

The Preparation of Poly[*N*(*n*-butoxymethyl) methacrylamide] Grafted Silk Fibers by Polymerization Using a Low pH System

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SYNOPSIS

The graft polymerizations of the *N*(*n*-butoxymethyl) methacrylamide (BMA) monomer onto silk fibers were effected after reducing the pH of the grafting system to 2.5 by the addition of a formic acid solution. We compared the grafting efficiencies, surface characteristics, and thermal behaviors, as well as the whiteness levels and the extent of reduction of the rate of yellowing following UV irradiation, with the equivalent features of poly(BMA)-grafted silk fibers, prepared under normal (pH 6) conditions. The grafting efficiency [as poly(BMA) weight gain] onto silk fiber that was attained was almost 100% through optimization of the pH environment in the polymerization system by the addition of formic acid. The stiffness of the silk fabrics observed, following the conventional grafting, was markedly higher than that of equivalent silks after the polymerization at pH 2.5. The rates of yellowness index increase, for these latter silk fabrics following UV irradiation, were also reduced, specifically in the initial irradiation period (up to 60 h).

The SEM of the grafted silk fabrics reveal the absence of granules on the surface of the grafted silk fiber, when the silk was grafted with poly(BMA), after reducing the pH of the grafting system to 2.5. These findings suggest that the BMA monomer was polymerized specifically within the silk fiber and not on the surface. It is suggested that the increase in the polymer weight gain, and the reduced adverse effect on the fabric handle, arise because of the modified polymer location. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Silk has outstanding mechanical properties, including high elastic modulus, moisture regain, and excellent fabric hand. In addition, silk is easily dyed with both acid and direct dyes.¹ However, silk does possess counterbalancing disadvantages, such as poor photoyellowing and wash and wear properties. Of these defects, the photoyellowing of silk is the major disadvantage, which limits its broader use as a textile fiber. This feature cannot be avoided, essentially because silk, as a natural protein fiber, inherently possesses chemical constituents, which re-

sult in polymer degradation and the loss of desirable features following exposure to either heat or sunlight. Research scientists have long been concerned with the development of an effective treatment or modification to reduce the consequential photoyellowing of exposed silk fabrics.²

Grafting and chemical modifications are the potential routes for improving the functional performances and to promote the wider utilization of silk fibers.³⁻⁴

The term "graft" is here employed, as in previous publications, to describe that polymeric material held by the fiber sample following the radical polymerization within the silk of the applied vinyl monomer.

Graft polymerization⁵⁻⁸ is anticipated to be a potentially powerful approach, capable of achieving a

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wide range of modifications to properties.⁹⁻¹¹ The grafting by radical polymerization of vinyl polymers, for example, poly(methacrylamide),¹² poly(methylmethacrylate)¹³ and poly(hydroxyethylmethacrylate),⁵ and poly(hydroxyethylmethacrylate/methacrylamide),⁶ to silk fibers has been extensively studied. In a series of investigations,¹⁴ we have shown that grafting can be achieved, with suitable monomers, without affecting the overall properties of the primary polymer substrate. However, the examination of alternative vinyl monomers for this purpose is only of recent origin.

In this previous study,¹⁴ the grafting of poly-*N*(*n*-butoxymethyl) methacrylamide (BMA) to the silks was achieved using approximately neutral conditions (pH 6.0), with an emulsifying agent system, which contained ammonium persulfate as initiator, with varying amounts of BMA monomer (with respect to the silk), at 80°C for 15 min. We demonstrated¹⁴ that poly(BMA) grafting onto silk was effective in reducing the rate of photoyellowing of the grafted silk fabrics that were subsequently exposed to UV. We also found that polymerization at pH 2.5 was more effective in not only increasing the grafting efficiency, but also in sustaining fabric handle, and fabric luster. It would, therefore, be relevant to compare positively the grafting efficiency and the product physical properties (including photoyellowing due to irradiation) of BMA graft-polymerized silk fibers, and fabrics produced at pH 6.0, with those produced in a system at a lower pH of 2.5.

