# Photoinitiated Graft Copolymerization of Hydroxyethyl Methacrylate onto Cotton Cellulose

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**SYNOPSIS**

The photoinitiated graft copolymerization of hydroxyethyl methacrylate (HEMA) onto cotton cellulose was studied using uranyl nitrate (UN) and ceric ammonium nitrate (CAN) photoinitiators. Optimization of various parameters of the graft-copolymerization reaction viz., time, temperature, initiator, and monomer concentration, was carried out. The optimized conditions of grafting were employed to cotton samples swollen in zinc chloride as well as sodium hydroxide. Graft add-on was found to be dependent on the nature of substrate and the concentrations of monomer and photoinitiator. UN was found to be the better photoinitiator, giving higher grafting with HEMA. The grafted samples showed initially decrease and then marginal increase in the moisture regain with increase in graft add-on. The dye uptake of both direct and reactive dyes decreased with increase in graft add-on.

## INTRODUCTION

Graft copolymerization of vinyl monomers onto cotton and analogous polysaccharides has been widely investigated. Grafting possesses great potential for tailoring the material properties to specific end uses. The use of ultraviolet light for the initiation of graft copolymerization is well known and there are several reports on photoinitiated grafting of cellulose with the use of photoinitiators such as dyes,[1] metal ions,[2] hydrogen peroxide,[3] etc.

HEMA has been grafted onto regenerated cellulose film using a series of water-soluble photoinitiators based on benzophenone and benzil chromophores.[4] Da Silva et al.[5] studied the photoinitiated grafting of acrylamide and HEMA onto cellulose substrates from the acetone/water solutions using isopropyl thioxanthane photoinitiator. The use of various organic solvents during radiation-induced graft copolymerization has been found to accelerate the diffusion of monomer into the substrate and enhance the graft add-on.[6,7]

In the present paper, the results on the photoinitiated graft copolymerization of HEMA onto cotton cellulose using uranyl nitrate and ceric ammonium nitrate as photoinitiators in aqueous medium have been reported. The effect of swelling of cotton on the graft add-on was also studied by using inorganic swelling agents such as sodium hydroxide and zinc chloride under optimum conditions. Determination of moisture regain and dyeability with direct and reactive dyestuffs was carried out to see the effect of grafting of this —OH-containing hydrophilic monomer on the properties of cotton.

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## EXPERIMENTAL

### Materials

#### Substrate

The scoured and bleached 30 count cotton yarn was used as cellulose sample. The swollen samples of cotton were prepared by using 24% (w/w) sodium hydroxide and 70% (w/w) zinc chloride at 20°C for 1 h each, followed by water-washing, and drying in air at room temperature.

#### Dyes

A direct dye, C. I. Direct Blue 86 and a reactive dye, C. I. Reactive Red 31 were used for dyeing the grafted cotton.

### *Chemicals*

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Co. was vacuum-distilled to make it free from the inhibitors. Uranyl nitrate (UN) and ceric ammonium nitrate (CAN) were the two photoinitiators used.

### Graft Copolymerization

The cellulose samples to be grafted were weighed to 1 g and immersed in 100 mL aqueous bath containing monomer and photoinitiator in a quartz conical flask. A Philips HPW 125 W mercury lamp was used as a source of UV radiation. The temperature range of 30–55°C was used and the reaction temperature was controlled by using a glycerine bath. The quartz flasks were irradiated for different time intervals varying from 1 to 6 h in an enclosed chamber containing a UV lamp. Afterwards, the irradiated samples were removed, washed with methanol, dried, and then extracted with boiling methanol–water (50 : 50) for 7 h each for three times to remove the homopolymer formed. After each extraction, the samples were washed with methanol and then with water followed by air-drying. The graft add-on was determined gravimetrically by weighing the samples before and after grafting.

The relations used were

$$\text{graft add-on (\%)} = \frac{w_2 - w_1}{w_1} \times 100$$

$$\text{graft yield (\%)} = \frac{w_2 - w_1}{w_3} \times 100$$

where $w_1$ = weight of the original control sample, $w_2$ = weight of the grafted sample, and $w_3$ = weight of the monomer taken initially for grafting reaction.

