

# Improving Graft Level during Photoinduced Graft-Copolymerization of Styrene onto Cotton Cellulose

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## SYNOPSIS

Styrene was graft-copolymerized onto cotton cellulose using photoinitiators uranyl nitrate (UN), ceric ammonium nitrate (CAN), and benzoin ethyl ether (BEE) under ultraviolet radiation. UN gave somewhat higher graft add-on. Preswelling of the substrate or using divinyl benzene in the grafting bath gave an increased level of graft, the later technique being more efficient. The moisture regain and tenacity decreased, whereas thermal stability increased in proportion to the graft add-on. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The graft-copolymerization process, for chemically modifying a polymeric substrate, has been accepted as an effective method to impart useful properties to the backbone polymer without significantly affecting the original ones. A number of vinyl monomers have been grafted onto various textile fibers, improving properties such as moisture regain, dyeability, and static charge reduction of synthetic fibers and enhancing the thermal stability of natural fibers.<sup>1-4</sup> The process of grafting of fibers has also benefited nontextile areas, such as in the use of styrene-divinyl benzene-grafted fibers in ion-exchange resins<sup>5</sup> and various grafted fibers in the absorption of heavy metal ions<sup>6</sup> and for a support for immobilization of enzymes.<sup>7</sup>

Of the various methods of initiation of grafting, photoinitiation using low-energy ultraviolet radiation possesses the least danger of damaging the polymer structure. However, the graft yields are generally low, since UV irradiation itself is not strong enough to initiate free-radical formation on the backbone polymer.<sup>8,9</sup> Photoinitiators of various types are, therefore, used for this purpose.<sup>10-15</sup>

The use of solvents and/or swelling agents has been shown to enlarge the fiber diameter, thereby

increasing the penetration of reactants, leading to increased graft add-on.<sup>16-18</sup> Similarly, mineral acids increase the grafting by opening up the structure of fiber.<sup>19</sup> Bifunctional monomers also have been tried, although their action is through different mechanisms. It has also been reported that divinyl benzene has a synergistic effect on the grafting of styrene.<sup>20,21</sup>

In the present study, the photoinitiators—uranyl nitrate, ceric ammonium nitrate, and benzoin ethyl ether—were used in the UV radiation-induced grafting of styrene onto cotton fibers. The effect of preswelling of the substrate prior to grafting using sodium hydroxide and zinc chloride as well as the effect of small additions of a bifunctional monomer, divinyl benzene, on the graft level of styrene onto cotton was studied. The grafted samples were subjected to analysis of moisture regain, tenacity, and thermal behavior.

## EXPERIMENTAL

### Materials

### Substrates

The cellulosic sample used was scoured and bleached 30 count cotton yarn. 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 thorough washing with water and air-drying.

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### Chemicals

Styrene, supplied by LOBA Chemie Indoaustral Co., and divinyl benzene (DVB), supplied by Ion Exchange (India) Ltd., were purified by mixing them well with 5% sodium hydroxide solution followed by separating out the pure monomers. These were further washed with 5% sodium chloride and then several times with distilled water, followed by drying. Methanol, benzene, sodium hydroxide, and zinc chloride of chemically pure grade were used.

### Initiators

Two inorganic photoinitiators, uranyl nitrate (UN) and ceric ammonium nitrate (CAN), and an organic photoinitiator, benzoin ethyl ether (BEE), were used.

### Measurement of Swelling

The degree of swelling of cotton fibers was measured by noting the change in diameter of the fiber on a Projection Microscope MP-3 (PZO, Warazawa, Poland) using a magnification range of 800 $\times$  and magnification/aperture of 40 $\times$ /0.65.

### Graft-Copolymerization

A Philips HPW 125 W mercury vapor lamp was used as a source of UV radiation. One gram of the cotton sample was immersed in 100 mL of methanolic solution of the monomer and initiator in a quartz conical flask. The temperature of reaction was maintained using a thermostatically regulated glycerine bath. The quartz flasks were stoppered and irradiated for different time intervals varying from 1 to 6 h in an enclosed wooden chamber containing the UV lamp. The distance between the lamp and the sample was about 12 cm.

