

# Graft Copolymerization of Vinyl Monomers onto Silk Fibers Initiated by a Semiconductor-Based Photocatalyst

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**ABSTRACT:** Graft copolymerization onto silk (*Bombyx mori*) was carried out with vinyl monomers (methyl methacrylate and acrylamide) and initiated by a semiconductor-based photocatalyst (cadmium sulfide). The utility of a semiconductor as an initiator in free-radical photografting and the effects of ethylene glycol and triethylamine with cadmium sulfide on graft copolymerization were explored. Depending on the reaction conditions, 10–48% grafting with methyl methacrylate and 4–26% grafting with acrylamide were achieved. The reaction conditions were opti-

mized, and the grafted fibers were characterized with scanning electron microscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetry analysis, and tensile strength measurements. The chemical resistance and water absorption of the grafted fibers were compared with those ungrafted fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2164–2175, 2007

**Key words:** catalysts; graft copolymers; photopolymerization

## INTRODUCTION

Over the decades, silk has been highly valued as a textile fiber because of its strength, elasticity, softness, absorbency, and affinity for dyes. Silk caught the interest of the scientific community more than a century ago and was used as a source of protein until the early part of the 20th century.<sup>1</sup> Of the different available silks, *Bombyx mori* is the most widely used worldwide and is the most important source of silk.<sup>2</sup>

The surface modification of the fibers has always been targeted to bring about changes in the properties, such as stiffness, softness, wrinkle resistance, abrasion resistance, and shrink proofing.<sup>3–5</sup> However, improvements in the performance properties of natural fibers, such as photoyellowing, wash and wear properties, moisture absorption, crease recovery, and water staining, have been successfully carried out by different research groups.<sup>6–8</sup>

Graft and block copolymerizations are novel methods for combining the physical and chemical properties of two or more different monomers into a single polymeric chain.<sup>9–12</sup> Of the different graft copolymerization methods, free-radical-induced polymerization is the easiest and most widely accepted procedure for this purpose.<sup>13</sup> Free-radical graft copolymerizations are generally initiated by variety of

species capable of generating primary free radicals via chemical reactions or thermal dissociation.

In the case of a free-radical mechanism, various initiator systems, such as 2,2-azobis-isobutyronitrile, benzoyl peroxide, ammonium persulfate, ceric ammonium nitrate,<sup>14</sup> Cr(VI),<sup>15</sup> and KMnO<sub>4</sub>/oxalic acid redox systems,<sup>16</sup> have been applied. In comparison with other grafting methods,<sup>17–19</sup> the free-radical process, followed by light-induced initiation, has an advantage because of its applicability at room temperature and its user-friendly nature. Moreover, the polymerization can be controlled with the intensity and wavelength of the applied illuminating systems.<sup>13</sup>

Semiconductor-based photocatalysis is one of the modern methods for the generation of initiating radicals in the photopolymerization of vinyl monomers.<sup>20</sup> Heterogeneous photocatalytic reactions with various semiconductors such as TiO<sub>2</sub>, ZnO, cadmium sulfide (CdS), and ZnS have been studied extensively over the last few decades.<sup>21</sup> The effectiveness of these semiconductors as photocatalysts depends on how well the radiation wavelength corresponds to the band-gap excitation energy of the semiconductor.<sup>22</sup>

Semiconductors are used for carrying out many organic transformations.<sup>23</sup> The applicability of semiconductor particles as photocatalysts for reduction/oxidation of water and for oxidation/reduction of contaminants in water in the presence of sacrificial electron donors/acceptors has been reported.<sup>24</sup> The catalytic efficiency depends on a major deactivation process involving e<sup>-</sup>-h<sup>+</sup> recombination. To suppress

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electron and electron-hole recombination and to make a continuous supply of valence band holes for reactive purposes, sometimes a sacrificial electron acceptor is added to scavenge the electron in the conduction band.<sup>25</sup> In addition to that, electron donors such as ethylene glycol, glycerol, and triethylamine are used to scavenge the electron holes so that the conduction band electrons are available for reaction; this increases the reactivity of the semiconductor.<sup>26</sup>

This work reports the results of the graft copolymerization of methyl methacrylate (MMA) and acrylamide (AAM) onto *B. mori* fibers with CdS as a semiconductor-based photocatalyst. The utility of a semiconductor as an initiator in free-radical photografting is explored. The effect of additives such as ethylene glycol and triethylamine with CdS on the graft copolymerization process is also reported. The structural and thermal properties and morphological structure of the grafted fibers have been characterized with differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), water absorption measurements, scanning electron microscopy (SEM), tensile strength measurements, chemical resistance measurements, and so forth.

## EXPERIMENTAL

### Materials

MMA was purified by repeated washing with a 4% aqueous NaOH solution and then washed with distilled water to make it free from alkali. The washed monomer was dried over anhydrous BaO for 24 h and distilled under nitrogen under reduced pressure.<sup>27</sup> The middle fraction was used for all experiments.

AAM, a white solid, was recrystallized from methanol and dried *in vacuo* over silica gel.<sup>28</sup> A freshly prepared aqueous AAM solution was considered for polymerization in each case.

CdS, obtained from CDH (Mumbai, India), was used without further purification. Acetone and petroleum ether (Merck, Mumbai, India) were distilled before use. *B. mori* fibers were supplied by a government firm (Sualkuchi, Assam, India).

### Light source

The excitation light source was a high-pressure mercury-vapor lamp (GE India, Ltd., New Delhi, India; 125 W and a radiation intensity of 750 W/m<sup>2</sup>). UV cutoff filters were employed to restrict the UV radiation.

### Methods

#### Pretreatment of the silk fiber

Silk fiber was stirred in a solution of NaOH (20 wt %) at room temperature for 2 h and then washed with a hydrochloric acid solution (1 wt %) followed by distilled water. The sample was dried later in an oven at 50°C.<sup>29</sup>

#### Graft copolymerization

A three-necked, 100-mL, round-bottom flask fitted with a stirrer, a thermometer pocket, and a nitrogen inlet was used to carry out the reaction. The reaction mixture, containing the monomer, photocatalyst (CdS), and triethylamine or ethylene glycol, and the silk fiber were placed in the flask. The pretreated silk samples were soaked in the reaction mixture for 24 h to ensure the incorporation of the monomer and other additives into the silk. The whole assembly was purged with the nitrogen gas and exposed to visible light (500–600 nm) for 1–7 h in different cases, and the reactions were carried out at three different temperatures (35, 45, and 55°C). At 45 and 55°C, a water bath with an electrical heating arrangement was employed. The flask was kept 10 cm apart from the light source in each case. To run the reaction at 35°C, a fan was fitted to the reaction system. After the stipulated time period, the silk fibers were taken out and washed with the appropriate solvent (depending on the monomer) several times. For the removal of the monomer and homopolymer, silk samples along with the homopolymer were precipitated in the necessary solvent. The silk samples were refluxed in a Soxhlet apparatus with the proper solvent, which depended on the polymer uploaded onto the fiber. The grafted fibers were dried to a constant weight and kept in a desiccator for further use. The grafting percentage, homopolymer formation, grafting efficiency, and total conversion were calculated. To optimize the grafting, the experiment was repeated with different reaction mixtures.