### Moisture Regain

The moisture regain of control and grafted cotton was determined by the oven-drying method.[8]

### Dyeing with Direct Dye

The grafted cotton samples were dyed with a direct dye, C. I. Direct Blue 86, at boil for 2% shade using 20% Glauber's salt as the exhausting agent. The total time of dyeing was kept at 1 h and the liquor ratio 50. The dye bath exhaustion values were calculated from the amount of dye remaining in the bath after dyeing by measuring the optical density of the dye solution.

### Dyeing with Reactive Dye

The dyeing with a reactive dye, C. I. Reactive Red 31, was carried out at about 80°C for 2% shade using 20 g/L Glauber's salt as exhausting agent and 15 g/L trisodium phosphate as alkali for reacting the dye to cellulose. The total time of dyeing was kept 1 h and the liquor ratio 50. The dyebath exhaustion values were calculated as in the case of dyeing with direct dye.

## RESULTS AND DISCUSSION

### Effect of Photoinitiator Concentration

The effect of photoinitiator concentration on the grafting of HEMA onto cotton cellulose was studied by varying the concentration in the range of 0.10 to 0.30% (w/v) for the two initiators, namely, UN and CAN. Figure 1 shows the changes in percent graft add-on with increase in the initiator concentration. The graft add-on increased with the initiator concentration giving the maximum value of 12.60% at 0.20% (w/v) UN and 11.26% at 0.25% (w/v) CAN. However, beyond these specific concentrations, further increase in the initiator concentrations brought about a decrease in the graft add-on. This phenomenon was ascribed to the fast termination of growing polymer chains owing to the presence of excess pho-

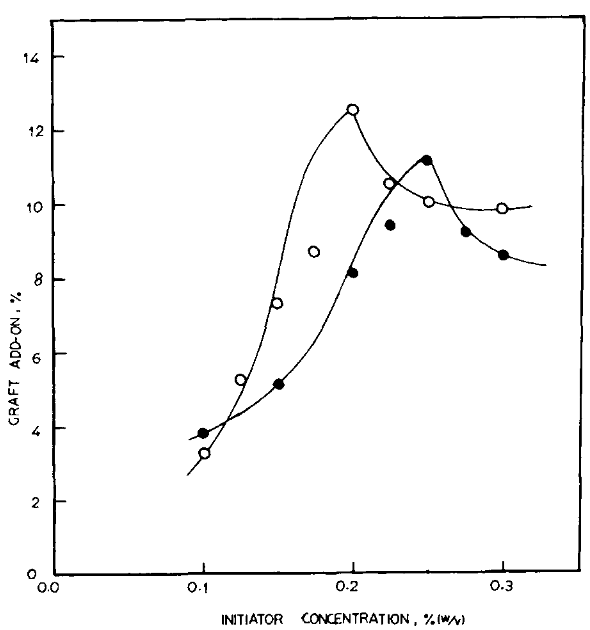


**Figure 1** Relation between initiator concentration and graft add-on: (○) UN photoinitiator; (●) CAN photoinitiator.

toinitiator. This effect was previously observed for other cellulosic systems by Cumberbirch and Holker[9] in case of grafting with acrylic acid.

### Effect of Reaction Time

Figure 2 shows the effect of the time of reaction on percent graft add-on. The graft add-on increased with increase in time of grafting from 1 to 3 h in the case of both the initiators. This would be due to the increasing extent of initiation and propagation of the graft copolymerization with time. Beyond 3 h, however, the graft add-on decreased progressively. The decrease in graft add-on was presumably due to the detrimental effect of UV radiation onto the grafted side chains at longer irradiation times in the presence of the initiator. Irradiation of the grafted cotton sample alone in the absence of initiator did not show any detrimental effect on the graft add-on. These results also support the earlier observation by Fouassier and Herdol[10] that longer irradiation times resulted in a decreased percent grafting in the case of methyl methacrylate grafting onto cellulose in the presence of benzophenone photoinitiator.

