

Photo-Induced Graft Copolymerization. III. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using Peroxydiphosphate as Photoinitiator

SUBASINI LENKA and PADMA L. NAYAK, *Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India.*

Synopsis

Photo-induced graft copolymerization of methyl methacrylate onto cellulose was investigated using peroxydiphosphate ion as the photoinitiator. The percentage graft yield increases with increasing both the monomer and initiator concentration. The reaction was carried out at three different temperatures, and the overall activation energy was computed. The kinetic data and other evidence indicate that the overall polymerization takes place by a radical mechanism. A suitable kinetic scheme has been suggested.

INTRODUCTION

During the last several years Nayak and co-workers have reported the graft copolymerization of a multitude of natural and synthetic fibers using a number of transitional metal ions.¹⁻³ The use of ultraviolet light for initiation of graft copolymerization is well known and numerous studies have been carried out on this subject with the use of various polymers as the base material. A number of anthraquinone,⁴ riboflavin,⁵ and other dyes have been used as photosensitizers for grafting vinyl monomers onto cellulose. Ogiwara and Kubota have reported that the ultraviolet light has a high accelerating effect on graft copolymerization of methyl methacrylate onto cellulose initiated by hydrogen peroxide⁶ or ceric ion.^{7,8} It has been observed that, in the absence of a sensitizer, a certain induction period was noticed.

Recently, we have reported the graft copolymerization onto cellulose,⁹ wool,¹⁰ silk,^{11,12} and nylon¹³ fibers using peroxydiphosphate as the initiator.

This communication presents the results of photo-induced graft copolymerization of methyl methacrylate onto cellulose using peroxydiphosphate as the photoinitiator.

EXPERIMENTAL

Egyptian cotton slivers were purified by our previous procedure.¹⁻³ Sodium hydroxide treated cotton (NaOH—cotton) was prepared by treating the purified cotton slivers with aqueous sodium hydroxide (12*N*) at room temperature for 1 h followed by washing and drying in air at room temperature. Cyanoethylated cotton was prepared by impregnating it with 0.5*N* sodium hydroxide for 1 h followed by padding to a pick up of about 100%. At this point, the sample was treated with acrylonitrile at 60°C for varying lengths of time. Finally, the sample

was scoured with dilute acetic acid, washed thoroughly with water, and dried at ambient condition. The crosslinked cellulose was prepared by immersing and wetting out it in a solution containing specified concentrations of formaldehyde and 2% ammonium chloride. Excess solution was removed by squeezing the materials to a wet pickup of 90–95%. The samples were dried at 60°C for 7 min and then heated in an oven at 120°C for 5 min.

Potassium peroxydiphosphate (PP, $K_4P_2O_8$) was obtained as a gift sample from F.M.C. Corp., U.S.A. All reagents used were of AR grade.

The graft copolymerization was carried out by adding the required amount of initiator, cellulose, and other additives, flushing with purified nitrogen gas, stoppering, and placing in a thermostat at the required temperatures. 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. Grafting does not occur in the absence of UV light, which is evident from various control experiments.

RESULTS AND DISCUSSION

The photo-graft copolymerization of methyl methacrylate onto cellulose fiber was investigated using peroxydiphosphate as photoinitiator. Figure 1 shows the change of graft percentage with time.

Figure 2 shows the results of graft yield, when monomer concentration is varied from $23.47 \times 10^{-2}M$ to $117.35 \times 10^{-2}M$ at different peroxydiphosphate concentrations (0.005M, 0.01M). The perusal of the result indicates that with increasing monomer concentration the graft yield progressively increases. The plot of R_p vs. [monomer] is linear (Fig. 3) with unity slope indicating the order with respect to monomer to be 1.

The effect of initiator concentration on graft yield was investigated by changing the initiator concentration from 0.005M to 0.025M at different monomer concentrations ($23.47 \times 10^{-2}M$, $46.94 \times 10^{-2}M$). The percentage graft yield increases progressively with increasing initiator concentration (Fig. 4).