The optimization of various parameters of grafting, viz., concentrations of the different photoinitiators and the styrene monomer and the time and temperature of the reaction was first carried out. The optimized conditions using UN photoinitiator were applied for graft-copolymerization of the swollen substrates. Further, the bifunctional monomer, 1% (w/v) DVB, was added to the styrene grafting bath under these optimum conditions for both the unswollen and swollen cotton substrates. After completion of the grafting reaction in each case, the samples were washed first with methanol, Soxhlet-extracted with benzene for 72 h, and then air-dried.<sup>22</sup> The graft add-on and graft yield were measured using standard formulae.<sup>23</sup>

### Moisture Regain

The moisture regain of control and grafted samples was determined by the oven-drying method.<sup>24</sup>

### Tenacity

Control and grafted cotton samples of 1 cm length were tested for tenacity on an Instron tensile tester, which recorded load-elongation curves with a chart speed of 50 mm/min by adjusting the full scale of the recorder for a load corresponding to 500 g.

### Thermal Analysis of Grafted Cotton

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a Stanton Redcroft Thermal Analyzer STA-780. The cotton sample was cut to approximately 1–2 mm length and 20  $\pm$  5 mg were taken for each analysis. The analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 10°C/min and with a chart speed of 200 mm/h.

## RESULTS AND DISCUSSION

In the optimization studies, the concentration of each of the photoinitiators, UN, CAN, and BEE, was varied between 0.10 and 0.40% (w/v) and the one that gave maximum graft add-on in each case was selected as optimum for further experiments. The time of reaction was then varied from 1 to 6 h to select the period giving maximum graft add-on. Similarly, by varying the temperature of the reaction in the range of 30–60°C, the optimum was noted. These optimized conditions of grafting parameters using different photoinitiators for grafting of styrene onto cotton yarn are given in Table I.

**Table I** Optimized Conditions of Grafting of Styrene onto Cotton

Grafting Parameter	Initiation		
	UN	CAN	BEE
Initiator concentration [% (w/v)]	0.20	0.20	0.30
Time (h)	4	4	4
Temperature (°C)	50	55	50
Monomer concentration [% (w/v)]	30	35	30
Maximum graft add-on (%)	19.12	13.24	18.00

### Effect of Monomer Concentration

Under the given optimum conditions of photoinitiation, the concentration of styrene was varied from 5 to 40% (w/v). The maximum graft add-on value was obtained at 30% (w/v) styrene for UN and BEE photoinitiators, whereas, in the case of the CAN photoinitiator, it was at 35% (w/v) styrene. These results are given in Table II. With a further increase in styrene concentration, however, the graft add-on decreased slightly. This may be due to the depletion of methanol in the grafting bath, which should be present in sufficient quantity to permit efficient swelling of the fiber as well as to allow the grafting reaction to proceed. With increase in the graft add-on, homopolymer formation also increased. This resulted in a slight initial increase in the graft yield, which decreased thereafter. UN appears to be a more efficient photoinitiator, giving higher graft add-on values as compared to CAN and BEE and, hence, only UN was used in all further grafting experiments.

Of the three photoinitiators used, one is organic (BEE), whereas the other two are inorganic (UN and CAN). Davis et al.<sup>20</sup> explained the mechanism of the action of photoinitiators during graft-copolymerization. The free radicals from the inorganic photoinitiators react with the aqueous methanolic grafting bath and produce  $\cdot\text{CH}_2\text{OH}$  radicals.<sup>25</sup> These solvent radicals yield grafting sites on the cellulose substrate by abstraction of hydrogen atoms. Additional sites may be created by the diffusion of the photoinitiator into the cellulose substrate by directly abstracting hydrogen atoms or by rupturing bonds in the cellulose chain molecules.

In the case of organic photoinitiators, radicals can be formed by homolytic cleavage. These radicals may then abstract hydrogen atoms from cellulose back-

bone. The nature of radicals formed as well as the stability and steric factors of the radicals determine their relative efficiencies.

### Effect of Preswelling

Since the graft add-on values obtained were not quite high even at the higher concentrations of styrene, the maximum being only 19.12% using 30% (w/v) styrene in presence of UN photoinitiator, grafting was carried out on preswollen cotton substrate. Table III gives the results of the graft add-on of sodium hydroxide-swollen and zinc chloride-swollen cotton substrates grafted in the presence of UN photoinitiator only. Preswelling of the substrate showed an improvement in grafting over that of the unswollen one. This is due to the higher accessibility and greater reactivity of the preswollen substrates since swelling opens up the fiber structure. Moreover, in the case of sodium hydroxide-swollen cotton, the graft add-on was found to be higher than that in the case of zinc chloride-swollen sample, under equivalent conditions of grafting due to the stronger swelling action exerted by sodium hydroxide than that by zinc chloride. It was observed, during the initial measurements on the lateral swelling of the substrate,<sup>23</sup> that sodium hydroxide causes a 33% swelling compared to about 26% using zinc chloride. The preswelling of the substrate prior to graft-copolymerization, thus, helps in obtaining higher graft levels that are dependent on the nature of action of the swelling agent.