#### Evaluation of the grafting parameters

The grafting percentage, grafting efficiency, homopolymer conversion, and total conversion were calculated by Fernandez et al.<sup>30</sup> on the basis of the increased weight of the silk fiber.

The grafting percentage (*G*) is the weight ratio of the grafted polymer to the original silk fibers:

$$G = \frac{\text{Weight of the grafted silk after the extraction of the homopolymer} - \text{Weight of the original silk}}{\text{Weight of the original silk}} \times 100$$

The homopolymer conversion ( $C_{\text{homo}}$ ) is the monomer fraction that affords the homopolymer:

$$C_{\text{homo}} = \frac{\text{Weight of the homopolymer}}{\text{Weight of the monomer}} \times 100$$

The grafting efficiency (GE) is the fraction of the total synthetic polymer that is grafted onto silk:

$$GE = \frac{\begin{array}{l} \text{Weight of the grafted sample after the} \\ \text{extraction of the homocopolymer} \\ - \text{Weight of the original silk} \end{array}}{\begin{array}{l} \text{Weight of the crude polymer product} \\ - \text{Weight of the original silk} \end{array}} \times 100$$

The total conversion ( $C_t$ ) of the monomer to the polymer is the monomer fraction that polymerizes:

$$C_t = \frac{\begin{array}{l} \text{Weight of the crude polymerization} \\ \text{product} - \text{Weight of the original silk} \end{array}}{\text{Weight of the monomer}} \times 100$$

### Characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of finely powdered grafted and ungrafted fiber samples were recorded with a Nicolet Impact 410 FTIR spectrophotometer with the KBr disc technique.

Thermal analysis

The thermal analysis was carried out with a Perkin-Elmer differential scanning calorimeter, and DSC thermograms were recorded at a heating rate of 10°C/min in a nitrogen environment.

TGA of the ungrafted and grafted silk fibers was carried out with a PerkinElmer thermal analyzer in the temperature range of 50–800°C at a heating rate of 10°C/min in a nitrogen environment.

SEM

The surface morphology of the grafted and ungrafted fibers was investigated with a Hitachi S-415 A scanning electron microscope (Japan) operating at an accelerating voltage of 10–15 kV and in the secondary electron image mode. The samples were coated with gold in a sputter coater *in vacuo* with a layer 15–20 mm thick.

Tensile properties

The stress–strain behavior of the grafted and ungrafted fibers under tension was evaluated with a

Zwick Z010 universal tensile testing machine (Germany) per the ASTM D 638 standard.<sup>31</sup>

The fiber samples were cut into 10-cm lengths, and care was taken to ensure that each specimen was free from abnormalities such as cut edges, creases, or wrinkles. The samples were selected randomly and conditioned at 25°C and 65% relative humidity.<sup>32</sup> The fibers were first clamped to the upper jaw and then carefully clamped to the lower jaw. The gauge length and rate of extension were 50 mm and 10 mm/min, respectively. After careful clamping in both jaws, a load was applied to the specimen until it broke. On average, 10 samples of each silk fiber were run under the same conditions.

Water absorption

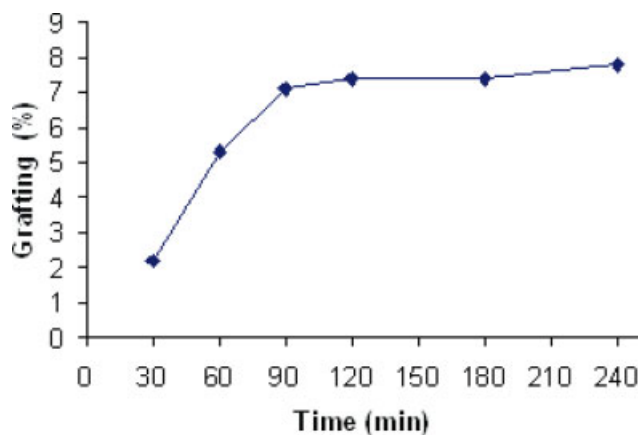
The water absorption measurements of the grafted and ungrafted silk fibers were compared with the standard method.<sup>33,34</sup> The weight of the dry silk fiber was recorded before the sample was soaked in deionized water until an equilibrium weight was achieved in the ambient environment. The determination of the water absorption by the fiber was practiced by centrifugation of the samples. The samples were placed on the strainer of a specially made centrifuge tube and centrifuged for 15 min. An arrangement was made so that the bottom of the tube allowed excess water to drain away from the sample. The centrifuge tube was sealed to ensure 100% relative humidity to prevent the desorption of water by the fibers. The samples were weighed, and this weight was considered the wet weight of the fiber; the samples were then dried in a vacuum oven at 40 ± 5°C for 24 h. The dry weight was recorded and compared with the earlier one. The water sorbency was calculated in terms of the water retention value [WRV (g of water/g of the dry sample)] and expressed as follows:

$$\text{WRV(g/g)} = \frac{\begin{array}{l} \text{Weight of the silk fiber (wet)} \\ - \text{Weight of the silk fiber (dry)} \end{array}}{\text{Weight of the silk fiber (dry)}} \times 100$$

The average values were estimated from five replicate measurements for each specific sample, and the results were reported.

Chemical resistance

The chemical resistance of the grafted and ungrafted fibers was measured with the ASTM D 443-87 method. Each fiber was dipped in the respective chemical for 24 h or more (in some cases), removed from the respective solvent, and washed in distilled water. The samples were weighed after drying in the



**Figure 1** Effect of the reaction time on the graft copolymerization of MMA onto silk fibers (reaction conditions: MMA = 1 mL; CdS = 0.005 g; silk fiber = 0.0598 g; temperature = 35°C; ethylene glycol = 0.02 mL). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

oven at 40°C for 10 h, and the loss/gain was calculated as a percentage.

