

Molecular Weight Distribution of the Methyl Methacrylate (MMA) Polymer Separated from the MMA-Grafted Silk Fiber

MASUHIRO TSUKADA,^{*,1} YOKO GOTO,¹ GIULIANO FREDDI,²
TAKASHI YAMAMOTO,³ and NOBUO NAKABAYASHI³

¹National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan,

²Stazione Sperimentale per la Seta, via G. Colombo 81, 20133 Milano, Italy, and

³Institute for Medical and Dental Engineering, Kanda, Tokyo 101, Japan

SYNOPSIS

The molecular weight distribution of poly-methyl methacrylate (poly-MMA) chains separated from MMA-grafted silk fibers obtained by using potassium persulfate (KPS) and tri-*n*-butylborane (TBB) as initiator of the graft-copolymerization reaction have been examined by gel permeation chromatography (GPC). GPC elution pattern of poly-MMA chains shows a bimodal molecular weight distribution. The two peaks have been identified as heavy and light component. The average molecular weight of the heavy component ranges from 48.5 to 200 kD for poly-MMA copolymerized by the KPS reaction system and from 336 to 816 kD for the poly-MMA copolymerized by the TBB reaction system. The light component has an average molecular weight lower than 1,000 D and its value is almost similar in all the samples examined. Scanning electron microscopy (SEM) analysis revealed the presence of MMA oligomers formed on the fiber surface during grafting. The molar ratio between poly-MMA chains and silk fibroin attains a constant value that seems to be specific for a certain reaction system. A linear correlation has been observed between the weight gain and the average molecular weight of the poly-MMA chains. These findings suggest the effect of grafting parameters on the molecular weight and molecular weight distribution of the grafted polymer, as well as its influence on the physical properties and textile performances of MMA-grafted silk fibers.

INTRODUCTION

Graft-copolymerization of vinyl monomers¹⁻³ onto silk fibers and chemical modification of silk⁴ have been the subject of many investigations during the last several years and has attracted considerable academic and practical interest. Grafting has been suggested as a potentially effective means of improving some characteristics of silk fiber, i.e., wrinkle recovery,⁵ wash and wear (W&W) properties, and light resistance, without affecting the handling, lustrous appearance, and outstanding physicomechanical properties of this fiber.

Graft copolymerization of methyl methacrylate (MMA) onto silk fibers has been extensively studied.^{1,5} The reaction of MMA with silk, using either chemical or photochemical initiation,⁶ rate of grafting, and weight gain were investigated by varying the concentration of monomer and initiator, temperature, reaction medium, etc. The textile performances as well as the physical properties and structural characteristics of MMA-grafted silk fibers were elucidated in relation to the weight gain.

Recently, the molecular weight distribution of the polymers and/or copolymers separated from the grafted substrate was studied by gel permeation chromatography (GPC).⁷⁻⁹ However, a detailed investigation of the molecular weight of the poly-MMA separated from grafted silk fibers has not yet been carried out. In our opinion, the evaluation of the

* To whom correspondence should be addressed.

characteristics of the grafted chains is of importance from the point of view of elucidating either the reaction mechanism of MMA grafting onto silk or the physicochemical properties of the grafted silk polymer.

Potassium persulfate (KPS) has been extensively used as water-soluble initiator for grafting MMA onto silk fibers. The weight gain usually does not exceed 80% and the grafting conditions adopted sometimes affect the physical and mechanical properties of silk fibers because of the high-temperature reaction system (about 70–80°C).¹

The use of tri-*n*-butylborane (TBB) as initiator has been recently reported as a useful method to prepare MMA-grafted silk fibers with a very high weight gain under relatively mild grafting conditions (reaction temperature about 37°C).^{10,11} The authors emphasized the role played by the pretreatment with FeCl₃ in enhancing the graft yield.^{11,12}

This article focuses on the characterization of poly-MMA separated from MMA-grafted silk fibers obtained by using either KPS or TBB as initiator. The molecular weight distribution of poly-MMA separated from grafted silk fibers was analyzed by GPC.

We think these results would contribute to improve our understanding of the effect of grafting parameters on the characteristics of the MMA polymer grafted onto silk fibers, as well as provide new tools for evaluating the physical properties of the graft copolymer.

