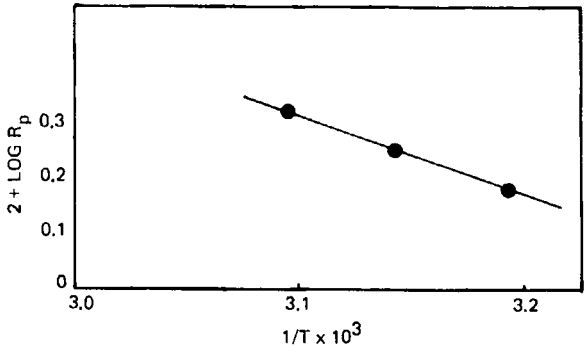


FIG. 7. Plot of log R_p vs 1/T.

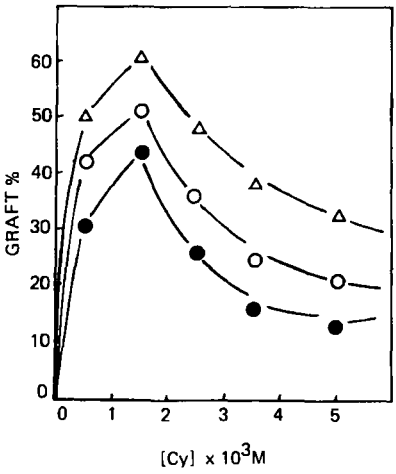


FIG. 8. Effect of [Cy] on graft yield: $[H_2O_2] = 23.7 \times 10^{-2}$ M; $[H_2SO_4] = 4.5 \times 10^{-2}$ M. Temperature = 50°C, time = 3 h, M:L = 1:100. (●) [MMA] = 28.16×10^{-2} M. (○) [MMA] = 46.94×10^{-2} M. (△) = 70.41×10^{-2} M.

The fall in graft yield beyond 7.5×10^{-2} M of sulfuric acid may be due to the coagulation of colloidal homopolymer in solution and within fibers which increase during the process of grafting. This retards the diffusion of both monomer and initiator into the fiber matrix for grafting to occur.

The graft copolymerization reaction is greatly influenced by increasing temperature (Fig. 6). The graft yield increases up to 50°C and then decreases. The decrease in graft yield beyond 50°C might be due to the greater possibility of combination rates of radicals.

From the Arrhenius plot of log R_p versus 1/T (Fig. 7), the overall activation energy was computed to be 7.0 kcal/mol. Using the value of $E_p - \frac{1}{2}E_t = 4 \sim 5$ kcal/mol given by Tobolsky [26], the activation energy of initiation E_d was calculated to be 5.0 kcal/mol from the relationship

$$E_d = 2E_a - (2E_p - E_t)$$

where E_p and E_t are energies of propagation and termination, respectively.

The effect of cysteine concentration was studied at fixed concentration of initiator, acid, and temperature (Fig. 8). The graft percentage

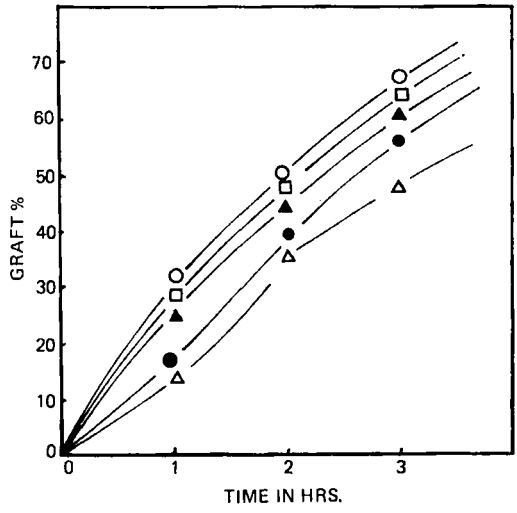
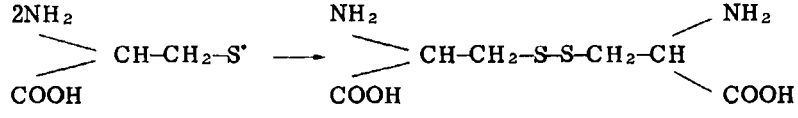


FIG. 9. Effect of solvents on graft yield: $[H_2O_2] = 15.8 \times 10^{-2}$ M; $[Cy] = 2.0 \times 10^{-3}$ M; $[H_2SO_4] = 4.5 \times 10^{-2}$ M; $[MMA] = 46.94 \times 10^{-2}$ M. Solvents = 10% v/v, temperature = 50°C, M:L = 1:100. (△) Solvent = acetone. (▲) Solvent = acetic acid. (●) Solvent = dimethylformamide. (□) Control. (○) Solvent = methanol.

increases up to 15.0×10^{-4} M and then decreases with a further increase of cysteine concentration. The decrease in graft yield beyond 15.0×10^{-4} M of cysteine concentration might be due to 1) the decrease in the concentration of cysteine radicals due to the formation of cysteine molecule:



2) the formation of more homopolymer, and 3) the formation of some species which might act as radical scavengers.

The graft copolymerization was also studied in the presence of different solvents. The graft yield follows the order (Fig. 9) methanol > control > acetic acid > dimethylformamide > acetone.

The dependence of graft yield on the nature of the solvents might be due to 1) the difference in ability of swelling cellulose molecules and 2) the difference in the capability of terminating the graft radicals as well as cellulose macroradicals via chain transfer.

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