In the present investigation, graft polymerization of BMA onto silk fibers was undertaken to improve the resistance to photoyellowing following UV irradiation, and to optimize the polymerization conditions towards this end. In this work, the physical properties of poly(BMA)-grafted silk fabrics, produced with and without the pH-reducing procedure using HCOOH, are analyzed. These studies should provide valuable technical information for improving the current grafting techniques.

EXPERIMENTAL

Materials

Habutae silk fabrics (plain weave *ca.* 60 g/m²) were used as a grafting substrate.

The *N*(*n*-butoxymethyl) methacrylamide (BMA) [Eq. (1)] was kindly provided by Mit-subishi Rayon Co., Ltd. to our requirements and was used without further purification.



The emulsifying agent (Newkalgen 1515-2H, Takemoto Yushi Co., Ltd), which contained a non-ionic emulsifying agent (polyoxyethylenonyl phenylether) and an anionic emulsifying agent (sodium dodecylbenzenesulfonate), was added at 10% on the weight of silk fabric. Then, 2.2% ammonium persulfate, on the weight of the BMA monomer, was added to the BMA plus silk fabric. Poly(BMA)-grafted silk fabrics, with different amounts of add-on, were thus prepared in the grafting system containing different amounts of BMA (15–60% on weight of fiber). The reduced pH of 2.5 for the grafting system was achieved by the addition of 2 mL/L formic acid solution. The pH of the grafting system, with or without the pH-reducing procedure of adding a formic acid solution, was, therefore, 2.5 and 6.0, respectively.

The poly(BMA)-grafted silk plain weave fabrics, with different values of polymer add-on, were thus produced (Table I).

The material to liquor ratio of 1 : 15 was maintained. The graft polymerization reaction was started at 40°C, was gradually raised from 40 to 80°C over a 15 min period, and then was maintained at this temperature for a further 45 min. At the end of the reaction, the treated silk was soaked at 80°C for 30 min in a solution containing 1 mL/L of an ether-type nonionic detergent (Nogen HC, Daiichi Kogyo Seiyaku, Ltd.). The silk was rinsed thoroughly with water to remove any unreacted BMA oligomers. The poly(BMA)-grafted silks used in this experiment, their grafting efficiencies, and their equilibrium regains, are presented in Table I.

Measurements

The percentage grafting efficiency (% *E*) was calculated from the increase in the weight of silk after grafting in the following manner:

$$\% E = (W_1)/W_2 \times 100$$

where W_1 and W_2 denote, respectively, polymer(BMA) add-on value and BMA amount (owf) contained in the grafting mixture system.

The % add-ons were measured according to the method described in a previous article.⁴⁻⁸

Heat flow DSC measurements were performed on a Rigaku Denki instrument (DSC-10A) at a heating rate of 10°C/min. The DSC sensitivity range and sample weight were 10.5 mL/s/10 mV and 2 mg, respectively. The open aluminium cell was swept with N₂ gas (flow rate 200 mL/min) during the course of the analysis. The onset of the induced DSC

Table I Physical Properties of Poly(BMA)-Grafted Habutae, Plain Weave Silks Graft-Polymerized Under Different Grafting Conditions

Sample	BMA ^a Amount (%)	Add-On (%)	Efficiency (E%)	Regain ^b (%)	Loop Length (mm)
Control	—	0	—	9.60	78
A-1 ^c	15	6.7	44.7	9.48	78
A-2	35	16.8	48.0	9.64	75
A-3	40	18.3	45.8	9.87	74
A-4	60	33.9	56.5	10.82	71
B-1 ^d	15	9.7	64.7	9.37	77
B-2	25	22.9	91.6	9.90	76
B-3	40	36.6	91.5	11.22	77

^a The amount of BMA was expressed as % of initial fiber weight.

^b Equilibrium regain.

^c A series of silks are those grafted without the pH-reducing procedure of the grafting system at pH 6.0.