### Effect of Bifunctional Monomer

The above results on grafting using preswollen substrates indicate that although there is an increase

**Table II Effect of Styrene Concentration on Graft Add-on and Graft Yield of Cotton Cellulose Using Different Photoinitiators**

Styrene Concentration [% (w/v)]	Graft Add-on (%)			Graft Yield (%)		
	UN	CAN	BEE	UN	CAN	BEE
5	5.54	0.00	3.86	1.10	0.00	0.77
10	10.84	3.18	5.76	1.08	0.31	0.57
15	14.16	4.95	9.20	0.94	0.33	0.61
20	16.38	7.60	11.10	0.81	0.38	0.55
25	17.26	9.46	13.12	0.69	0.37	0.52
30	19.12	13.20	18.00	0.63	0.44	0.60
35	18.90	13.24	17.52	0.54	0.38	0.50
40	18.40	12.75	16.36	0.46	0.32	0.40

**Table III** Effect of Styrene Concentration on Graft Add-on of Unswollen and Swollen Cotton Cellulose in Absence and Presence of DVB Using UN Photoinitiator

Graft Add-on (%)	Styrene Concentration [% (w/v)]					
	5	10	15	20	25	30
Unswollen	5.54	10.84	14.16	16.38	17.26	19.12
NaOH-swollen	—	19.23	—	24.50	—	26.46
ZnCl <sub>2</sub> -swollen	—	17.20	—	21.74	—	24.10
Unswollen, with DVB	12.75	17.38	22.36	28.30	35.46	40.50
NaOH-swollen, with DVB	—	27.84	—	38.46	—	47.84
ZnCl <sub>2</sub> -swollen, with DVB	—	26.10	—	35.52	—	44.28

in the graft add-on the levels are not very high, the maximum increase being about 38% (from 19.12 to 26.46%) for sodium hydroxide-swollen cotton using the UN photoinitiator. The bifunctional monomers have been found to give extremely large enhancements in graft levels when used in very small amounts in the grafting baths containing monofunctional monomers.<sup>26</sup> The effect of the addition of DVB to the styrene grafting bath was, therefore, studied using the unswollen and swollen substrates. These results also are given in Table III.

Thus, under optimized conditions of UN-photoinitiated grafting, viz., 0.20% (w/v) UN, 4 h, and 50°C in the presence of 1.0% (w/v) DVB, the concentration of styrene was varied from 5 to 40% (w/v) in the grafting bath. The graft add-on increased with increase in the styrene concentration. Moreover, the data indicate that the graft add-on value at each styrene concentration was significantly higher in the presence of DVB than that in its absence for both unswollen as well as preswollen substrates. Thus, at 30% (w/v) styrene concentration, the graft add-on increased from 19.12% to 40.50% with the addition of 1% (w/v) DVB for unswollen cotton, whereas for sodium hydroxide-swollen cotton, it reached a further higher value of 47.84%.

The effect of the addition of DVB to the styrene grafting bath can be four-fold. Thus:

- (i) Polystyrene graft chains are formed onto the cellulose backbone due to the graft-copolymerization reaction, and the bifunctional DVB molecule can form a cross-link between two such graft chains. In this case, the graft add-on will not increase. In fact, further growth of the graft chains will be terminated.
- (ii) Simultaneous occurrence of the graft-copolymerization reaction and homopolymer-

ization will also produce polystyrene homopolymer chains loosely held in the grafting bath. The DVB molecule may form a cross-link between two such polystyrene homopolymer chains present in the bath. This reaction also will not affect the graft level. On the contrary, to some extent, the growth of homopolymer chains will be restricted, thus making more styrene monomer available for grafting. Such a styrene-DVB copolymer was easy to extract from the grafted substrate. To confirm this, another experiment of copolymerization between 30% (w/v) styrene and 1% (w/v) DVB, under the conditions of grafting but in absence of the substrate, was carried out and the product was found to dissolve in benzene over a period of 12 h, which was considerably less than that used for extracting the grafted samples (viz., 72 h). The loose styrene-DVB copolymer thus is removed completely during the extraction of the substrate after completion of grafting. The bulkiness of such a loose copolymer will not allow its penetration inside the fiber structure and, hence, it will be present only near the fiber surface, making it easier to dissolve during the extraction process.