EXPERIMENTAL

MMA-grafted silk fibers were prepared according to two different initiator mixture systems:

1. *KPS system*: Degummed *Bombyx mori* silk fibers were immersed in a solution of aqueous KPS (0.1%) as initiator that contained MMA monomer as the grafting agent emulsified by nonionic surfactant at a temperature of 75–80°C for 1–4 h. The graft mixture system was intermittently stirred. The material-to-liquor ratio of 1 : 100 was maintained.
2. *TBB system*: Degummed silk fibers, 0.8 g, were immersed in 30 mL water at 25°C for 5 min and subsequently in solutions of FeCl₃ at different concentration at 25°C for 1 min. To this were added 5 g MMA and 0.4 mL TBB as initiator at a temperature of 35–37°C for 1 h. The reaction was stopped by pouring the mixture into 250 mL methanol.

After the desired reaction time, silk fibers were taken out and washed thoroughly with water three or four times. The washed and air-dried samples were dried in a forced air oven at 100–105°C to achieve a constant weight, placed in a desiccator over silica gel for 30 min, and weighed, the correction being made for the weight increase upon treatment with the MMA solution alone; thus, the weight gain was obtained. If necessary, the grafted silk samples were extracted with acetone at 55°C for different periods of time to remove unreacted MMA oligomers formed during the copolymerization reaction.

The grafted MMA chains were separated from the MMA-grafted silk fibers by acid hydrolysis. About 0.3 g MMA-grafted silk fibers were hydrolyzed in the 6*N* HCl/acetic acid mixture system (6/1 v/v) at 110°C for 24 h. Fibrous precipitate thus obtained was dissolved in tetrahydrofuran (THF).

Gel permeation chromatograms were recorded with a Tosoh HLC-802A equipment with refractive index (RI) detector. The liquid chromatograph consists of a series of four TSK-GEL columns: G1000H, G2000H, G3000H, and G4000H so a wide range of molecular weights may be studied. THF was used as eluent and was purified by refluxing for 48 h over potassium metal followed by vacuum distillation. The purity of the eluent was examined by refraction meter. The GPC columns were calibrated with known standards of polystyrene samples supplied by Tosoh. For each experiment, 3 mg/mL of sample were used. The flow rate of the eluent was 1 mL/min. The standard program provided by Tosoh CP-8000 along with the molecular weight distribution data analyzer was used for the determination of the molecular weight data.

Infrared spectra were measured with a Japan Spectroscopic Co., Ltd. spectrophotometer (IR-G) in the spectral region 1900–400 cm⁻¹. KBr pellets of the MMA-grafted silk fibers with weight gain of 56% obtained using KPS as initiator were prepared for the IR measurement.

The surface of grafted silk fibers was examined before and after acetone extraction with a JEOL JAX-333S scanning electron microscope (SEM) at 15 kV acceleration voltage after gold coating.

RESULTS AND DISCUSSION

SEM and IR Spectroscopy Analyses

The scanning electron micrographs of MMA-grafted silk fibers with a relatively low weight gain, i.e., those obtained with the reaction initiated by KPS after