^d B series of silks are those grafted with the pH-reducing procedure of the grafting system at pH 2.5.

peak theoretically provided the sample temperature assessment at which the observed change occurred. However, the identification of this feature from the recorded curves is often difficult and, assuming that the nature of the induced change remains unaffected, with the same heating rate, sample size, and presentation, then comparative information can be realistically provided from observations of movements in the recorded peak temperatures.

Infrared spectra were measured with a Perkin-Elmer FT-IR Spectrophotometer (1760×) in the spectral region 2000–400 cm⁻¹. KBr pellets were prepared for the IR measurement.

Poly(BMA)-grafted habutae silks were irradiated from a Carbon arc using a phadoemeter (WEL-25AX-HC-EC) from Suga Test Instrument Co., Ltd. Yellowness index values were calculated on a Color Computer (SM-3) from Suga Test Instrument Co., Ltd. The Whiteness (*W*) of each sample was calculated in the following manner:

$$W(L^*, a^*, b^*) = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}}$$

$$L^* = 116(Y/100)^{1/3} - 16$$

$$a^* = 500[(X/98.05)^{1/3} - (Y/100)^{1/3}]$$

$$b^* = 200[(Y/100)^{1/3} - (Z/118.10)^{1/3}]$$

where *L**, *a**, and *b** denote, respectively, the lightness, blueness, and yellowness values evaluated by a Suga Test Instrument AUD-SCH-2U colorimeter.

The Stiffness of silk fabrics was evaluated from measurements based upon the “hart loop” method (D-type), described in the JIS standard L1096-6.19.4.

RESULTS AND DISCUSSION

Equilibrium Regain

In Figure 1, the equilibrium regain values of the graft polymerized silk fibers are shown as a function of the % polymer add-on. For extents of add-on up to 15%, both sets of regain values (from the BMA-grafted silk fibers with or without the pH-reducing procedure) show no significant difference from the control sample. Above 15% polymer add-on, the equilibrium regains gradually rise with increasing

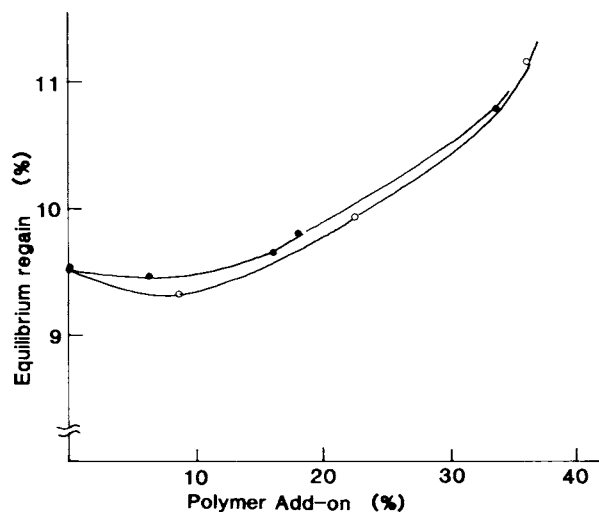


Figure 1 Equilibrium regain of poly(BMA)-grafted silk fibers produced in different grafting conditions. (●) Normal graft polymerization, (○) graft polymerization with formic acid.

polymer content. This has been attributed to the influence of the hydrophilic properties of the BMA polymer, inserted in the silk fibroin matrix. No significant difference between the poly(BMA) grafted silks from either polymerization process, with and without the pH-reducing procedure, was apparent.

Polymer Add-on and Fabric Stiffness

The measured polymer weight gains by the silk fibers in the BMA graft polymerizations are shown in Table I. The levels of poly(BMA) add-on to silk fiber, with the pH-reducing procedure using HCOOH, were higher than those achieved without the pH-reducing procedure. The loop length of the grafted silk fabrics with the pH reducing procedure remained unchanged, as compared with the untreated control, regardless of the grafting while, in contrast, the loop length for the grafted silks, produced without the pH-reducing procedure, decreased (and did not increase) with rising add-on. These findings suggest that the stiffness of the sample remained unchanged, regardless of the grafting that occurred after reducing the pH of the grafting system to 2.5. It is therefore desirable, when preparing grafted silks, to maintain the desirable hand of the fabric by the use of a pH-reducing procedure, such as the one described here.

