

# Properties of Poly(styrene)-“Grafted” Silk Fibers and Molecular Weight of Poly(styrene)

GIULIANO FREDDI,<sup>1\*</sup> YOSHIO ISHIGURO,<sup>2</sup> NOBUTAMI KASAI,<sup>3</sup> JOHN S. CRIGHTON,<sup>4</sup> and MASUHIRO TSUKADA<sup>5</sup>

<sup>1</sup>Stazione sperimentale per la Seta, via G. Colombo 81, 20133 Milano, Italy, <sup>2</sup>Yokohama Center for Quality Control and Consumer Service, Kitanaka Dori, Yokohama 231, Japan, <sup>3</sup>Kobe Women's University, Suma, Kobe 654, Japan, <sup>4</sup>University of Leeds, Department of Textiel Industries, Leeds LS2 9JT, UK, and <sup>5</sup>National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan

## SYNOPSIS

Poly(styrene) was grafted onto silk fibers in an aqueous medium, using ammonium persulphate initiator. Add-ons of up to 100% were achieved. The add-on increased linearly with the monomer concentration of the grafting system, all other factors remaining constant. The yield of the reaction attained about 80% and the extent of homopolymerization was negligible. The equilibrium moisture regain decreased noticeably with increasing add-on. Breaking load showed a tendency to increase in the 0–55% range of poly(St) content, while elongation at break and work of rupture decreased. The DSC endothermal peak at 315°C slightly shifted towards higher temperature by graft-copolymerization, and a new endothermal transition appeared beyond 400°C. TG measurements showed an increase of weight retention beyond 300°C for poly(St)-“grafted” silk fibers. The dynamic mechanical behavior was characterized by a shift to lower temperature of the loss modulus peak. The transverse dimension of the fibers increased with increasing add-on. The polymeric residue remaining after alkaline dissolution of silk fibroin showed a porous texture with a sponge-like morphology. The molecular weight of poly(St) removed from silk increased up to 120 kDa in the 0–55% add on range and then remained constant. The “Poly(St)/Silk” molar ratio increased linearly over the add-on range examined. © 1996 John Wiley & Sons, Inc.

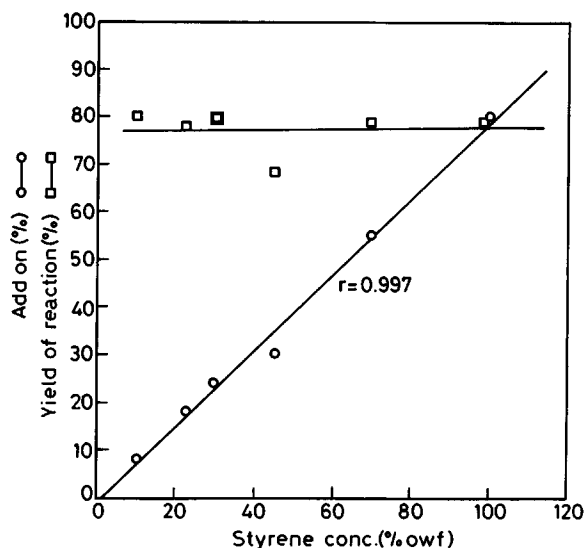
## INTRODUCTION

The graft-copolymerization of vinyl monomers onto *Bombyx mori* silk fibers, in particular, grafting with methacrylamide,<sup>1,2</sup> is widely applied on an industrial scale as weighting treatment, aiming at increasing silk weight in order to compensate for the loss resulting from degumming. However, in recent years grafting is regarded not only as an effective means to increase silk weight, but also as a powerful method to improve the textile performance of silk, such as crease recovery, dimensional stability, rub resis-

tance, photoyellowing, oil and water repellency, color fastness, etc.<sup>3–8</sup>

Among the grafting agents applied onto silk, styrene (St) was popular during the early 70s. The bulk and fullness of handle of such poly(St)-“grafted” silk fibers provided aesthetic appeal. Significant improvement in crease recovery was achieved at about 30% add-on.<sup>9</sup> Beyond this value the fibers became too stiff. Resistance to aqueous soil was also improved. The increased affinity for disperse dyes let to envisage the possibility of developing new textile goods by blending silk with man-made fibers.<sup>10</sup> However, because the use of styrene also entailed some disadvantages (fiber hydrophobicity, electrostatic charge, soft loss, air pollution), it was gradually replaced by other grafting agents with a softer impact on both silk fibers and processing plants.<sup>1</sup>

\* To whom correspondence should be addressed.



**Figure 1** Add-on and yield of reaction of poly(St)-"grafted" silk fibers as a function of styrene concentration in the grafting system.