The effect of temperature on graft yield was investigated within the temperature range of 30–40°C. With increasing temperature the graft yield increases. This is expected since increasing the temperature would favorably influence the swellability of cellulose, the solubility of monomer diffusion of both monomer

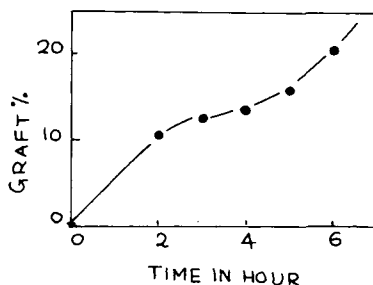


Fig. 1. Percentage conversion with time: $[PP] = 0.01M$; $[H^+] = 0.15M$; $[MMA] = 46.94 \times 10^{-2}M$; temp = 30°C; M:L = 1:100.

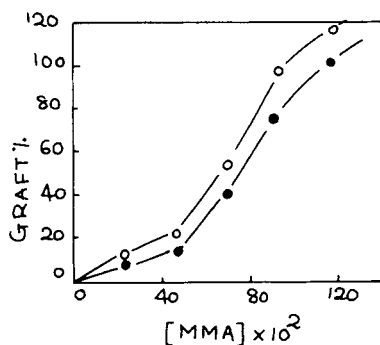


Fig. 2. Effect of [MMA] on graft yield: $[H^+] = 0.15M$; time = 6 h; temp = $30^\circ C$; M:L = 1:100; (●) $[PP] = 0.005M$; (○) $[PP] = 0.01M$.

and initiator, the rate of PP decomposition, and the initiation and propagation process of the graft formation. The net effect of all these parameters leads to higher grafting. From the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 5), the overall activation energy was computed to be 18.4 kcal/mol.

Since peroxydiphosphate ion is catalyzed by acid, it is necessary to study the effect of acid concentration on graft yield. The acid concentration was varied from 0.03M to 0.3M at different monomer concentrations. The graft yield was found to be increased with sulphuric acid concentration up to 0.15M, after which it decreases with further increase of acid concentration (Fig. 6).

The reaction of peroxydiphosphate which is both a peroxide and oxyanion, i.e., oxyanion derivative of $H-O-O-H$ are acid-catalyzed. Due to high neg-

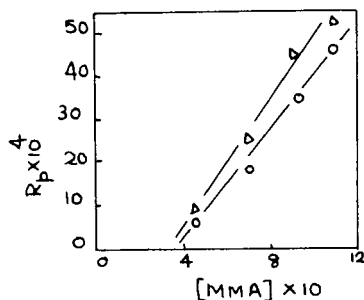


Fig. 3. Plot of R_p vs. [MMA]: (○) $[PP] = 0.005M$; (Δ) $[PP] = 0.01M$.

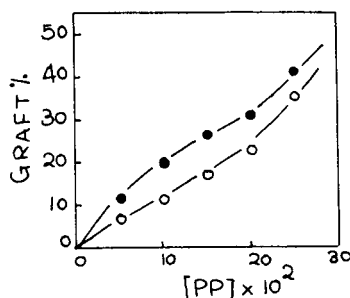


Fig. 4. Effect of [PP] on graft yield: $[H^+] = 0.01M$; time = 6 h; temp = $30^\circ C$; M:L = 1:100; (○) $[MMA] = 23.47 \times 10^{-2}M$; (●) $[MMA] = 46.94 \times 10^{-2}M$.

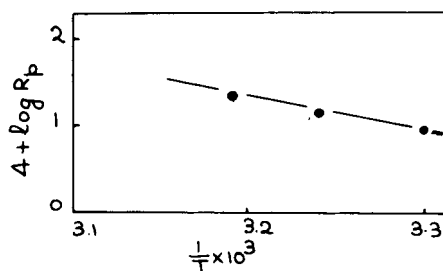


Fig. 5. Arrhenius plot of $\log R_p$ vs. $1/T$.

ative charge, PP is protonated giving rise to various species like $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^-$, $H_4P_2O_8$, $H_5P_2O_8^+$, $H_6P_2O_8^{2+}$. Maruthamuthu and Santappa^{14,15} have reported that the reaction rate as well as the concentration of $H_3P_2O_8^-$ and $H_4P_2O_8$ increases with increasing acid concentration. In the lower acid concentration range, probably the most active species, $H_3P_2O_8^-$, might be formed, which interacts with various other species, giving rise to a large number of free radicals, thus enhancing the graft yield.