Thermal Behaviors

Figure 2 shows the DSC curves for the poly(BMA)-graft polymerized silk fibers. The untreated control silk fiber displayed a major endothermic peak at 313°C, which has been attributed to the thermal decomposition of silk fibroin, presented in an oriented β' configuration.¹⁵ The DSC curve from the silk fiber containing poly(BMA), produced by the pH-reducing procedure at an add-on level of 36.6%, indicated, in addition to the major peak, which shifted to 324°C, a small broad endothermal effect at 240–250°C.

The DSC curves of the grafted silk fibers [Fig. 2 (b)], with the pH-reducing procedure, essentially do not differ from the grafted silk fiber [Fig. 2 (c)], without the pH-reducing procedure. The position of the major endothermic peak in both cases shifted to a higher temperature, following the poly(BMA) grafting. As discussed in a previous article, the broad, but shallow, endotherm at around 240–250°C has been assigned to the thermal decomposition of the graft poly(BMA) present in the silk fibroin matrix.

Infrared Spectra

To assist in the characterization of the molecular structure of the graft poly(BMA)-silk fibers, the infrared spectra were observed (Fig. 3). The spectra of the untreated control silk samples showed absorption bands at 1969 and 1654 cm^{-1} (amide I), 1521 cm^{-1} (amide II), 1260 and 1231 cm^{-1} (amide III), and 1079, 689, and 635 cm^{-1} (amide V). It was not possible to observe any significant difference between the absorption bands of either of the graft poly(BMA)-silk fibers [Fig. 3 (a, b)] and the control silk fiber [Fig. 3 (c)].

Change in Whiteness Following Irradiation

In a previous article, we demonstrated that there was a considerable effect following the grafting of poly(BMA) onto silk fiber without the pH-reducing procedure. In comparison with untreated fabrics, a reduced rate of yellowness index increase following

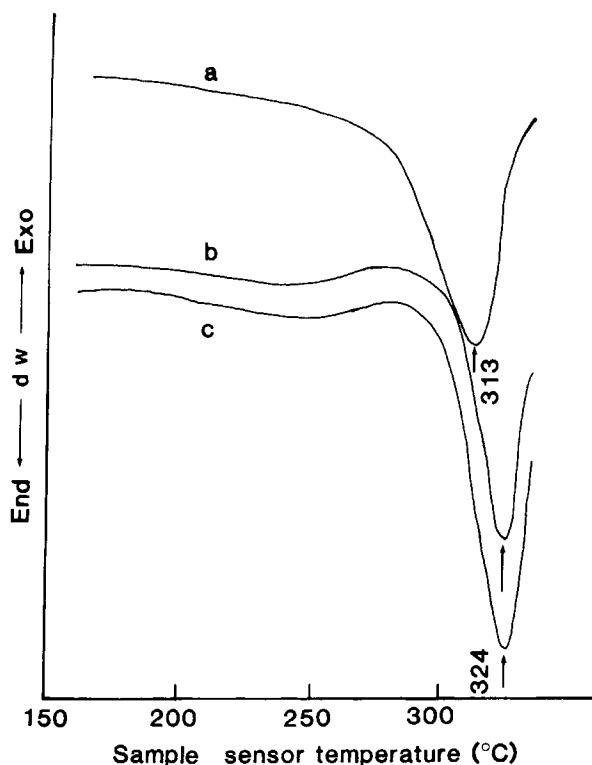


Figure 2 DSC curves of untreated control (a) and poly(BMA)-grafted silk fibers, obtained in different grafting conditions. (b) Prepared with formic acid with add-on of 36.6%. (c) Prepared without formic acid with add-on of 33.9%.