The application of the graft-copolymerization techniques is currently confined to the textile field. However, silk is becoming an attractive material not only for textile but also for nontextile uses.<sup>11</sup> Applications in the biotechnological (enzyme immobilization) and biomedical (sutures) fields have already been reported,<sup>12</sup> and "grafted" silk fibers may present characteristics exploitable for nontextile applications.<sup>13</sup> In this respect, some drawbacks (stiffness, hydrophobicity, homopolymerization, etc.) that limit the use of certain grafting agents for the production of textile silk goods might then become less important for manufacturing other silk-based materials.

The study of silk fibers modified with various grafting agents covers both scientific and technological aspects. The latter may lead to improve the current processing techniques, while the former mainly focus on the fine structural changes induced

by grafting, as well as on the polymer-substrate interactions. The molecular weight of the polymer may exert an influence on the properties and performance of the resulting graft-copolymer.<sup>14,15</sup> In a previous study on poly(methyl methacrylate)-"grafted" silk fibers<sup>16</sup> we reported that the molecular weight of poly(MMA) increased with increasing add-on, while the "Poly(MMA)/Silk" molar ratio attained a constant value characteristic of the initiation system used. The present study deals with the characterization of the physical, mechanical, and thermal properties of poly(St)-"grafted" silk fiber, as well as with the determination of the average molecular weight of poly(St) separated from silk fibers. It is noteworthy that in this study, as well as in the previous ones,<sup>1</sup> the term "grafted" silk is employed to describe the material obtained from *in situ* polymerization and subsequent monomer/oligomer extraction. In fact, it is recognized that the polymer may be not only chemically bonded but also physically held within the fiber structure.

## EXPERIMENTAL

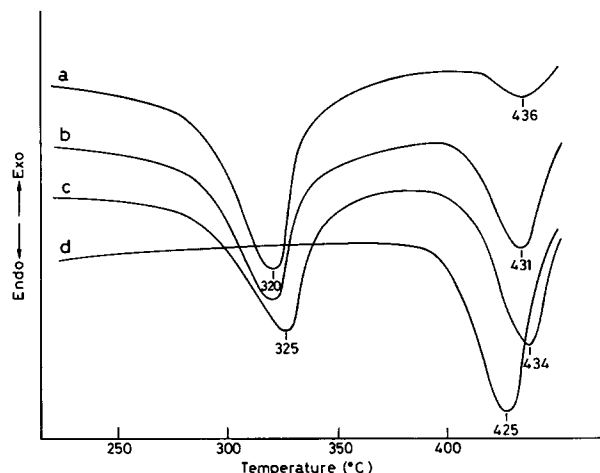
### Materials

Silk yarn, obtained from reeling of *Bombyx mori* cocoons, was degummed with an aqueous solution of 0.7% Marseille soap (w/v), at 98°C for 1 h. The yarn was thoroughly rinsed several times with deionized water and then dried at room temperature before being used as grafting substrate.

Dried fibers were immersed in the grafting system containing different amounts of styrene monomer (from 10 to 100% on weight of fibers (owf)), 1.8% owf ammonium persulphate (APS), and 1 g/L nonionic surfactant (Noigen HC, Daiichi Kogyo Seiyaku LC., Ltd.). APS and styrene were commercial products purchased from Wako Pure Chemical Indus-

**Table I** Equilibrium Moisture Regain and Tensile Properties of Poly(St)-"Grafted" Silk Fibers

Add-on (%)	Moisture Regain (%)	Breaking Load (g)	Tenacity (g/den)	Elongation at Break (%)	Work of Rupture (gf × mm)
Control	9.8	448 ± 9.5	3.2	17.7 ± 0.3	3432 ± 144
8	8.6	449 ± 7.7	3.1	14.5 ± 0.3	2442 ± 143
18	5.7	475 ± 5.9	3.0	14.2 ± 0.3	2599 ± 117
24	4.9	462 ± 17.6	2.8	14.8 ± 0.4	2323 ± 165
55	3.8	481 ± 6.3	2.5	13.6 ± 0.2	2545 ± 113
80	3.5	455 ± 10.8	2.0	13.2 ± 0.2	2143 ± 141



**Figure 2** DSC curves of poly(St)-"grafted" silk fibers with 24% (a), 55% (b), and 80% (c) add-on, and of poly(St) separated from the fibers with 55% add-on (d).

tries, Ltd. The pH of the grafting systems was adjusted to 3.0 by adding about 2 g/L formic acid. The material-to-liquor ratio was maintained at 1 : 15. The temperature was gradually raised from 35 to 80°C over 30 min and then held constant for 60 min. At the end of the polymerization the yarn was soaked in a solution containing 1 g/L nonionic detergent at 80°C for 30 min, rinsed thoroughly with water, and dried at room temperature. The percentage of weight increase of silk yarn (add-on) and the extent of polymerization (yield of reaction) were calculated as follows:

$$\text{Add-on (\%)} = [(W_2 - W_1)/W_1] \times 100$$

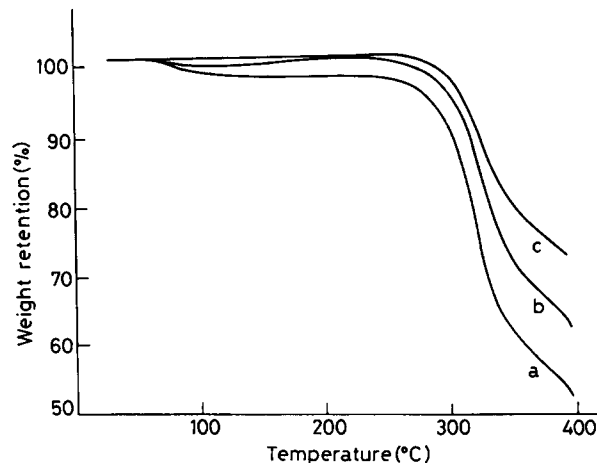
$$\text{Yield of reaction (\%)} = [(W_2 - W_1)/W_3] \times 100$$

where  $W_1$ ,  $W_2$ , and  $W_3$  denote the weight of the original silk sample, that of the same sample after grafting and that of the monomer, respectively.

Poly(styrene) was separated from poly(St)-"grafted" silk fibers by alkaline treatment. About 0.1 g of fibers were immersed in a solution containing 0.8 g NaOH, 20 mL of sodium hypochlorite, 20 mL of deionized water. The temperature was raised to 65°C in 20 min and held constant for 3 h. The undissolved residue was collected by centrifugation, rinsed with water, and dried before subsequent analysis.

### Measurements

Equilibrium moisture regain was determined in standard conditions at 20°C and 65% relative humidity (R.H.).

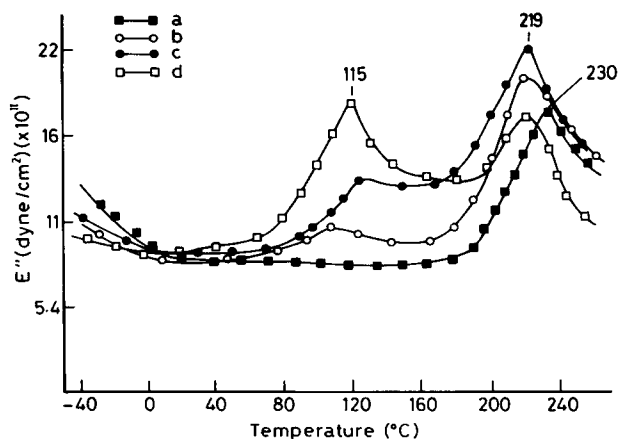


**Figure 3** TG curve of untreated (a) and poly(St)-"grafted" silk fibers with 55% (b) and 100% (c) add-on.

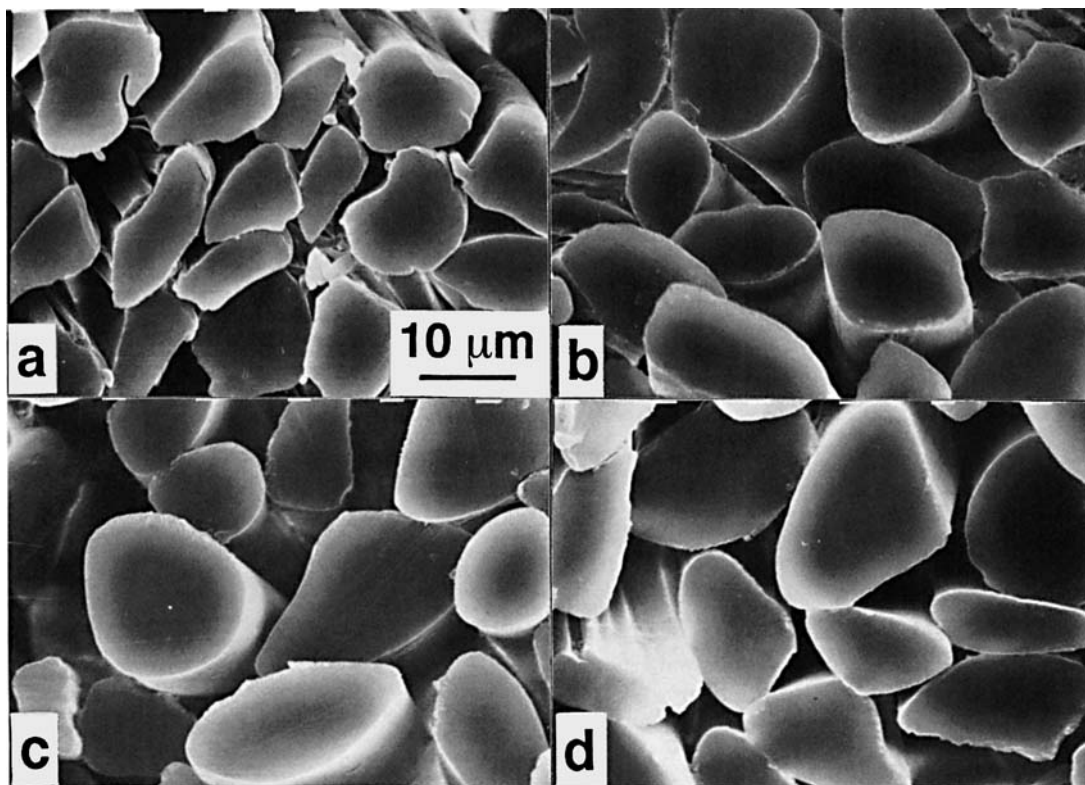
Tensile properties were measured with an automatic tensile testing machine (Tensilon UTM-II, Toyo Baldwin Co., Ltd.) in standard conditions. Each value is the average of 20 measurements.