## RESULTS AND DISCUSSION

### Graft copolymerization of MMA with a semiconductor-based photocatalyst

Effect of the variation of the exposure time

The effect of the exposure time on grafting was investigated with other variables, such as the initiator, additive, and temperature, kept constant. The grafting percentage against the radiation exposure time is plotted in Figure 1. An increasing trend was observed in the initial stage of the grafting up to a certain level. The increase in the grafting with increased exposure time was probably due to the generation of more active sites on the backbone of the fiber. The leveling off of the graft conversion after a certain time period was due to the predominance of homopolymerization over grafting and the termination of growing grafted chains by excess primary radicals that formed in the reaction mixture.

Effect of the variation of the reaction temperature

The grafting was carried out at three different temperatures (35, 45, and 55°C), and the reaction times and results are shown in Table I. The yield and other parameters increased with increasing temperature up to 55°C. The increasing trend in the rate of grafting within certain temperature ranges can be ascribed to a greater activation energy. The swellability of the fibers and the diffusion rate of the monomer into the fibers are influenced by increases

**TABLE I**  
Effect of the Reaction Temperature on Grafting

Reaction time (h)	Graft yield (%) <sup>a</sup>			Total conversion (%) <sup>b</sup>			Homopolymer formation (%) <sup>b</sup>		
	35°C	45°C	55°C	35°C	45°C	55°C	35°C	45°C	55°C
2	10.20 (±0.07)	15.08 (±0.09)	19.32 (±0.12)	11.61 (±0.08)	17.40 (±0.16)	21.48 (±0.24)	10.52 (±0.07)	15.23 (±0.09)	19.35 (±0.29)
4	18.67	21.52	25.16	17.40	19.84	21.12	15.89	16.57	16.98
6	20.06	22.57	23.35	26.54	28.62	32.55	21.65	22.43	23.78
7	21.77	24.41	25.26	29.25	30.83	32.89	24.25	25.14	24.79

The reported data are the averages of five experiments. The figures in parentheses indicate the standard deviations. The reaction conditions were as follows: 1 mL of MMA, 0.01 g of CdS, 0.2 mL of ethylene glycol, and 0.05 g of silk.

<sup>a</sup> Based on the weight of silk.

<sup>b</sup> Based on the total monomer taken.

**TABLE II**  
Effect of the Material-to-Liquid Ratio on Grafting

Reaction time (h)	Graft yield (%) <sup>a</sup>		Grafting efficiency (%) <sup>b</sup>		Homopolymer formation (%) <sup>b</sup>	
	1 : 15 ratio	1 : 100 ratio	1 : 15 ratio	1 : 100 ratio	1 : 15 ratio	1 : 100 ratio
2	10.20	15.77	9.27	9.62	10.52	25.45
4	18.67	37.84	10.06	10.24	15.89	41.23
6	24.59	48.45	10.26	11.04	21.65	45.27

The reaction conditions were as follows: 1–10 mL of MMA, 0.01 g of CdS, 0.2–2 mL of ethylene glycol, 0.05 g of silk, and 35°C.

<sup>a</sup> Based on the weight of silk.

<sup>b</sup> Based on the total monomer taken.

in the temperature.<sup>26</sup> An increasing trend in the results was also observed as the reaction time proceeded up to certain level. At the stipulated time (7 h) and reaction temperature, an increasing trend was not observed as shown in earlier cases when other conditions remained the same. This was probably due to the increase in the viscosity of the reaction mixture, as a high viscosity reduces termination more than it shows propagation. However, because of the extreme viscosity (viscosity increases due to increases in the amount of ethylene glycol in the reaction mixture), it may trap the primary radicals in a solvent cage and cause termination to occur faster than propagation.<sup>35</sup>

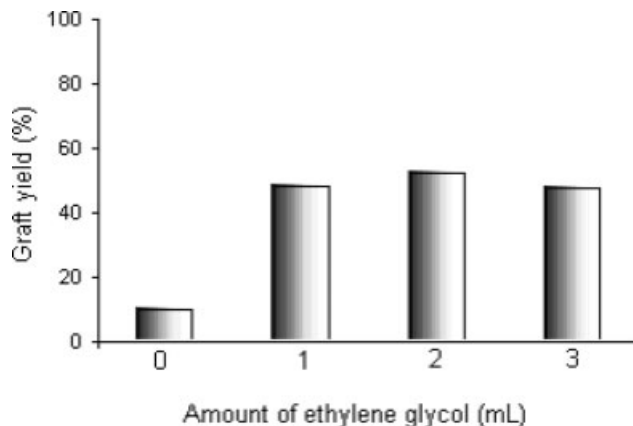
#### Effect of the material-to-liquid ratio

The effect of grafting on the variation of the material-to-liquid ratio is reported in Table II. The material-to-liquid ratio was varied by changes in only the quantities of the monomer and additive (swelling agent); the amount of the material was kept constant. The increase in the ratio from 1 : 15 to 1 : 100 enhanced the grafting, whereas a further increase in the

amount of the monomer reduced the grafting with increasing homopolymer formation. Therefore, an increase in the material-to-liquid ratio resulted in a dilution of the reactants. The dilution reduced the collision probability of the reaction ingredients, thereby reducing grafting.<sup>36</sup> Thus, the enhancement in the grafting up to a material-to-liquid ratio of 1:100 indicates that this particular amount of the liquid offers the most appropriate environment for collision probability among the reactants.

#### Effect of ethylene glycol on grafting

Ethylene glycol along with semiconductor-based photocatalysts has shown prominent effects on the photopolymerizations of different monomers.<sup>20</sup> It has been used in the graft copolymerizations of vinyl monomers onto silk fiber. The effect of the amount of ethylene glycol on grafting was observed with other variables kept constant, such as the amount of the initiator, monomer, and silk fiber, the temperature, and the exposure time. The graft copolymerization was also observed without ethylene glycol, and there was little conversion. The graft yield (%) against the amount of ethylene glycol is reported in Figure 2. An increase in the grafting was observed up to a certain amount of ethylene glycol (2 mL in 10 mL of the monomer). This may have been due to an increase in the viscosity of the reaction mixture.<sup>20</sup> However, an increase in the homopolymer formation also increased the viscosity to a certain extent.