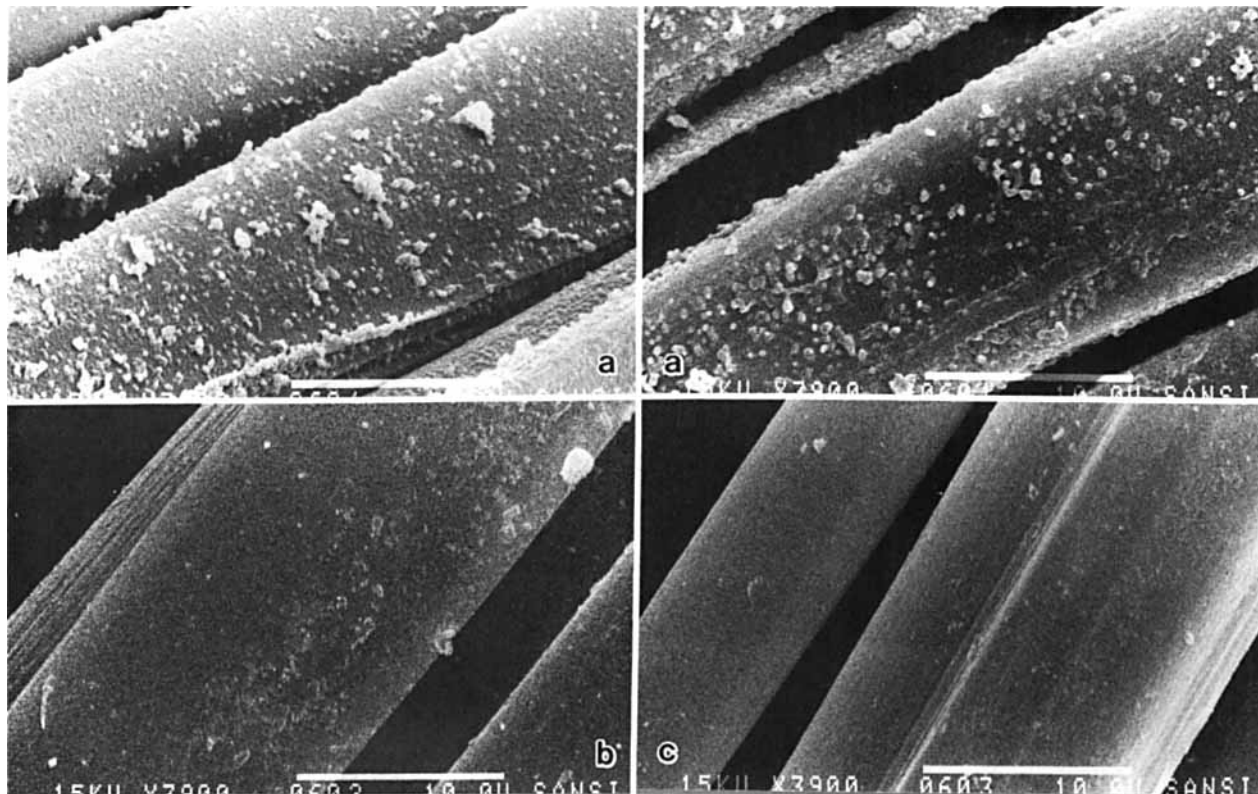


Figure 1 Scanning electron microscopic observation of MMA-grafted silk fiber prepared by grafting using KPS with weight gain of 56%. (a), before acetone extraction; (b) and (c), after acetone extraction for 20 min and 90 min, respectively.

water washing, show the presence of several small granules adhering to the fiber surface [Fig. 1(a)]. This observation is in agreement with the results of the morphological characteristics of MMA-grafted silk fiber already reported in a previous paper.¹ These granules probably consist of unreacted MMA oligomers formed during the graft-copolymerization reaction.

After a 20-min extraction with hot acetone [Fig. 1(b)], almost all granules were removed from the surface of the grafted silk fiber and after 1.5 h of extraction the fiber surface appeared as smooth as that of the ungrafted silk [Fig. 1(c)].

MMA-grafted silk fibers with a weight gain of 56%, obtained by using KPS as initiator, were analyzed by infrared spectroscopy before and after acetone extraction [Figs. 2(b) and (c)]. It is interesting to note that MMA-grafted silk fibers, either before or after acetone extraction, show sharp absorption bands at around 1728, 1192, 1628 (amide I), and 1512 cm^{-1} (amide II), the two latter absorption bands being characteristic of the β -structure of silk fibroin¹³ as appears from the IR spectrum of the control silk [Fig. 2(a)]. It is reasonable that

the absorption band at 1728 cm^{-1} is attributed to the carbonyl group of the side chains of the MMA polymer in the silk fiber. Since MMA-grafted silk fibers after acetone extraction do not show the presence of MMA oligomers on their surface (Fig. 1), these IR spectra give evidence that the MMA polymer is grafted inside the fiber and not on the fiber surface.