Heat flow differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki instrument (DSC-10A) at a heating rate of 10°C/min. The DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open aluminium pan was swept with  $N_2$  gas during the course of the heating process.

Thermogravimetric analyses (TG) were run under  $N_2$  on a Rigaku Denki Co., Ltd. instrument. The heating rate was 10°C/min and the temperature range studied was from 25 to 400°C.



**Figure 4** Loss modulus curves ( $E''$ ) of untreated (a) and poly(St)-"grafted" silk fibers with 24% (b), 80% (c), and 100% (d) add-on.



**Figure 5** SEM photographs (cross-sectional view) of untreated (a) and poly(St)-"grafted" silk fibers with 24% (b), 55% (c), and 80% (d) add-on.

Dynamic mechanical (DMA) properties were measured using a Toyoseiki Rheograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from  $-50$  to  $260^{\circ}\text{C}$ , and samples were heated at  $2^{\circ}\text{C}/\text{min}$ . Sample length was 15 mm, with initial tension of 30 gf.

The longitudinal and cross-section surfaces of untreated, poly(St)-"grafted" silk fibers, and poly(St) separated from the fibers were examined with a JEOL JAX-333S scanning electron microscope (SEM), after gold coating, at 15 keV acceleration voltage.

Size exclusion chromatography (SEC) was run with a Japan Spectroscopic Co., Ltd. TRI ROTAR-V instrument, equipped with a UV detector (Jasco, UVIDEC-100-S) operating at 260 nm. The separation system consisted of a series of Shodex A-80M columns, so that a wide range of molecular weight was studied. The low molecular weight fraction was selectively analyzed by using a Finepack GEL 101 column. Tetrahydrofuran (THF) was used as mobile phase after purification by 48 h refluxing over potassium metal followed by vacuum distillation. The flow rate and sample concentration were 1 mL/min

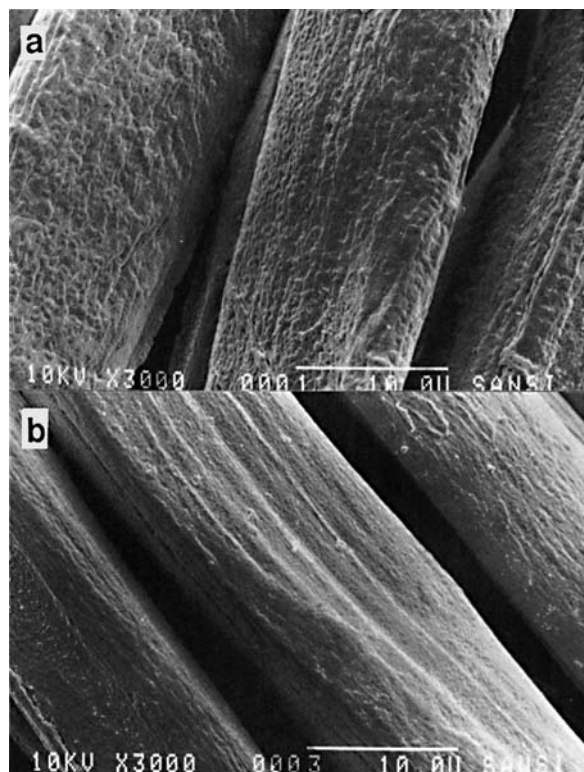
and 3 mg/mL, respectively. The SEC system was calibrated with a series of poly(styrene) standards.

## RESULTS AND DISCUSSION

### Add-On and Tensile Properties

Poly(St)-"grafted" silk fibers of increasing add-on values were obtained by raising the concentration of monomer in the reaction system. The add-on increased linearly with monomer concentration (Fig. 1). Other grafting agents<sup>17</sup> have shown a closely similar behavior when applied onto silk fibers in aqueous medium by using a chemical redox system (APS) as initiator. The extent of polymerization reached a limiting value of about 80%, remaining constant over the entire add on range examined. Homopolymerization, for instance, polymer deposition on the fiber surface, was negligible. This feature, as well as the high yield of the grafting reaction, is an important prerequisite for the application of grafting processes on an industrial scale.