**Figure 2** Effect of ethylene glycol on the graft copolymerization of MMA onto silk fibers (reaction conditions: MMA = 10 mL; temperature = 35°C; CdS = 0.01 g; exposure time = 6 h; silk fiber = 0.0598 g).

#### Graft copolymerization of AAm with a semiconductor-based photocatalyst

##### Effect of the variation of the exposure time

The effect of the exposure time on the grafting of AAm onto silk fiber was investigated, with other variables kept constant, such as the initiator, additive, and temperature. The graft yield, total conversion, and homopolymer formation on grafting are reported in Table III. An increasing trend was observed as the reaction time proceeded up to a cer-

**TABLE III**  
Effect of the Exposure Time on the Graft Copolymerization of AAm onto Silk Fibers

Reaction time (h)	Graft yield (%) <sup>a</sup>	Total conversion (%) <sup>b</sup>	Homopolymer formation (%) <sup>b</sup>
2	11.95	25.26	24.33
4	16.23	33.92	31.21
6	26.47	44.26	40.12
7	27.54	48.54	42.57

The reaction conditions were as follows: 10 mL of 1M AAm, 0.01 g of CdS, 1 mL of ethylene glycol, 0.05 g of silk, and 35°C.

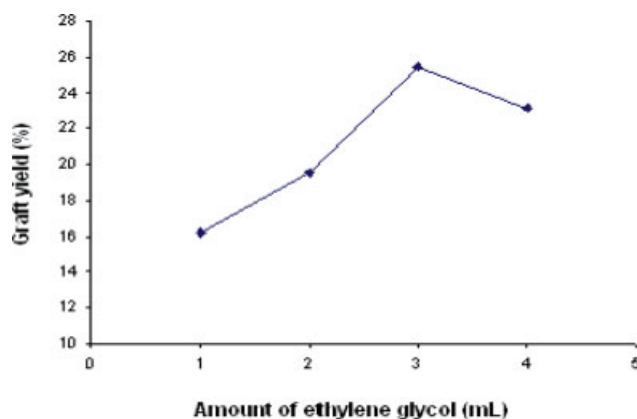
<sup>a</sup> Based on the weight of silk.

<sup>b</sup> Based on the total monomer taken.

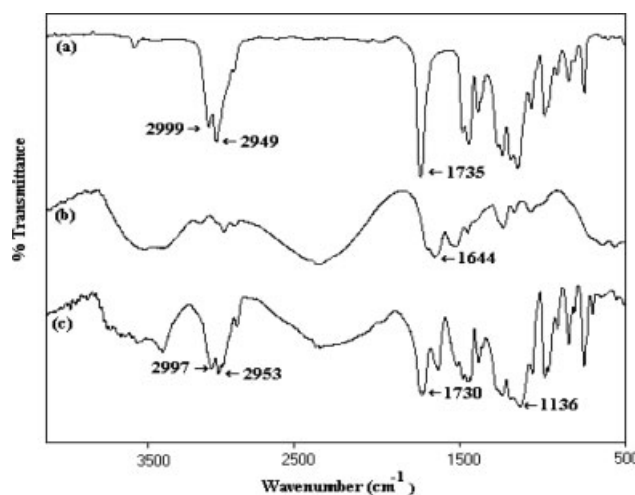
tain level (6 h). The increasing trend was as not prominent as earlier after 6 h of exposure under the same conditions. The increase in grafting with an increase in the exposure time was probably due to the generation of more active sites on the backbone of the fiber. In comparison with the grafting process with MMA onto the same silk, AAm/CdS/ethylene glycol generated more homopolymer formation along with the grafted product.

#### Effect of ethylene glycol on grafting

It has already been reported that ethylene glycol along with semiconductor-based photocatalysts has shown prominent effects on the photopolymerizations of different monomers.<sup>20</sup> The effect of the amount of ethylene glycol on grafting was observed with the other variables kept constant, such as the amount of the initiator, monomer, and silk fiber, the temperature, and the exposure time. The graft yield (%) against the amount of ethylene glycol is reported



**Figure 3** Effect of ethylene glycol on the graft copolymerization of AAm onto silk fibers (reaction conditions: 1M AAm = 10 mL; CdS = 0.01 g; temperature = 35°C; silk fiber = 0.05 g; exposure time = 4 h). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

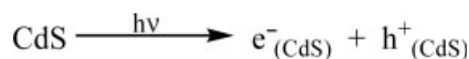


**Figure 4** FTIR spectra of (a) PMMA, (b) ungrafted silk, and (c) 10.20% grafted silk fibers.

in Figure 3. In the case of MMA/CdS/ethylene glycol; an increasing trend was observed with an increase in ethylene glycol up to a certain amount (2 mL with 10 mL of the monomer); after that, it showed a decreasing trend. A similar trend was also observed for the graft copolymerization of AAm onto silk fiber. This may have been due to an increase in the viscosity of the reaction mixture, as a high viscosity reduces termination more than it shows propagation.<sup>20</sup>