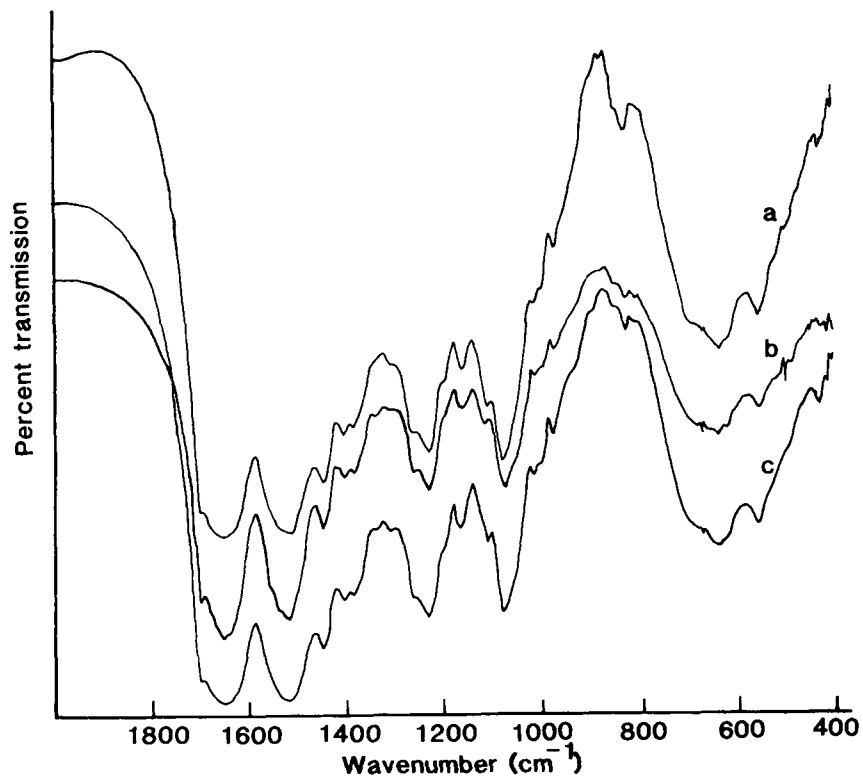


Figure 3 Infrared spectra of the control (a) and the poly(BMA)-grafted silk fibers, produced in different grafting conditions. (b) Poly(BMA)-grafted silk fibers with add-on of 36.6%, produced with formic acid. (c) Poly(BMA)-grafted silk fibers with add-on of 33.9%, produced without formic acid.