Grafting with poly(St) caused a drastic decrease of equilibrium moisture regain, the extent of reduc-



**Figure 6** SEM photographs (longitudinal view) of poly(St) separated from poly(St)-“grafted” silk fibers with 24% (a) and 80% (b) add-on.

tion being larger in the low add on range (<50%) (Table I). The higher hydrophobicity of “grafted” silk fibers may be related to the poly(St) chains present in the nonordered volumes of the fiber, which either masked the groups responsible for binding water or acted as a barrier against moisture diffusion. The decreased moisture content is known to cause slight to drastic changes in silk fiber properties, with variable consequences not only on silk processing (dyeing, printing, etc.), but also on the end-use and maintenance of silk goods. While handle and comfort may be negatively influenced by a lower degree of moisture absorption, crease recovery, water staining and “wash and wear” may present improved performance.

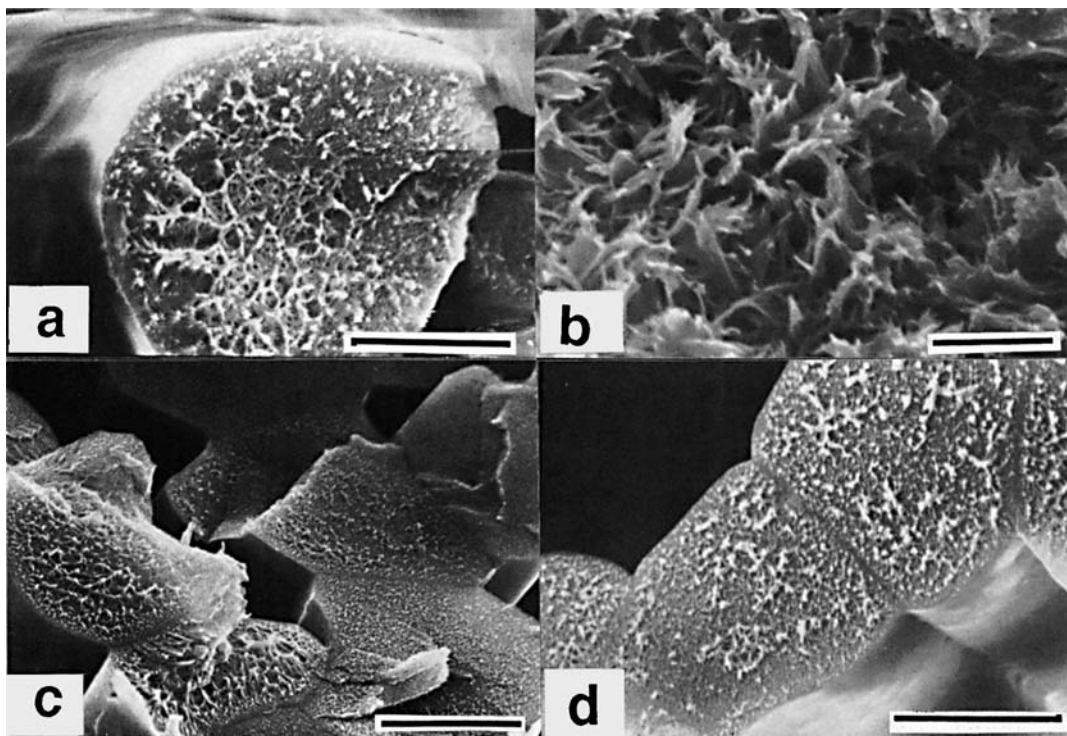
The observed tensile properties of “grafted” silk fibers are listed in Table I. The observed breaking loads show a tendency to increase with increasing add on, especially in the 0–55% range of poly(St) content. This behavior is in agreement with our previous findings,<sup>6,13,17,18</sup> showing that grafting frequently results in the increase of silk fiber strength. The tenacity of poly(St)-“grafted” silk fibers decreased with increasing add-on. This behavior is

mainly due to the fiber swelling following loading with the polymer (see SEM results). Both the elongations at break and the works of rupture of poly(St)-“grafted” silk fibers were significantly lower than the corresponding values of the control sample. Comparing the grafted samples, a tendency for further decreases of elongation and work of rupture was observed, especially at high add-on. These results suggest that grafting may exert a strong influence upon the extensibility of silk fibers. In fact, the new polymer chains growing within the amorphous regions of the fibrous substrate might perturb the arrangement of the fibroin molecules and partially impede their mobility when subjected to tension. Steric hindrance, as well as the decrease of moisture content might be considered responsible for the observed changes in elongation. Work of rupture decreased as well, because the drop of elongation occurred at constant breaking load values.

### Thermal Behavior

The study of the thermal properties of “grafted” silk fibers involves both scientific and technological aspects. The former mainly focus on the study of the interactions between the loaded polymer and the fibrous substrate, while the latter deal with the effects of the thermal treatments to which the fibers undergo during processing.