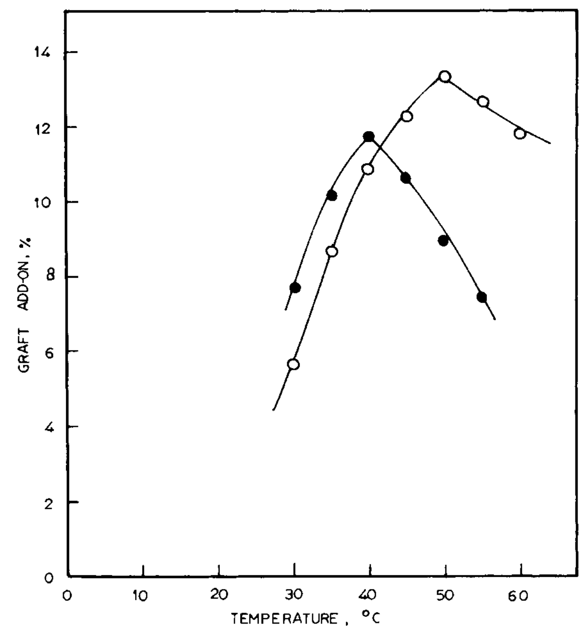


Figure 3 Relation between temperature of reaction and graft add-on: (○) UN photoinitiator; (●) CAN photoinitiator.

### Effect of Reaction Temperature

Figure 3 shows the effect of the reaction temperature on the percent graft add-on for both the initiators. The graft add-on showed an increase with increasing temperature and reached a maximum value of 13.40% at 50°C for UN and 11.80% at 40°C for CAN. Further increase in reaction temperature, however, showed an adverse effect on graft add-on. This was attributed to the increased extent of radical termination at higher temperature of reaction.

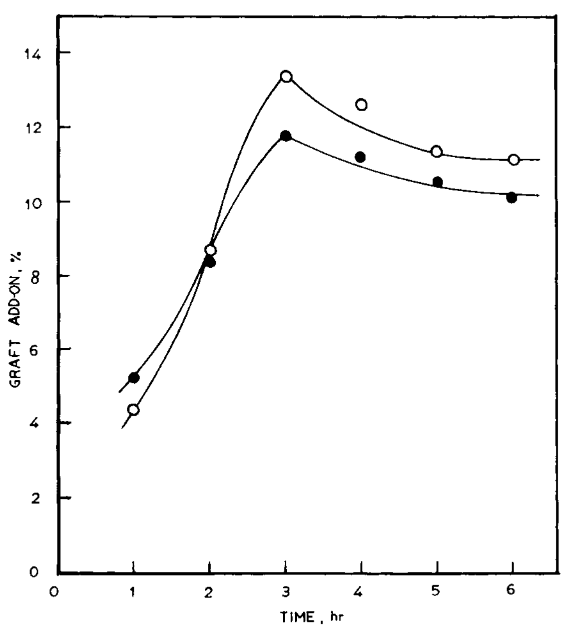


Figure 2 Relation between time of reaction and graft add-on: (○) UN photoinitiator; (●) CAN photoinitiator.

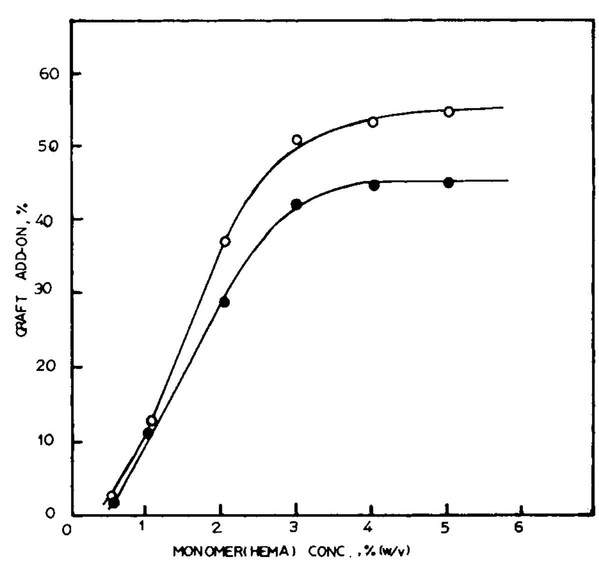


Figure 4 Relation between HEMA concentration and graft add-on: (○) UN photoinitiator; (●) CAN photoinitiator.