Earlier, the same method was reported for the extraction of styrene-DVB cross-linked homopolymer while grafting onto polypropylene and polyethylene films.<sup>21,27</sup> In those cases, the values of the graft add-on were as high as 92%.

- (iii) One end of the DVB molecule may become bonded to a growing polystyrene graft chain already present on the cellulose backbone and the other end will attract a loose polystyrene homopolymer chain. This will

greatly enhance the graft add-on level as the length of the graft chain is considerably increased due to the bridging by DVB.

- (iv) One end of the DVB molecule may attach to the growing polystyrene graft chain and the other end is free to initiate growth of a new polystyrene chain via scavenging reactions. This type of reaction will also contribute to the enhancement of the graft level.

Thus, by adding a small amount of DVB to the styrene grafting bath, the graft add-on considerably increases in terms of the graft chain length. DVB may not enhance the number of polystyrene graft chains.

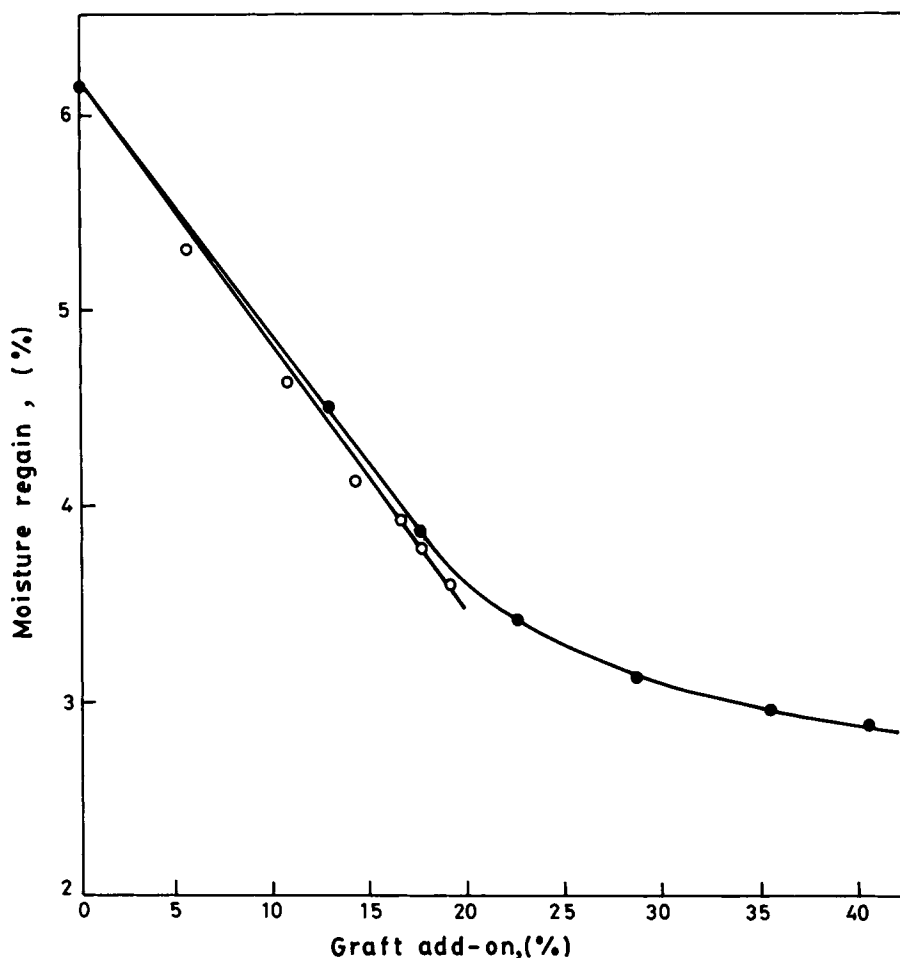
The infrared spectra of styrene-grafted cotton samples, both in the absence and the presence of DVB in the grafting bath, indicated the appearance of a peak at  $1620\text{ cm}^{-1}$  due to the introduction of an

aromatic C—C stretch in the fiber structure. This is obvious since both monomers have similar reactive groups. This was also observed earlier by Guthrie and Haq.<sup>28</sup>