The differential scanning calorimetry profile of untreated silk fibers is characterized by a broad and large endothermic transition starting beyond 250°C, with a peak temperature at around 315°C, attributed to the thermal decomposition of silk fibroin with oriented  $\beta$ -sheet structure<sup>19</sup> (curve not shown). Poly(St)-“grafted” silk fibers with 24, 55, and 80% add-on [Fig. 2(a),(b),(c), respectively] displayed a slight upward shift of the decomposition temperature. It is noteworthy the apparent higher thermal stability conferred on silk by the loaded poly(St). These results are in good agreement with our previous findings on silk fibers treated with other grafting agents.<sup>17</sup> The DSC curves of poly(St)-“grafted” silk fibers showed additional endothermic transition peaks at temperatures of about 430–435°C, the size of which increased with increasing add-on. These transitions can be attributed to the depolymerization of poly(St), as demonstrated by the DSC profile of the polymer separated from the fibers. The presence of separate thermal transitions in the DSC curves of poly(St)-“grafted” silk fibers may be considered indicative of incompatibility between the polymer and the fibrous substrate.



**Figure 7** SEM photographs (cross-sectional view) of poly(St) separated from poly(St)-“grafted” silk fibers with 60% (a, b), 80% (c), and 100% (d) add-on. Scale bar: (a): 5  $\mu\text{m}$ ; (b): 1  $\mu\text{m}$ ; (c) and (d): 10  $\mu\text{m}$ .

Figure 3 shows the TG curves of untreated and poly(St)-“grafted” silk fibers. Two zones of weight loss can be observed. The former, at approximately 100°C, is due to the loss of moisture. Its intensity decreased with increasing add-on, in agreement with the behavior of the moisture regain data listed in Table I. The latter is located at around 300°C, and can be associated with the beginning of fiber degradation, because it coincides with the strong endothermic transition of the DSC curves. It is interesting to note that its onset temperature shifted to higher values with increasing add on, suggesting that loading silk with poly(St) may result in an improved resistance to thermal treatments at elevated temperatures.

Figure 4 shows the temperature dependence of the dynamic loss modulus ( $E''$ ) of untreated and poly(St)-“grafted” silk fibers with increasing add-on. The  $E''$  curve of untreated silk [Fig. 4(a)] is characterized by a prominent loss peak starting at about 180°C, with a peak temperature at 230°C. The onset temperature of the loss peak can be associated to the glass transition temperature ( $T_g$ ) of silk fibroin.<sup>20</sup> Below  $T_g$ , silk fibers exhibited a noticeable thermal

stability, as shown by the absence of significant changes in the value of loss modulus. Following grafting, the DMA pattern of poly(St)-“grafted” silk fibers displayed two main transitions; one beyond 200°C, corresponding to the loss peak of silk fibroin, the other at a lower temperature, with an intensity roughly proportional to the add on. The peak temperature of the latter transition is located in the range 100–115°C, while the onset value is at about 80°C. Because this value corresponds to the glass transition temperature of poly(St),<sup>21</sup> we can attribute the low temperature loss peak to the thermally induced molecular motion of poly(St).

The loss peak of poly(St)-“grafted” silk fibers slightly broadened and shifted to lower temperature. Silk fibers treated with other grafting agents exhibited a rather similar behavior.<sup>5,7,22</sup> Because the prominent loss peak has been attributed to the molecular motion of the fibroin chains in the crystalline regions,<sup>23</sup> it can be inferred that the interatomic vibrations within the chain segments of the ordered regions became less restrictive after grafting. However, our previous results on the crystalline structure of grafted silk fibers<sup>4–6,22</sup> exclude direct involvement

**Table II** Molecular Weight of Poly(*St*) Separated from Poly(*St*)-“Grafted” Silk Fibers

Add-on (%)	Molecular Weight (kD)		<sup>a</sup> Poly( <i>St</i> ) : Silk Molar Ratio
	Heavy Chain	Light Chain	
24	60	4-2	1.1
55	120	6-2	1.5
80	120	6-2	2.2
100	120	6-2	2.7

<sup>a</sup> Calculated by dividing the mol wt of poly(*St*) by the mol wt of silk fibroin (330 kD).

of the  $\beta$ -sheet ordered volumes in grafting. It follows that the above effects on loss modulus should be caused by the polymer present not only in the amorphous but also in the laterally ordered regions of the fibers, within the fringed fibril volumes located at the end of the crystalline elements.