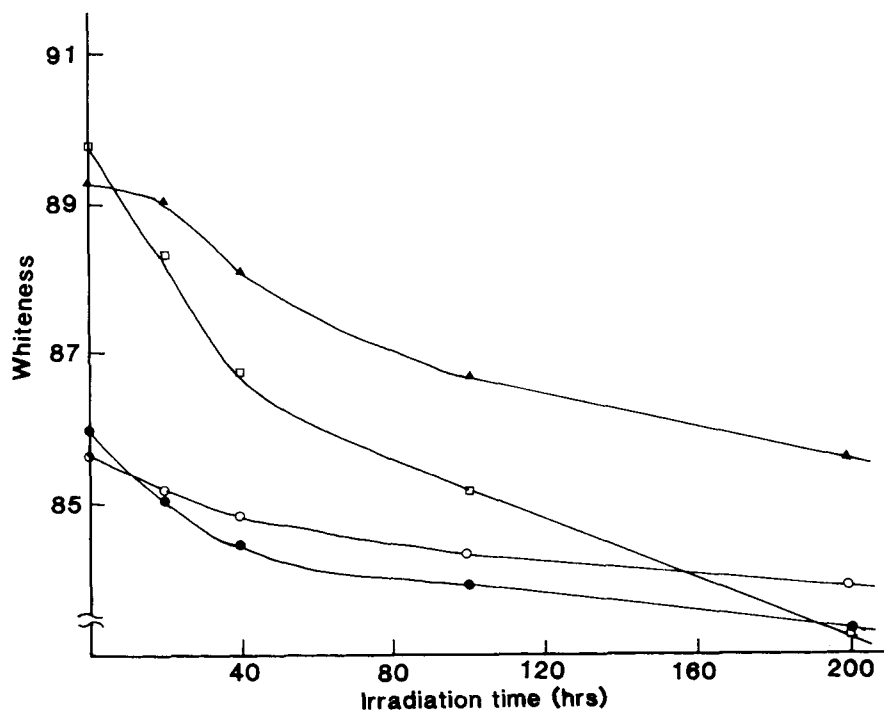


Figure 4 The whiteness of the control (□) and poly(BMA)-grafted silk fabrics with different add-on values following carbon arc irradiation (385 nm; 490 W/m²), as a function of irradiation time. (▲) Poly(BMA)-grafted silk fibers with add-on of 33.9%, produced without formic acid. (●) Poly(BMA)-grafted silk fibers with add-on of 9.7%, produced with formic acid. (○) Poly(BMA)-grafted silk fibers with add-on of 22.9%, produced with formic acid.

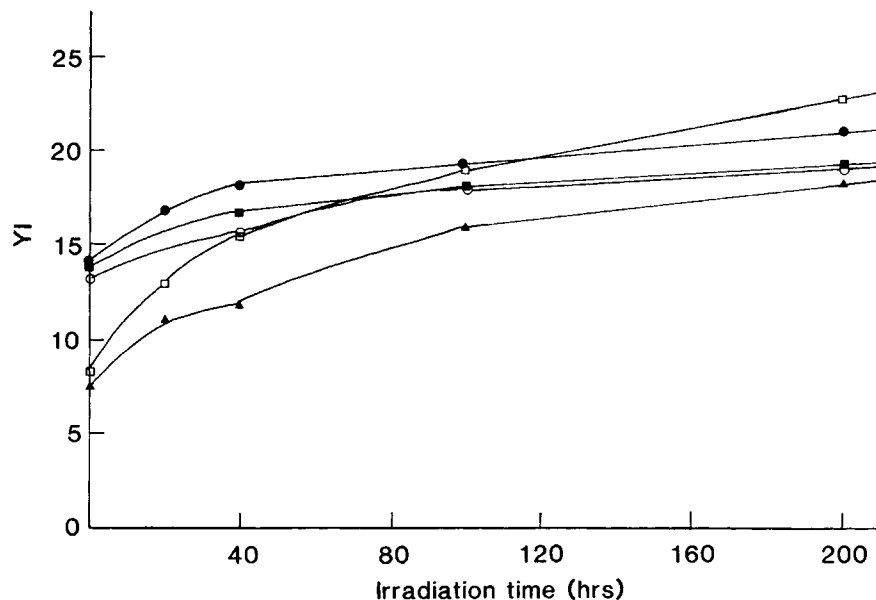


Figure 5 Yellowness index of the control and poly(BMA)-grafted silk fibers. The samples are identified in Figure 4.

UV irradiation was observed. It is valuable to compare the relative resistances to photodegradation of grafted silk fibers, produced both with and without the pH-reducing procedure. Figure 4 shows the reductions of whiteness of the poly(BMA) grafted silk, following exposure to carbon arc irradiation (major wavelength 385 nm and intensity 490 W/m^2). The whiteness of the control (untreated silk) exhibited a gradual decrease, particularly in the initial period of irradiation. The rate of photoyellowing of the grafted silk fiber, without the pH-reducing procedure, was retarded by the poly(BMA) treatment. The initial whiteness values (Fig. 4), as well as yellowness index values (Fig. 5), of the poly(BMA)-grafted silk fabrics from the pH reducing procedure show an initial fall compared to the control silk, but upon prolonged exposure to UV, further changes in whiteness are small. The procedure of poly(BMA) grafting onto silk, with and without the pH-reducing system, are both effective in decreasing the rate of photoyellowing. The extents of this reduction increase with increasing polymer add-on, particularly when no pH control is employed.