The graft copolymerization of MMA onto cellulose was studied in the presence of different water-miscible solvents. From the graft yield obtained the order of different solvents is as follows:

formic acid > methanol > acetic acid > ethanol

The variation of the graft yield with the solvents depends on ability of swelling the fiber, miscibility with monomer, formation of the solvent radicals from the primary radical species by chain transfer, participation of the solvent radical in the activation of fiber and termination of the graft radical by combination with solvent radical.

The cellulose was subjected to different modifications prior to grafting. The percentage graft follows the sequence:

unmodified > NaOH—cell > cyanoethylated-cell > crosslinked-cell

The same observation was noticed by Nayak et al.³ while grafting methyl methacrylate onto modified cellulose using peroxydiphosphate as the initiator by thermal method.

The average molecular weight \bar{M}_w and degree of polymerization of the grafted poly(methyl methacrylate) was determined by using the relationship

$$[\eta] = 9.6 \times 10^{-5} \bar{M}_w^{0.69}$$

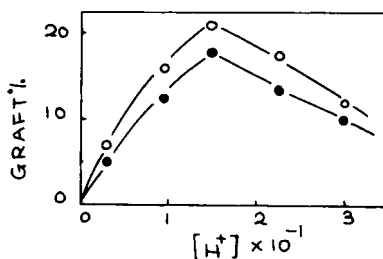


Fig. 6. Effect of [acid] on graft yield: [PP] = 0.01M; time = 6 h; temp = 30°C; M:L = 1:100; (●) [MMA] = $28.16 \times 10^{-2}M$; (O) [MMA] = $46.94 \times 10^{-2}M$.

TABLE I

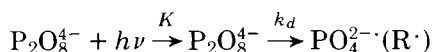
Graft (%)	$\bar{M}_w \times 10^{-5}$	$D\bar{P} \times 10^{-3}$
10.00	5.12	5.12
20.00	5.38	5.38
55.00	6.97	6.97
98.00	7.12	7.12

The perusal of the result (Table I) indicates that the average molecular weight as well as the degree of polymerization increases with increasing graft-on percentage. This might be due to mutual termination.

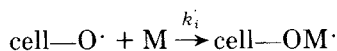
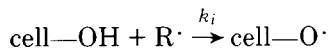
The percentage of moisture regain was calculated. The perusal of the result indicates that, with the increase of the percentage of grafting, the percentage of moisture regain decreases. The reduction in moisture regain after graft copolymerization suggests that the synthetic polymer chains act as diffusion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

Mechanism

When PP molecules are subjected to incident light, they decompose to yield the phosphate ion radical ($\text{PO}_4^{2\cdot-}$). These phosphate ion radicals might interact with the hydroxyl groups present in the cellulose backbone, producing cellulose macroradicals, which initiates grafting. The reaction scheme is presented below:

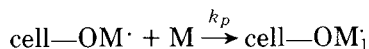


Initiation:

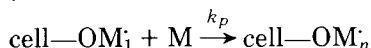


(cell-OH = cellulose, cell-O \cdot , and cell-OM \cdot = cellulose radicals)

Propagation:



⋮



Termination:



Applying steady state assumptions, the rate of polymerization R_p may be expressed as

$$R_p = k_p(k_i/k_t)^{1/2}[\text{cell-OH}]^{1/2}[\text{M}]$$

The plot of R_p vs. $[\text{M}]$ is linear, which satisfies the above reaction scheme.

This project is financed by CSIR, New Delhi, India by Project No. 2 (135)/79-EMR-II. One of the authors, S. Lenka, thanks CSIR for the award of Research Associateship.

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Received October 16, 1981

Accepted April 5, 1982