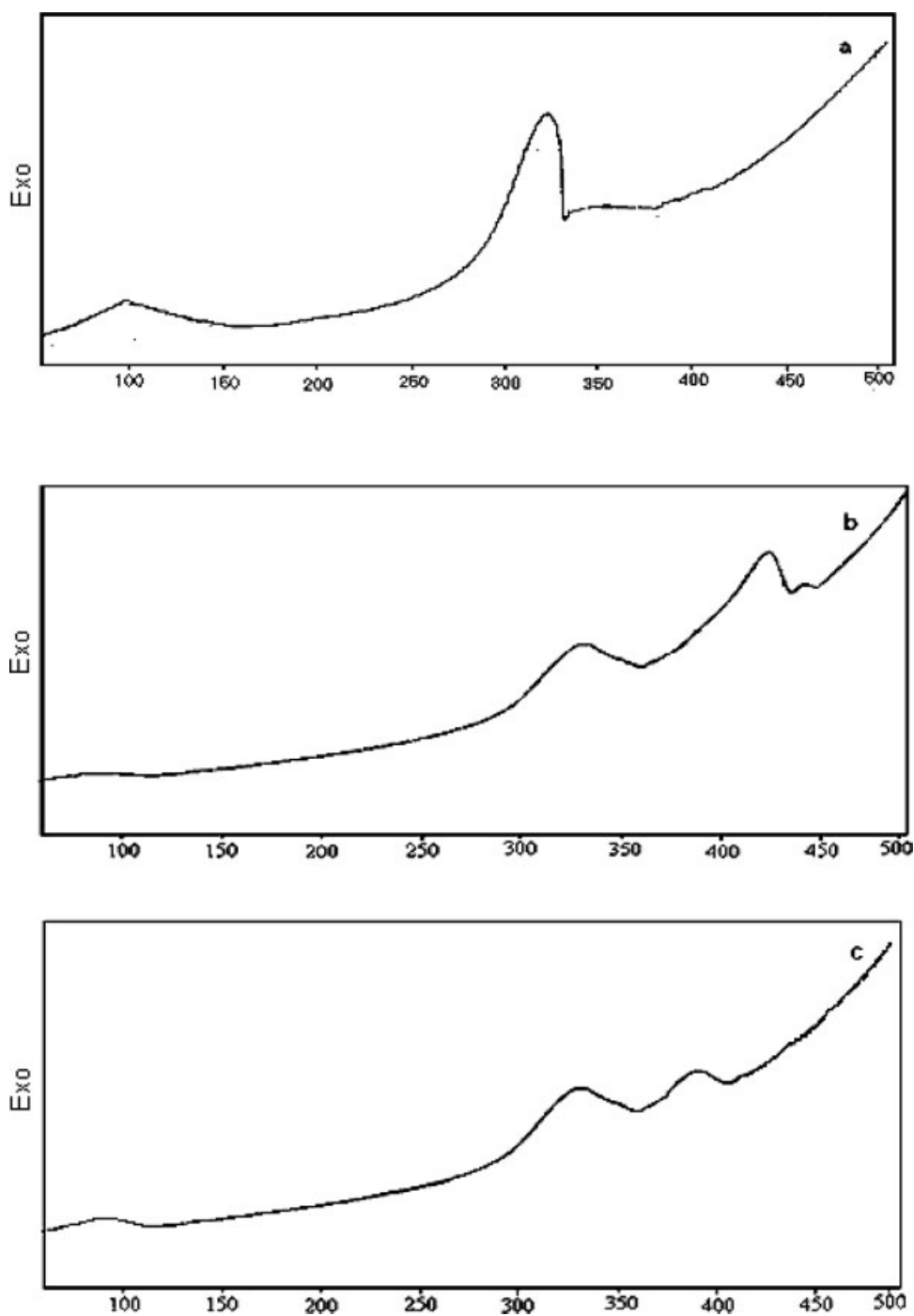
#### Reaction schemes for the graft copolymerization of vinyl monomers (MMA and AAm) onto silk fibers

The reaction scheme for the generation of free radicals on the fiber backbone and the initiation step may be represented by the following scheme, in which the semiconductor in the presence of light generates an electron in the conduction band and a positive hole is created in the valence band:<sup>35</sup>



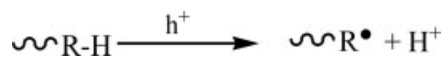
**TABLE IV**  
Characteristic Bands of IR Spectra of AAm-Grafted Fibers

Frequency (cm <sup>-1</sup> )	Conclusion
1645	C=O stretching vibration of the amide group (amide I)
1514	N-H bending vibration of the amide group (amide II)
2926	-CH <sub>2</sub> - stretching vibration of CH <sub>2</sub> =CH-



**Figure 5** DSC thermograms of (a) ungrafted silk, (b) 10.20% MMA grafted silk, and (c) 11.95% AAm grafted silk.

The positive hole can easily transfer the charge to a silk macromolecule by generating a free radical and proton:



where  $\sim\text{RH}$  and  $\sim\text{R}^\bullet$  represent the silk molecule and silk monomer radical, respectively. The propagation and termination steps possibly may proceed

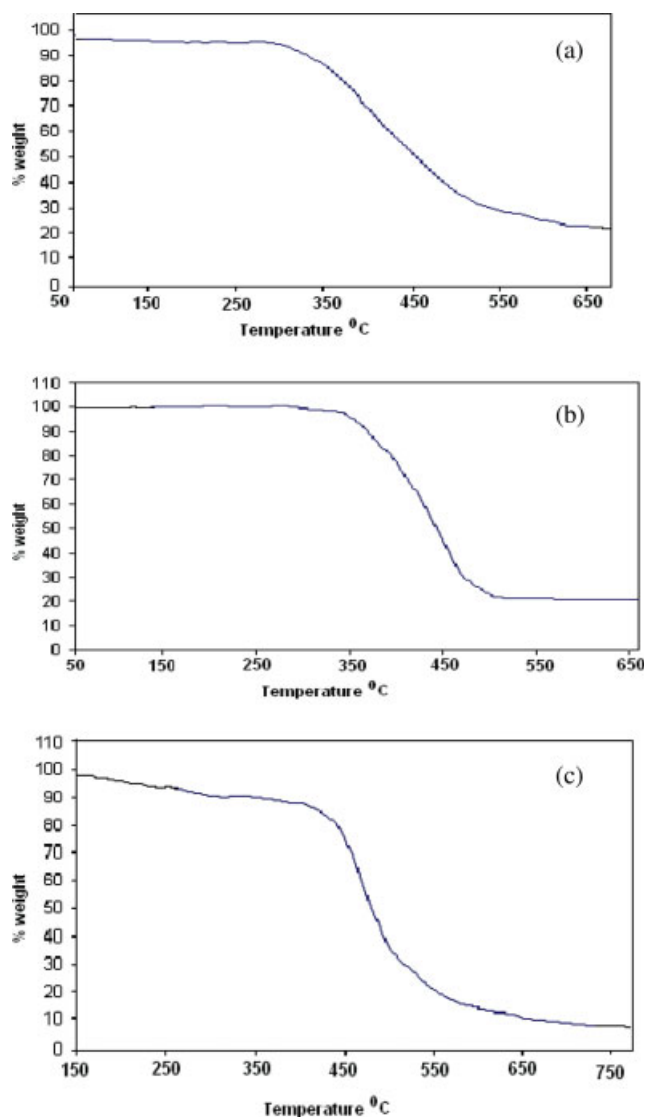
as follows (M stands for the monomer):

Initiation:



Propagation:

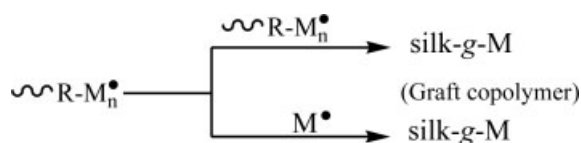




**Figure 6** TGA curves for (a) ungrafted silk fiber, (b) MMA-grafted silk fiber, and (c) AAm-grafted silk fiber. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



Termination:



In this scheme, monomer free radicals are generated during the reaction and further produce the homopolymer along with the grafted product.