To achieve an insight into the mechanisms both of the grafting of the poly(BMA) onto silk and of the reduction in the photoyellowing of treated silks by UV irradiation, a schematic representation of the poly(BMA)-grafted silk fibers and a possible scheme to explain the improved protection from photo yellowing is shown in Figure 6. If the pH of the polymerization system is reduced by formic acid,

the polymerizations are considered to proceed mainly within the silk fibers and not on their surface. In contrast, graft polymerizations of BMA to silk, without pH control, occur on the surface of the silk fiber. It is suggested that there are BMA oligomers present on the surface of the fiber in the latter systems, which absorb the UV irradiation energy, and act as a screen preventing the active UV components from reaching the photosensitive fibroin elements. In a previous article, where we describe the poly(methylmethacrylate) CMMA grafting onto

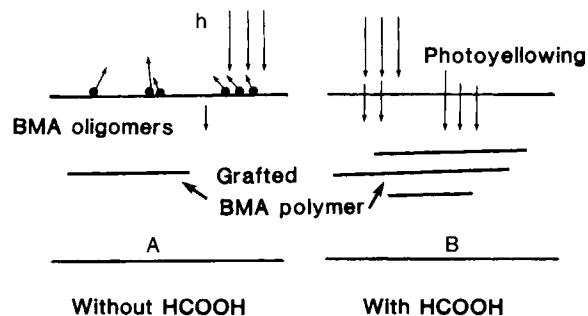


Figure 6 Schematic representation of the prevention of photoyellowing, following irradiation by UV (carbon arc, 385 nm). (A) Photoyellowing of poly(BMA)-grafted silk was prevented because of the absorption of incident light energy by the BMA oligomer granules on the fiber surface. (B) Graft BMA polymer was present primarily in the core of the silk fibroin following irradiation; photoyellowing can occur.