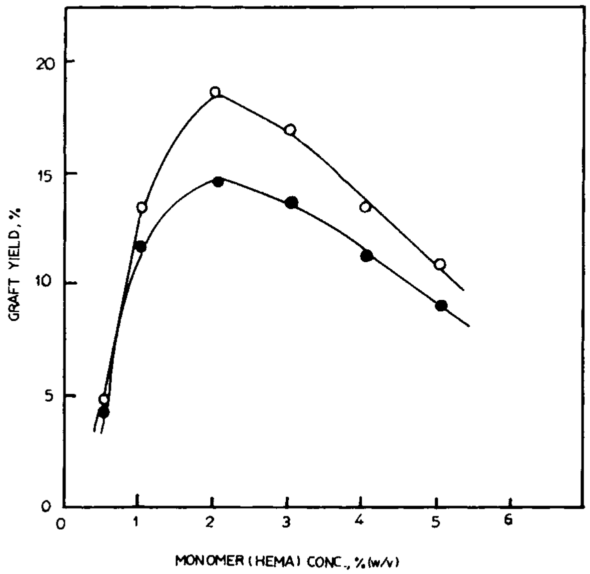


**Figure 5** Relation between HEMA concentration and graft yield: (○) UN photoinitiator; (●) CAN photoinitiator.

## Effect of Monomer Concentration

The HEMA concentration was varied between 0.5 and 5.0% (w/v) to see the effect on graft add-on. These results have been plotted in Figure 4, which shows that there is significant enhancement in the graft add-on values with increase in the monomer concentration and finally a leveling off of graft add-on for both the photoinitiators. In these studies, UN appears to be more efficient, giving higher graft add-on values as compared to those by using CAN, at each concentration of HEMA used. The maximum graft yield was observed at 2% (w/v) HEMA for both the initiators (Fig. 5), suggesting thereby that the utilization of monomer is better at this concentration than that at any other concentration of HEMA used. Although higher graft add-on values have been obtained beyond 2% (w/v) HEMA, there is correspondingly higher homopolymer formation also, which has the effect of lowering the graft yield at higher monomer concentrations.