### FTIR spectroscopy

The FTIR spectra of pure poly(methyl methacrylate) (PMMA), ungrafted silk, and silk-g-MMA are shown in Figure 4.

In the spectrum, PMMA showed a characteristic band at  $1735\text{ cm}^{-1}$  for the carbonyl group of the ester stretching vibration [Fig. 4(a)]. The sharp peak at  $1730\text{ cm}^{-1}$  for the grafted fiber indicated the presence of PMMA chains on the *B. mori* fiber, which was not prominent in the IR spectra of ungrafted silk fiber.<sup>35</sup> On the other hand, the bands at  $2997$  and  $2953\text{ cm}^{-1}$  in Figure 4(c) confirmed the free  $-\text{CH}_3$  vibration, and the band at  $1136\text{ cm}^{-1}$  for the  $-\text{C}-\text{C}-\text{O}-$  stretching further confirmed the formation of MMA-grafted silk, which is not prominent in Figure 4(b). The band for  $\text{NH}-$  stretching for ungrafted silk fiber was shifted from  $3447$  to  $3411$  and  $3295\text{ cm}^{-1}$  in Figure 4(c).

Similarly, IR spectra of polyacrylamide-graft-silk (PAAm-g-silk) were also recorded and are reported in Table IV. The grafted silk fiber showed the characteristics bands at  $1645$  and  $1514\text{ cm}^{-1}$ , which might be attributed to the  $\beta$  conformation of the crystalline regions. The IR spectra of the grafted silk fiber were not distinguishable, in that the monomer and silk had the same kind of functional group, that is,  $-\text{CONH}-$ . The band at  $2926\text{ cm}^{-1}$  for  $-\text{CH}_2-$  stretching was observed for the grafted silk fiber and may confirm the incorporation of polyacrylamide (PAAm) into the fiber.

### Characterization of the grafted product

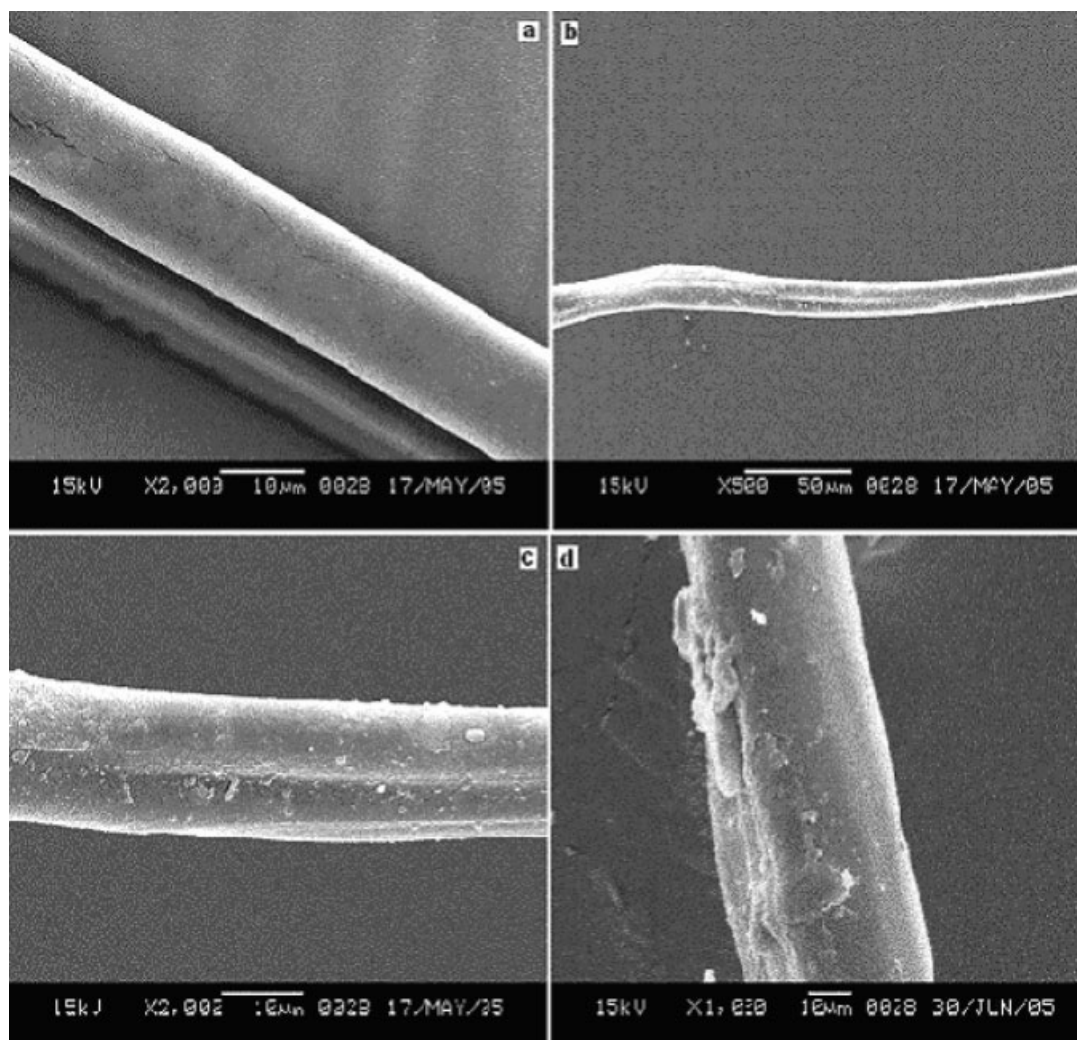
#### DSC thermograms

DSC thermograms of grafted [poly(methyl methacrylate)-graft-silk (PMMA-g-silk) and PAAm-g-silk] and ungrafted silk fibers are reported in Figure 5(a-c). The DSC thermogram of the ungrafted fiber shows one exotherm at  $320^{\circ}\text{C}$ , which is possibly due to the decomposition of the fiber. The grafted product shows two exotherms at  $330$  and  $410^{\circ}\text{C}$ , which are possibly due to the decomposition of the grafted fiber. The shifting of the initial decomposition temperature from  $320$  to  $380^{\circ}\text{C}$  for the grafted fibers