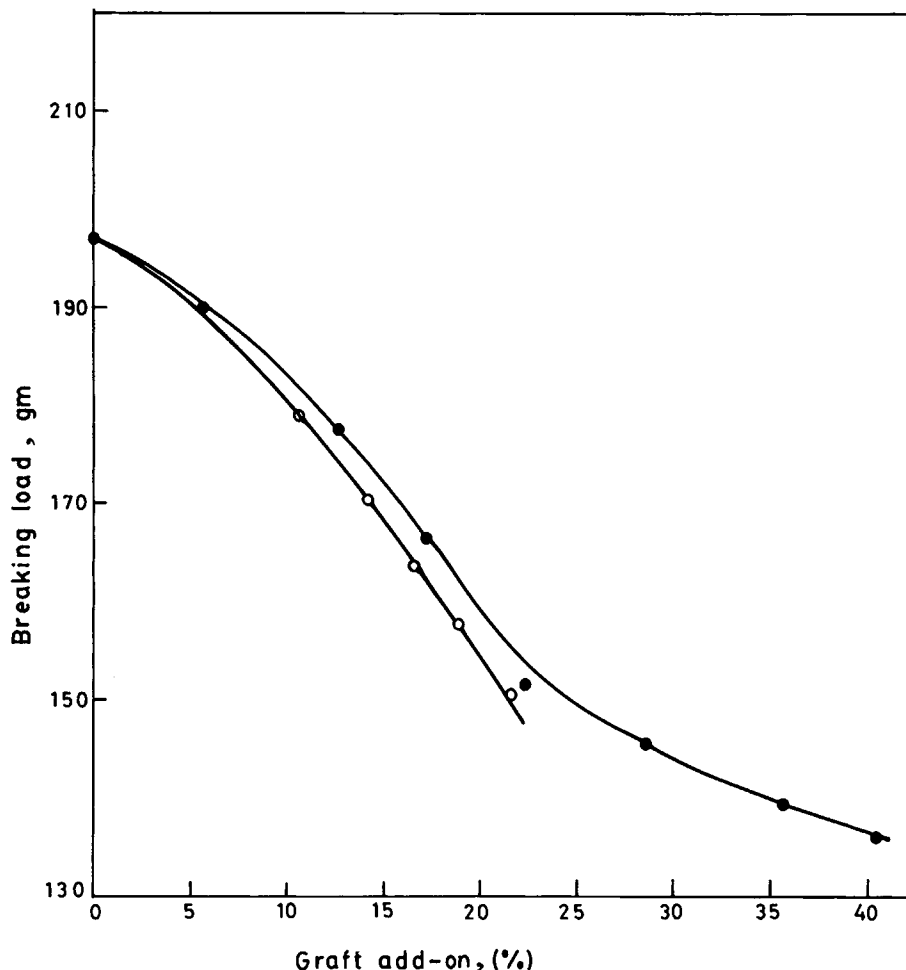
### Moisture Regain and Tenacity

The moisture regain values for the grafted substrates decreased gradually with increase in the styrene graft add-on, depending solely on the level of graft add-on (Fig. 1). The decrease in moisture regain is attributed to the introduction of hydrophobic groups in the fiber structure.

The tensile strength of the grafted cotton yarns was also found to decrease progressively with increase in the graft add-on (Fig. 2). With increase in graft add-on, the extent of cross-linking in the fiber substrate increases, which makes the fiber



**Figure 1** Effect of styrene graft add-on on moisture regain of cotton: (○) without DVB; (●) with DVB.



**Figure 2** Effect of styrene graft add-on on breaking load of cotton: (O) without DVB; (●) with DVB.

brittle and rigid and decreases its breaking load. Thus, as far as tensile properties are concerned, the grafted side chains act as a dead load contributing toward the decrease in tenacity.