The infrared spectrum for the grafted cotton has

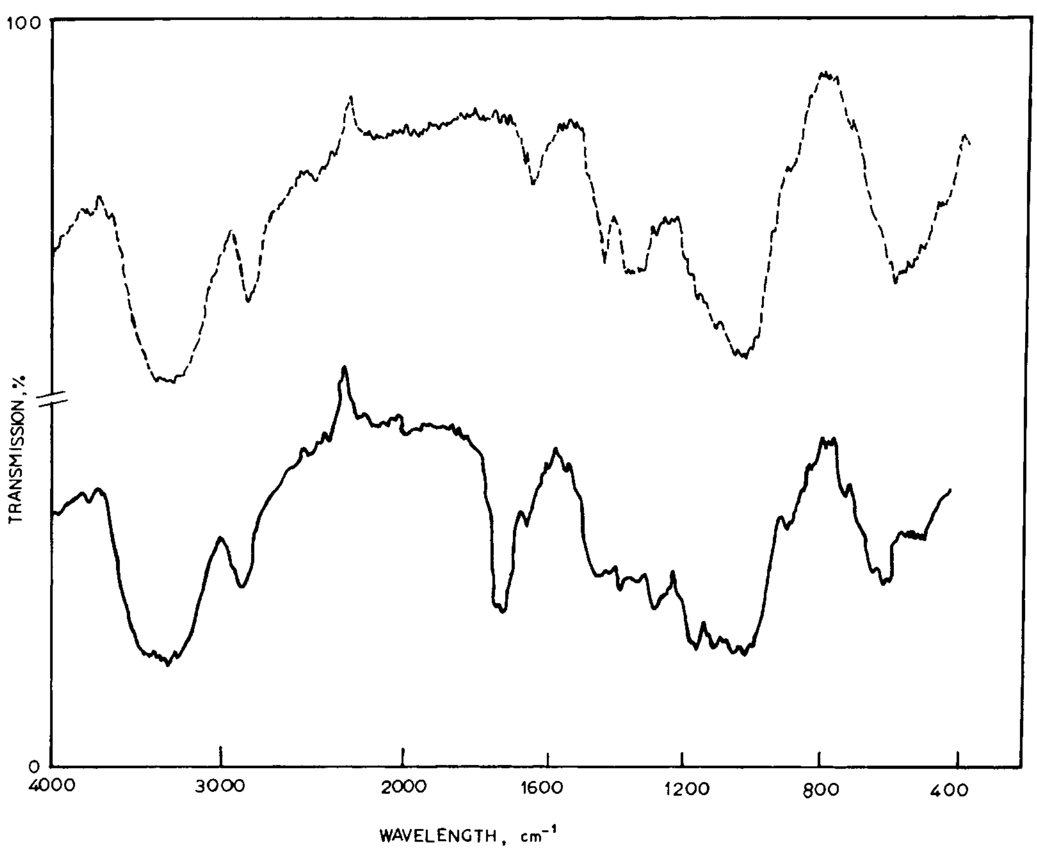


**Figure 6** Infrared spectra of samples: (- - -) control cotton; (——) HEMA-grafted cotton.

**Table I Effect of Swelling on Graft Add-on of HEMA onto Cotton Cellulose**

| HEMA Concentration (%) (w/v) | Cotton Sample | Graft Add-on (%) | |
|---|---|---|---|
| | | UN Initiation[a] | CAN Initiation[b] |
| 1.0 | Unswollen | 13.40 | 11.80 |
| | NaOH-swollen | 27.35 | 24.30 |
| | $ZnCl_2$-swollen | 24.10 | 23.12 |
| 2.0 | Unswollen | 37.22 | 29.06 |
| | NaOH-swollen | 49.74 | 44.74 |
| | $ZnCl_2$-swollen | 46.80 | 42.26 |
| 3.0 | Unswollen | 50.98 | 42.12 |
| | NaOH-swollen | 56.22 | 51.56 |
| | $ZnCl_2$-swollen | 54.45 | 50.32 |

[a] UN initiation: 0.20% (w/v) UN, 50°C, 3 h.
[b] CAN initiation: 0.25% (w/v) CAN, 40°C, 3 h.

been given in Figure 6. The additional peak obtained at 1700 $cm^{-1}$ confirms the introduction of ester carbonyl groups in the fiber structure.

## Effect of Swelling

The grafting of HEMA onto swollen cotton was carried out under optimized conditions of time, temperature, and UN and CAN photoinitiator concentrations by varying the concentration of HEMA in the range of 1–3% (w/v). These results are presented in Table I which indicate that swollen cotton gives very high graft add-on values than those for unswollen cotton at each concentration of HEMA used. The higher graft add-on values in the case of swollen cotton were mainly attributed to the higher accessibility and greater reactivity of swollen cotton than the unswollen cotton. Moreover, in the case of NaOH-swollen cotton, the graft add-on was found to be higher than that in the case of $ZnCl_2$-swollen sample at each concentration of HEMA used, due to more swelling action of NaOH than that of $ZnCl_2$ under the conditions used for swelling. However, the effect of swelling was less pronounced at the higher concentrations of HEMA.

## Moisture Regain and Dyeability

The moisture regain values for the control cotton and those for the NaOH-swollen cotton samples were 6.13 and 9.18%, respectively. On grafting HEMA onto the unswollen samples, using UN and CAN photoinitiators, and onto the swollen samples, using only UN as photoinitiator, it was observed that, initially, at low graft add-on level, the moisture regain decreased markedly, followed by a small