**TABLE V**  
Weight Losses of Ungrafted and Grafted Silk Fibers at a Heating Rate of  $10^{\circ}\text{C}/\text{min}$

Nature of silk	Temperature ( $^{\circ}\text{C}$ )			
	5% weight loss	10% weight loss	15% weight loss	50% weight loss
Ungrafted	306	337	361	450
MMA-grafted	350	370	379	444
AAm-grafted	214	350	420	479





**Figure 7** SEM micrographs of (a–d) MMA-grafted and (e–h) AAm-grafted silk fibers. The graft yields were (a) 0, (b) 10.20, (c) 18.67, (d) 24.59, (e) 11.95, (f) 16.38, (g) 17.25, and (h) 26.4 %.

indicate the increased thermal stability of the grafted fiber, whereas the homopolymer (PMMA) alone shows an exotherm around 360–380°C due to degradation.<sup>37</sup> The result was similar when the grafting was carried with a conventional initiator.<sup>38</sup>

The DSC thermogram of the grafted fiber (PAAm-g-silk) shows two exotherms at 330 and 360°C. The shifting of the exotherm can also be observed as in the earlier case, and this indicates the improvement of the thermal stability of the grafted fiber.

#### Thermal behavior from TGA

The thermal behavior of ungrafted and grafted silk fibers was analyzed with TGA. TGA was performed at a heating rate of 10°C/min. TGA curves for ungrafted and grafted fibers are plotted in Figure 6(a–c). The initial decomposition temperature was noted

from the TGA thermograms for the grafted and ungrafted fiber. The initial decomposition temperature for the ungrafted fiber was 306°C, whereas it was 350 and 370°C for the MMA-grafted and AAm-grafted fibers, respectively. This shows the higher thermal stability of the grafted fiber.

In terms of the weight loss, the grafted fibers showed a 10% weight loss at 370 (MMA-grafted) and 350°C (AAm-grafted) versus 337°C for the ungrafted fiber. A similar trend was observed in other values of the weight loss of the fibers (Table V), although the AAm-grafted fibers showed unusual behavior in the first phase of heating.

#### SEM studies

Morphological studies of ungrafted and grafted silk (PMMA-g-silk and PAAm-g-silk) fibers were per-

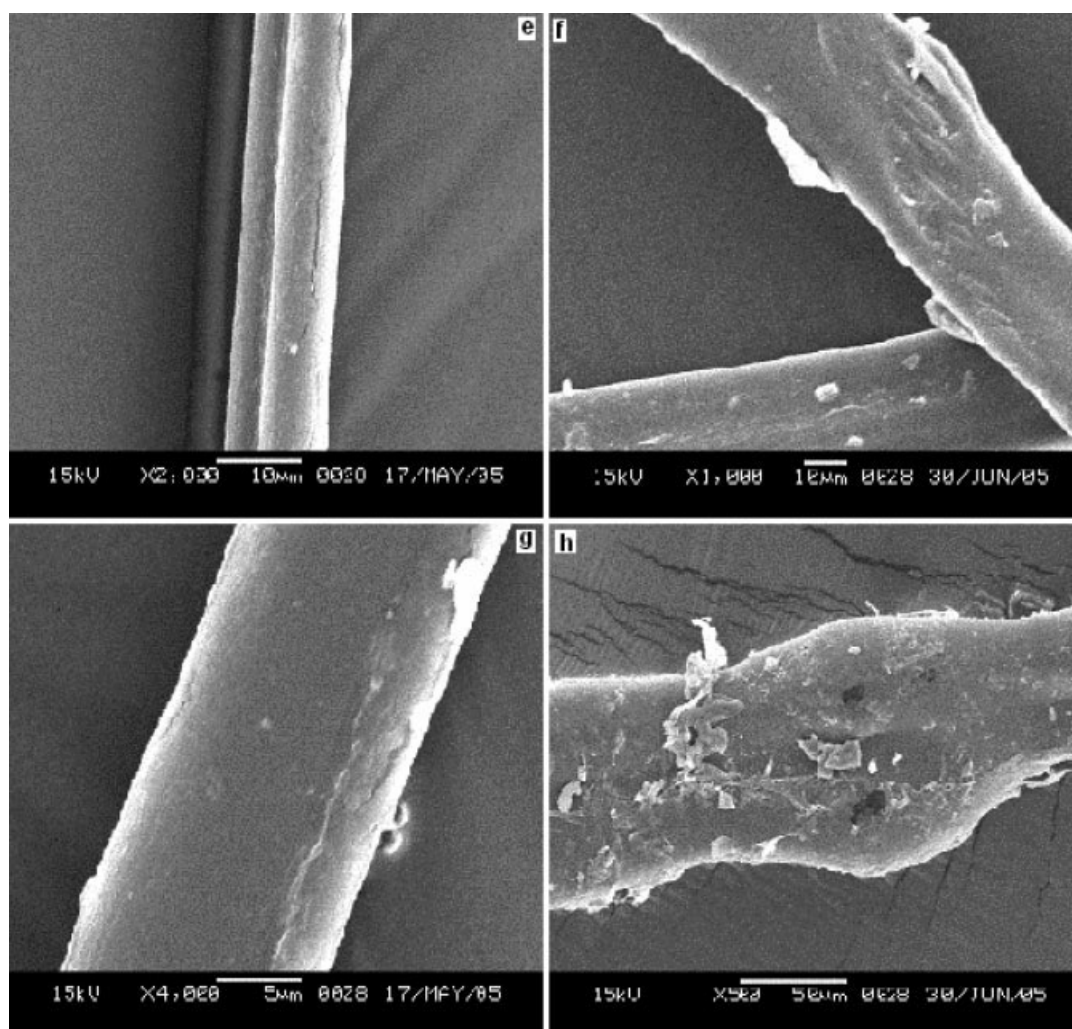


Figure 7 (Continued)

formed with SEM. The SEM micrographs of ungrafted and grafted fiber are shown in Figure 7(a–h). As semiconductor-based photografting is likely to occur on the surface of the fibers, grafting should leave its mark on the surface morphology of the fibers.<sup>37</sup> The smoothness and evenness of the fiber surface were observed in the micrograph of the ungrafted fiber. The change in the surface morphology after grafting with the monomers was clearly revealed by the SEM micrograph, as grafting affected the surface of the silk fibers. The unevenness of the surface resulted from the deposition of the polymer, which formed during the graft copolymerization with the monomers. The cracks in the surface of the ungrafted fiber [Fig. 7 (a)] were filled by the monomer that uploaded during the graft copolymerization in the grafted fiber [Fig. 7 (c)]. The roughness of the surface of the grafted fiber increased as the grafting percentage increased. These results are quite similar to those of Tsukada<sup>39</sup> for grafted fibers (PMMA loading silk), demonstrating the presence of granules that appeared chemically bonded and/or physically adhered to the surface of the

grafted silk fibers. However, the changes in the thermal and mechanical properties may support the idea that grafting is not merely a surface phenomenon.