#### Scanning Electron Microscopy Analysis

One of the most noticeable changes induced by grafting is the increase of the transverse dimension of silk fibers due to loading of polymer within the nonordered volumes of the fiber. The cross-sections of untreated and poly(*St*)-“grafted” silk fibers were examined by SEM (Fig. 5). Compared to the untreated sample [Fig. 5(a)] “grafted” silk fibers [Fig. 5(b)–(d)] showed a noticeable increase of the cross-sectional area. The higher the add-on, the larger the area of the cross-section. This observation is consistent with previously reported results,<sup>17</sup> showing that the fiber size increases linearly with increasing the amount of polymer loaded. These morphological changes may influence to some extent the intrinsic properties of silk, such as handle, luster, tensile behavior, dye absorption, etc. It is interesting to note that the cross-section surface of grafted silk fibers appeared as smooth as that of the untreated sample, without showing morphological details attributable to the presence of a foreign polymer loaded into the fibers.

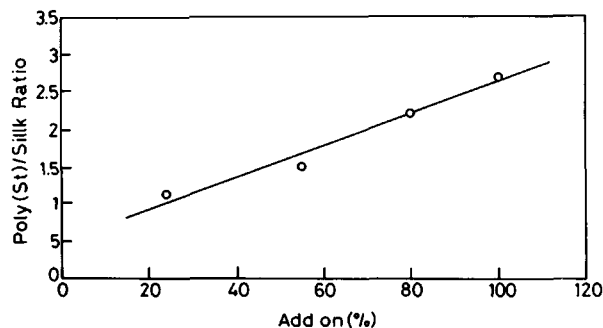
After treating poly(*St*)-“grafted” silk fibers with an alkaline solution, variable amounts of undissolved residues were recovered. Their morphology was examined by SEM (Figs. 6 and 7). It is worth mentioning that even after complete dissolution of the proteinic substrate, the residue maintained the shape of the original silk filament. This indicates that the reagents (monomer, initiator, etc.) diffused homogeneously into the fibers during grafting, lead-

ing to the formation of an interconnected polymeric network by aggregation of the growing polymer chains. Moreover, these microscopic observations imply the absence of spatial restrictions for the location of the polymer. As shown by the shape of the fiber cross-sections (Fig. 5), the fiber size increased gradually with a radial symmetry. The surface of the undissolved residue showed a porous texture (Fig. 6). The higher the add-on, the denser the texture. The fractured surfaces of the poly(*St*) residues showed a sponge-like morphology formed by thin interconnected sheets delimiting voids of variable size (Fig. 7).

#### Molecular Weight of Poly(styrene)

The average molecular weight of poly(*St*) separated from silk fibers with increasing add on was determined by size exclusion chromatography. All the samples displayed a fairly similar elution pattern, with an intense and sharp peak in the high molecular weight region and a series of minor peaks in the low molecular weight region. Table II lists the average molecular weight values of both heavy and light poly(*St*) fractions, as well as the “Poly(*St*)/Silk” molar ratio. The average molecular weight of the heavy fraction reached a maximum value of 120 kDa at 55% add-on, and then remained unchanged. The light fraction showed one broad peak at about 6 kDa (4 kDa for the sample with 24% add-on), accompanied by a series of minor peaks eluting in the proximity to the total permeation volume ( $V_t$ ) of the column. The “Poly(*St*)/Silk” molar ratio increased linearly with the add-on, the calculated values fitting a regression curve (Fig. 8) with a correlation coefficient ( $r$ ) of 0.986.

It is interesting to compare these results with those reported in a previous study on poly(MMA)-“grafted” silk fibers prepared by using a reaction



**Figure 8** Behavior of the “Poly(St)/Silk” molar ratio as a function of add-on of poly(St)-“grafted” silk fibers. The value of the “Poly(St)/Silk” molar ratio is calculated by dividing the molecular weight of poly(St) (obtained by SEC) by the molecular weight of silk fibroin (330 kDa).

system with KPS as initiator.<sup>16</sup> The behavior of poly(St) closely resembled that of poly(MMA) in the low add on range (0–55%), with both molecular weight and molar ratio increasing rapidly until about 120 kDa and 1.5, respectively. These findings seem to suggest that during the first stages of the graft-copolymerization reaction the increase of add-on is sustained by both initiation of new polymer chains and elongation of those already initiated. However, at higher add on values (>55%), while the molecular weight of poly(MMA) continued increasing, that of poly(St) attained a limiting value and then remained constant, as shown by the linear increase of the “Poly(St)/Silk” molar ratio.

These results indicate the presence of a threshold value for the molecular weight of poly(St) graft-copolymerized onto silk fibers. This behavior might be attributed to either chemical or steric factors, though the contribution of both effects cannot be excluded. The composition of the grafting system, the reaction conditions, the extent of swelling of the fibrous substrate, the diffusion of reagents, the shape and size of the growing poly(St) chains, the interactions with the surrounding fibroin molecules, etc., might have influenced the stages of activation/termination of the graft-copolymerization reaction, therefore limiting the maximum molecular weight attainable during grafting.