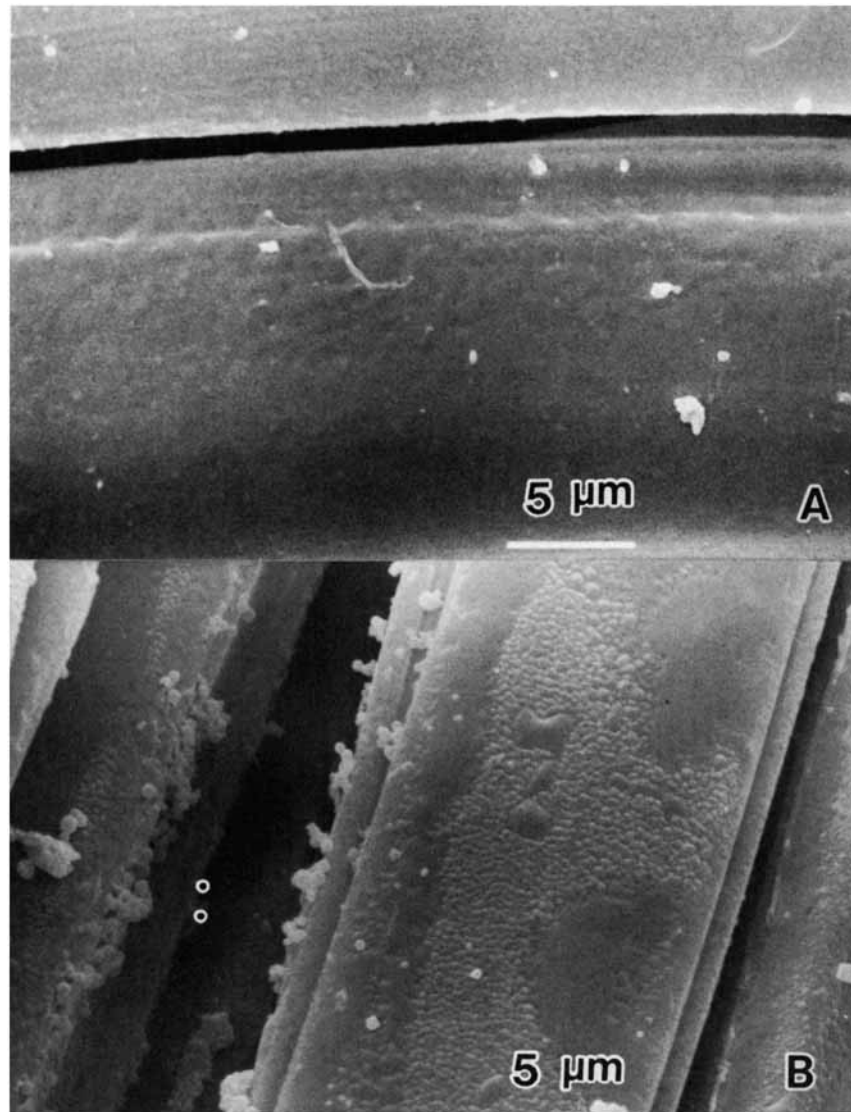


Figure 7 SEM of the poly(BMA)-grafted silk fibers produced by the different grafting conditions. (A) Silk graft, produced with formic acid; polymer add-on 36.6%. (B) Silk graft, produced without formic acid; polymer add-on 33.9%.

silk, we concluded that the several small granules, observed on the surface of the silk fibers possessing high polymer weight gain values, could be MMA oligomers, as these adhering particles are easily removed by extraction with hot acetone for 20 min. It was determined that these MMA oligomers possessed a mol wt of only 1000.

Surface Characteristics

Figure 7 shows the SEM photo micrographs of the poly(BMA)-grafted silk fibers, produced with (A) and without (a), which is the formic acid pH reducing procedure.

The surfaces of the grafted silk fibers with the pH reducing procedure appeared smooth, which was similar to those of the control silk fibers. However, the photomicrographs of the poly(BMA) graft silk fibers, achieved without the pH reducing procedure, revealed the presence of regular surface granules. These observations suggested that by reducing the pH of the polymerization medium, the result is an overall increase in the polymer add-on and a decrease in the number of BMA oligomers that chemically or physically bond to the surface of the silk. Polymerizations at low pH result in poly(BMA) held within the silk matrix of the fiber core. These results are consistent with the experimental obser-

vations of the weight gains and stiffnesses of the graft polymerized silk fabrics.

CONCLUSION

The equilibrium regains and IR spectra of the grafted silk fibers, prepared either under normal procedures or in a reduced pH environment, show little dependence upon the BMA grafting conditions. Polymerization of BMA occurred preferentially inside the silk fiber and not on the surface of the silk fiber when the reduced pH procedure was employed. As a consequence, an increase in the grafting efficiency and a reduced influence on the fabric handle (demonstrated by the stiffness) was apparent. The rates of yellowness index increase, following irradiation by UV of these polymer grafted silks, were, however, slightly reduced if compared with those of poly(BMA)-silks prepared under normal conditions.

The greater reduction in the rate of change of the yellowness index for the grafted silks, prepared by normal procedures, suggests that the BMA oligomers on the surface of the silk fiber specifically absorb the UV irradiation energy, thus limiting the photo degradation of the core silk fibroin. The presence of the surface granular form of the BMA oligomer is due to the formation of a monomer-complex by the action of BMA with silk fibroin. The precise mechanism for the BMA oligomer formation requires more detailed analysis.

The evidence presented above has supported the understanding that the polymerization, when the pH-reducing procedure of the grafting system was employed, occurred preferentially within the silk fiber and not on the surface of the silk fibers. The higher grafting efficiency, and the minimal change the handle of the silk fabrics achieved when the polymerizations were at pH 2.5, are closely related to differences in the graft polymerization modes for

BMA in systems with and without pH control. The reduction in the rate of increase in the yellowness index following UV irradiation is believed to be due to the BMA oligomers held on the surface of the silk fibers, which absorb the UV irradiation energy.

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