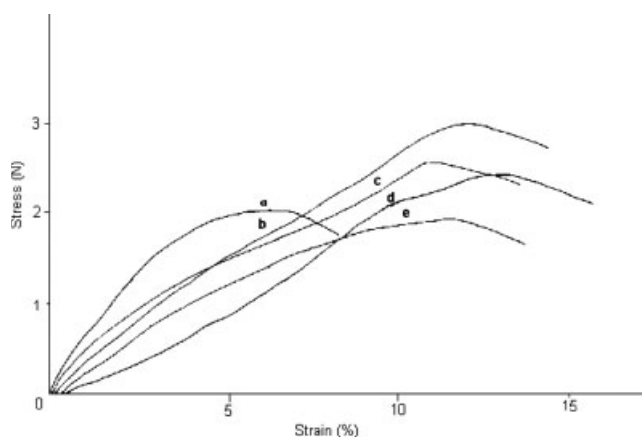


Figure 8 Stress-strain curves for ungrafted and grafted fibers: (a) ungrafted silk fiber, (b) MMA-g-silk (37.84% grafted), (c) MMA-g-silk (48.45% grafted), (d) AAm-g-silk (17.38% grafted), and (e) AAm-g-silk (26.47% grafted).

**TABLE VI**  
Effects of Chemicals on the Weight of Ungrafted and Grafted Fibers

Chemical	Weight loss after dipping for 24 h (wt %) <sup>a</sup>		
	Ungrafted silk	PMMA-g-silk	PAAm-g-silk
Acetic acid	7.14	15.38	18.75
Concentrated HCl	Dissolved	Slightly dissolved	Dissolved
60% NaOH	Dissolved	12.28	Slightly swollen
Benzene	4.95	3.47	4.61
Toluene	2.88	2.24	2.39
Concentrated HNO <sub>3</sub>	Dissolved	Slightly swollen	Partially dissolved

<sup>a</sup> The reported data are the averages of five experiments.

### Tensile strength

The stress–strain curves for ungrafted and grafted fibers with MMA and AAm are shown in Figure 8. Grafting resulted in an increase in the yield point and slope of the stress–strain curve. The elongation at break increased from 7 to 12% for the MMA-grafted fiber and to 14% for the AAm-grafted fiber. The decrease in the yield point for the grafted fiber could be observed as the grafting percentage increased. A similar nature was observed for the AAm-grafted fiber. On the other hand, the MMA-grafted fiber showed a high yield but a lower elongation at break than the AAm-grafted fiber. In the case of the MMA-grafted fibers, a lower elongation at break was expected because the flexibility of PMMA was lower than that of the PAAm uploaded fiber at room temperature. The increase in the elongation at break for the grafted fiber indicates that because of grafting, many of the intermolecular forces holding the chains together are broken, and this facilitates the slippage of molecules.<sup>40</sup> Furthermore, acrylic polymers except for MMA have glass-transition temperatures below room temperature, and this makes grafted polymers more easily extendable. This phenomenon is also reflected in a comparison of the slopes of stress–strain curves. With grafting, the slope gradually decreases; that is, the modulus of elasticity decreases.

### Chemical resistance

The effects of different chemicals on ungrafted and grafted silk fibers are reported in Table VI. When

treated with acetic acid, NaOH, benzene, and toluene, ungrafted and grafted silk fibers (PMMA-g-silk, 24.59% grafting; PAAm-g-silk, 26.47% grafting) lost their weight to some extent. In a 60% NaOH solution, the ungrafted silk fiber was dissolved, but both types of grafted fibers showed resistance toward the alkali. Moreover, nitric acid could not fully dissolve the grafted silk fiber even after 7 days.

Upon grafting, an overall improvement in the chemical resistance was observed. The weight loss in every case was reduced in the case of grafted fibers, but the MMA-grafted fibers showed better chemical resistance than the AAm-grafted fibers. This may be due to the nature of the hydrophobic side chains of the MMA polymer filled in the fiber.

### Water sorbency

The grafting of silk with PMMA imparted the hydrophobic nature of PMMA to the silk, as is evident from the WRVs of the ungrafted and grafted silks (Table VII). As the grafting percentage increased, WRV decreased. The low rate of grafting (%) did not show much variation of WRV from that of ungrafted silk. With an increase in the grafting on silk, the surface was covered with PMMA, which made the surface more hydrophobic and thereby reduced WRV.

A similar trend was also observed for the AAm-grafted fiber. The results showed that WRV of the grafted silk decreased with an increase in the grafting (Table VIII). The decrease in WRV might have been due to the decrease in the cohesive force of the highly swollen fiber.<sup>41,42</sup>

**TABLE VII**  
WRVs of Ungrafted and PMMA-Grafted Silk Fibers

Sample	Grafting (%)	WRV (g/g) <sup>a</sup>
Ungrafted silk	—	3.2
Grafted silk	2.51	3.1
	6.42	2.8
	10.20	2.6
	18.67	2.5
	21.52	2.4
	48.45	2.0

<sup>a</sup> The reported data are the averages of five experiments.

**TABLE VIII**  
WRVs of Ungrafted and AAm-Grafted Silk Fibers

Sample	Grafting (%)	WRV (g/g) <sup>a</sup>
Ungrafted silk	—	3.2
Grafted silk	4.56	3.0
	11.95	2.9
	16.23	2.7
	26.23	2.3
	26.47	2.0

<sup>a</sup> The reported data are the averages of five experiments.

## CONCLUSIONS

A semiconductor-based photocatalyst, in combination with additives ( $\text{Et}_3\text{N}$  and ethylene glycol), appears to be a promising initiator for the graft copolymerization of MMA and AAm onto silk fibers. However, variations in the amounts of the additives and the nature of additives have pronounced effects on the grafting process. SEM clearly illustrates the unevenness of the surface of grafted fibers. On grafting, an increase in the thermal stability has been observed. Moreover, the grafted fibers show increased chemical resistance, increased elongation at break, decreased slopes of stress-strain curves, and decreased WRVs to some extent.

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