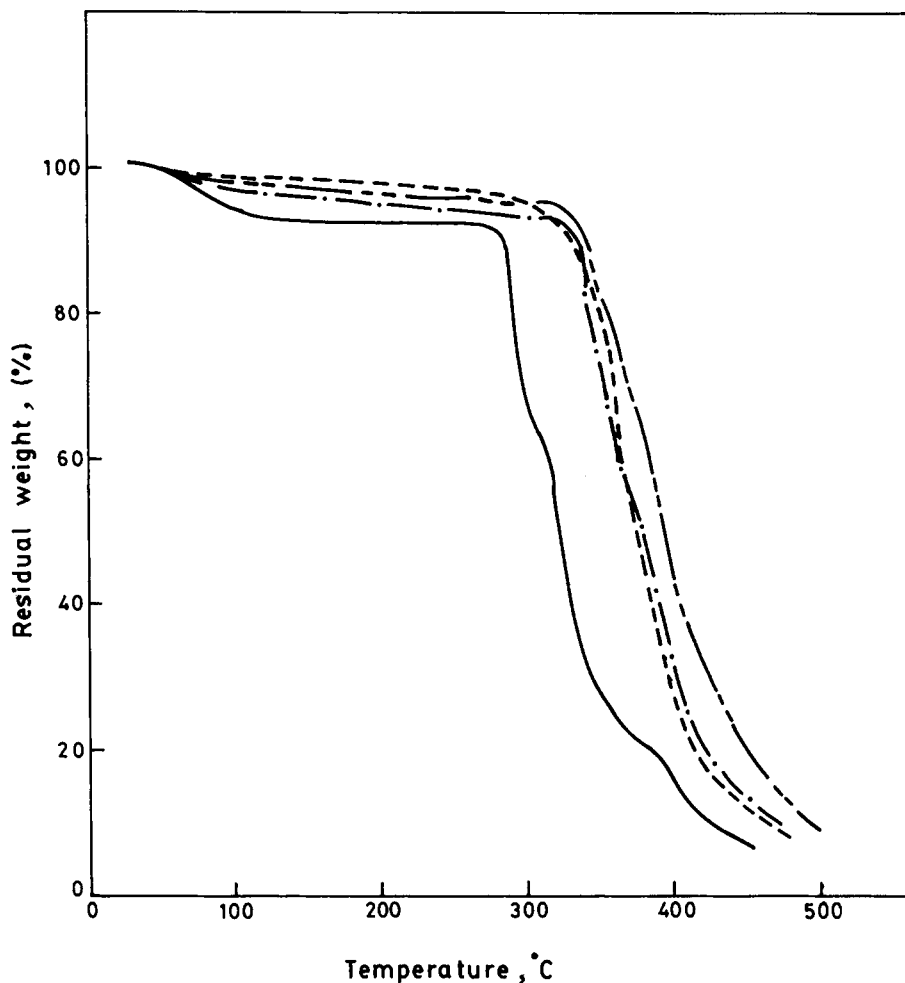
#### Thermal Behavior of Grafted Cotton

The differential thermal analysis (DTA) of the styrene-grafted cotton in the absence as well as in the presence of DVB showed a new endothermic peak at 410–425°C due to the polystyrene copolymer. With increase in graft add-on, the peak became larger with a simultaneous decrease in the endothermic peak due to cellulose decomposition at 341°C. Because of the hydrophobic nature of the graft, the moisture desorption endothermic peak at 100–110°C slowly disappeared with increasing graft add-on. Instead, a small endothermic peak, due to

the glass transition temperature of polystyrene at 75–80°C, in the DTA curves appeared for the samples having a high graft level. The very slight appearance of this peak is indicative only of shorter polystyrene graft chains.

The thermogravimetric analysis (TGA) of the grafted samples indicated that, with increase in the graft add-on, the thermal stability of cotton increased (Fig. 3). The thermal decomposition also started at higher temperature with correspondingly higher levels of graft add-on. Thus, for a weight loss of 10%, the temperature of decomposition increased from 280°C for ungrafted cotton to 335°C for cotton having a graft add-on of 40.50%.

It may be concluded that in order to enhance the graft levels, especially when using low-energy sources like UV, it is useful either to preswell the substrate or to make use of a bifunctional monomer



**Figure 3** Effect of temperature of decomposition on weight loss of cotton: (—) control cotton; (---) 10.84% styrene graft; (- · - ·) 19.12% styrene graft; (- - -) 40.50% styrene graft (with DVB).

in very small quantities in the grafting bath, the latter being the easier method. The textile properties of the substrate in such a case (i.e., grafted in the presence of a lower amount of a bifunctional monomer) are dependent solely on the level of graft addition, irrespective of the absence or presence of the bifunctional monomer.

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