## CONCLUSIONS

The results reported in this study contribute additional information on the properties of poly(St)-

“grafted” silk fibers, a grafting system known since the early 70s and already exploited for silk finishing on an industrial scale. The physical, mechanical, and thermal properties of silk fibers underwent noticeable changes, whose trend appears consistent with the results obtained by treating silk with other grafting agents. These findings suggest that the grafting processes share some common basic features regardless of the grafting agent used. These mainly concern the effect induced on fine structure and morphology of silk fibers loaded with large amounts of polymer that accumulates in the nonordered volumes of the fiber. By selective degradation of silk fibroin it has been possible to verify that poly(St) grows inside the fiber forming an interconnected polymeric network. These findings provide interesting details on the structure and texture of the composite material originated by grafting. The molecular weight of poly(St) attained a limiting value of 120 kDa at about 50–55% add-on, while the “Poly(St)/Silk” molar ratio increased linearly over the entire add-on range examined. Though it appears that there are only limited margins for the application of styrene grafting to silk processing, we think that some properties of St-grafted silk fibers might be exploited for other uses. For examples, the high degree of hydrophobicity attained by poly(St)-“grafted” silk fibers, combined with the good mechanical properties, the inertness towards biological attack, and the excellent biocompatibility of silk fibroin might give an impulse for the development of new materials suitable for nontextile applications.

## REFERENCES

1. M. Tsukada, H. Shiozaki, and G. Freddi, *Melliand Textilberichte*, **74**, 778 (1993).
2. W. Schindler and A. Dietel, *Melliand Textilberichte*, **74**, 81 (1993).
3. M. Tsukada, G. Freddi, M. Matsumura, H. Shiozaki, and N. Kasai, *J. Appl. Polym. Sci.*, **44**, 799 (1992).
4. M. Tsukada, G. Freddi, H. Shiozaki, and N. Pusch, *J. Appl. Polym. Sci.*, **49**, 593 (1993).
5. M. Tsukada, G. Freddi, P. Monti, and A. Bertoluzza, *J. Appl. Polym. Sci.*, **49**, 1565 (1993).
6. M. Tsukada, G. Freddi, P. Monti, A. Bertoluzza, and H. Shiozaki, *J. Appl. Polym. Sci.*, **49**, 1835 (1993).
7. M. Tsukada, H. Shiozaki, J. S. Crighton, and N. Kasai, *J. Appl. Polym. Sci.*, **48**, 113 (1993).
8. M. Tsukada, H. Shiozaki, and J. S. Crighton, *J. Appl. Polym. Sci.*, **48**, 1409 (1993).
9. Y. W. Lee and K. E. Song, *Seric. J. Korea*, **27**, 47 (1985).



10. H. Shiozaki, Proc. Symp. *Seta: Conoscenze Attuali e Prospettive Future*, Como, Oct. 21-23, 1993, p. 244.
11. T. J. Bunning, H. Jiang, W. Wade Adams, R. L. Crane, B. Farmer, and D. Kaplan, in *Silk Polymers. Materials Science and Biotechnology*, ACS Symposium Series 544, American Chemical Society, Washington, DC, 1994, p. 353.
12. M. Demura, T. Takekawa, T. Asakura, and A. Nishikawa, *Biomaterials*, **13**, 276 (1992).
13. G. Freddi, M. R. Massafra, S. Beretta, S. Shibata, Y. Goto, H. Yasui, and M. Tsukada, *J. Appl. Polym. Sci.*, to appear.
14. N. Kuramoto, K. Suda, and K. Nagai, *J. Appl. Polym. Sci.*, **27**, 1713 (1989).
15. M. D. Fernandez, M. J. Fernandez, and G. M. Guzman, *J. Appl. Polym. Sci.*, **27**, 3439 (1989).
16. M. Tsukada, Y. Goto, G. Freddi, T. Yamamoto, and N. Nakabayashi, *J. Appl. Polym. Sci.*, **44**, 2197 (1992).
17. G. Freddi, M. R. Massafra, and M. Tsukada, Proc. Aachen Textile Conference *Forward-looking Fibre Modification and Textile Construction*, Aachen, Nov. 22-23, 1994, DWI Reports no. 114, 1995, p. 73.
18. M. Tsukada, G. Freddi, Y. Ishiguro, and H. Shiozaki, *J. Appl. Polym. Sci.*, **50**, 1519 (1993).
19. H. Ishikawa, M. Tsukada, I. Toizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).
20. J. Magoshi, Y. Magoshi, N. Nakamura, N. Kasai, and M. Kakudo, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1675 (1977).
21. J. F. Rudd, in *Polymer Handbook, Physical Constants of Poly(styrene)*, V/81, J. Brandrup, E. H. Immergut, Eds., Wiley, New York, 1989.
22. M. Tsukada, N. Kasai, and G. Freddi, *J. Appl. Polym. Sci.*, **50**, 885 (1993).
23. M. Nagura, K. Goto, and H. Ishikawa, *Kobunshi Ronbunshu*, **34**, 389 (1977).

Received August 10, 1995

Accepted January 12, 1996