**Table II Effect of Graft Add-on of HEMA on Moisture Regain of Cotton Cellulose**

| HEMA Concentration (%) (w/v) | UN Initiation | | | | CAN Initiation | |
|---|---|---|---|---|---|---|
| | Unswollen | | NaOH-Swollen | | Unswollen | |
| | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) |
| 0.0 | 0.00 | 6.13 | 0.00 | 9.18 | 0.00 | 6.13 |
| 0.5 | — | — | 10.05 | 8.59 | — | — |
| 1.0 | 13.40 | 5.65 | 26.37 | 8.65 | 11.80 | 5.64 |
| 2.0 | 37.22 | 5.74 | 47.57 | 8.88 | 29.06 | 5.69 |
| 3.0 | 50.98 | 5.86 | 55.21 | 8.94 | 42.12 | 5.78 |
| 4.0 | 53.65 | 5.92 | 63.64 | 8.98 | 44.98 | 5.81 |
| 5.0 | 54.42 | 5.95 | 67.95 | 9.02 | 45.30 | 5.84 |

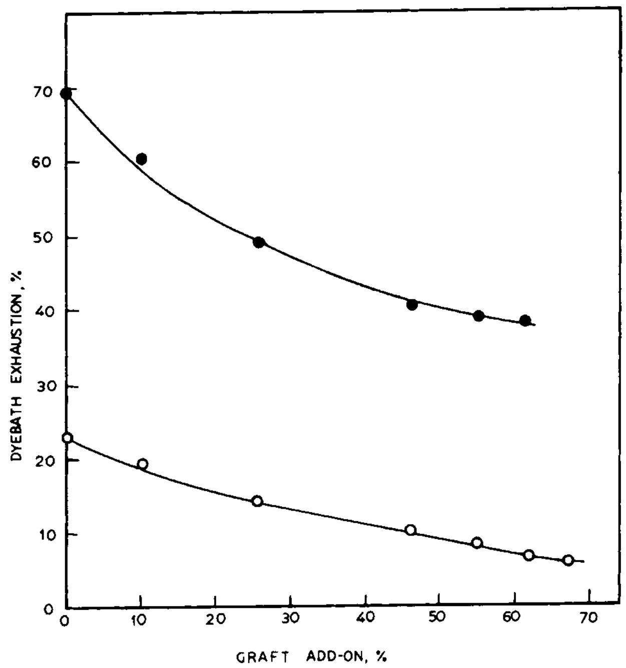


**Figure 7** Relation between HEMA graft add-on and dye bath exhaustion: (○) C. I. Direct Blue 86; (●) C. I. Reactive Red 31.

steady rise with further increase in graft add-on. These results are given in Table II. The measurement of the diameter of the grafted samples indicated increase over that of the control swollen cotton. When these samples were subjected to dyeing with direct and reactive dyes, a decrease in the dye uptake of both the dyes with increase in the graft add-on was observed as shown in Figure 7.

It is a well-known fact that the moisture regain and the dyeability primarily depend on the accessible nature of substrate. The direct dye dyeing and the moisture sorption depend on the hydrogen bonding capabilities of the hydroxyl groups present in the substrate, whereas the reactive dyes form actual covalent bonds with the —OH groups of the substrate. This, in turn, implies that such —OH groups are accessible to the agents, namely, dyestuffs or moisture. Initially, when the cotton samples are grafted with HEMA, the moisture regain as well as the direct dye uptake decreases as a result of the nonavailability of cellulosic —OH groups for hydrogen bonding. This may be, perhaps, caused by the steric hindrance of the bulky HEMA molecules. As the graft add-on increases further, lesser and lesser amounts of cellulosic —OH groups are made available for dyeing or for moisture sorption.

However, as compared to the molecular size of the dyestuffs, the molecular size of water molecule is extremely small. The HEMA-grafted samples make the cellulosic —OH groups inaccessible; however, the —OH groups due to HEMA grafted chains are, although in a very small amount, accessible to moisture. Hence, the dye uptake of both direct and reactive dyes goes on decreasing with increase in the graft add-on, whereas the moisture sorption decreases initially at low graft add-on level and then goes on increasing very marginally. At a graft add-on value as high as 67.95%, thus, the moisture regain value of swollen cotton increases only to 9.02%, which happens to be less than that for the swollen control sample.

In conclusion, it may be stated that the use of proper conditions of grafting reaction leads to a considerably high amount of graft add-on even with the use of low energy UV radiations. The system substrate–monomer–photoinitiator also plays an important role in determining the actual amount of graft add-on.

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