The surface of silk fibers grafted by the TBB initiator system appears almost completely covered by a layer of MMA polymer. MMA oligomers, if present, should be trapped by this material looking like a rubbery mass, as suggested in a previous paper.¹¹

GPC Analysis

The average molecular weight and the molecular weight distribution of poly-MMA separated from grafted silk fibers with different weight gain were determined by GPC. Figure 3 shows the GPC chromatograms of poly-MMA chains separated from silk fibers copolymerized with the KPS reaction system. The GPC pattern clearly shows two kinds of peaks: The major peak (heavy component) at the lower-

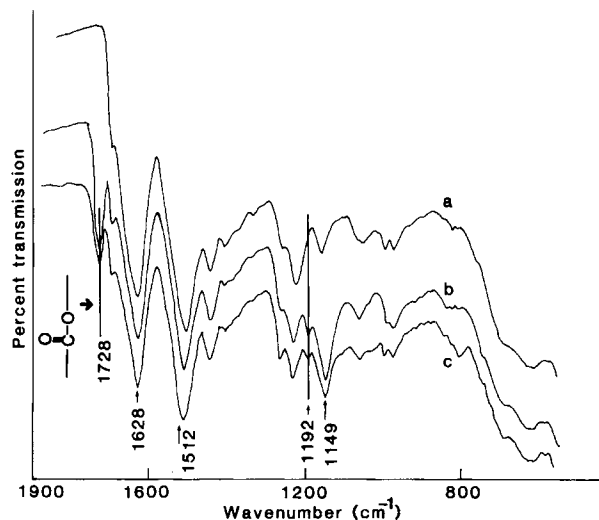


Figure 2 Infrared spectra of the MMA-grafted silk fibers prepared by grafting using KPS with weight gain of 56%. (a), control silk fiber; (b), before acetone extraction; (c), after acetone extraction for 1.5 h.

count region becomes broader and displaces to higher molecular weight values as the weight gain increases, while the minor peak (light component) corresponding to the higher-count region presents constant elution properties despite the different graft yield of the four samples examined. Figure 4 shows the GPC results of poly-MMA chains separated from silk fibers grafted using TBB as initiator. Also in this case, the elution pattern presents a bimodal molecular weight distribution. The major and

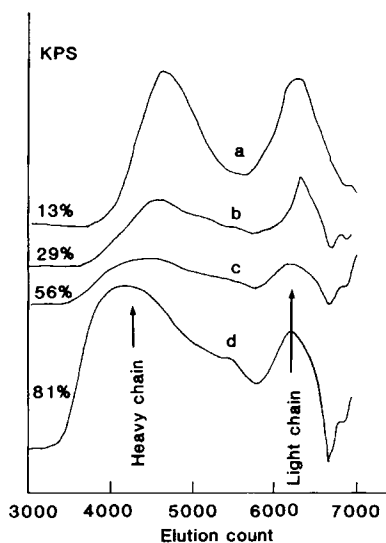


Figure 3 Gel permeation chromatograms of poly-MMA chains separated from silk fibers copolymerized in the KPS reaction system with different values of weight gain.

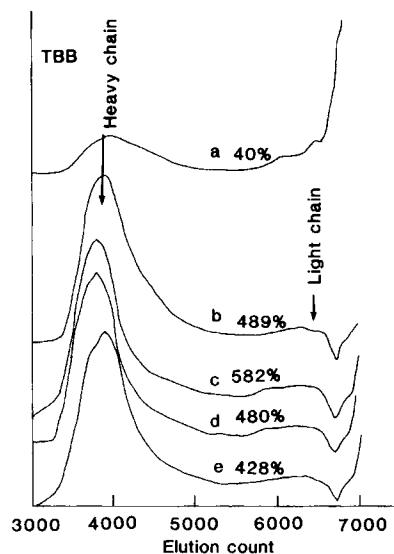


Figure 4 Gel permeation chromatograms of poly-MMA chains separated from silk fibers copolymerized in the TBB reaction system with different values of weight gain.

minor peaks are still present, but their relative intensity is different from that observed in the other samples. Moreover, the heavy component is eluted at lower counts, compared to the corresponding component in Figure 3. The average molecular weight of the poly-MMA chains was calculated on the basis of calibration with polystyrene standards and is listed in Tables I and II with the corresponding weight gain values and the poly-MMA/silk molar ratio. The average molecular weight of the poly-MMA heavy component initiated by TBB is noticeably higher than that of the corresponding component initiated by KPS, even for the sample with a weight gain of only 40%. The former shows

Table I Effect of Weight Gain on the Molecular Weight of the MMA Polymer Separated from the MMA-Grafted Silk Fibers

Weight Gain (%)	Molecular Weight		PMMA/Silk (mol ratio ^a)
	Heavy Chain	Light Chain	
14	48,500	845	0.9
30	63,100	600	1.5
56	126,000	935	1.5
82	200,000	935	1.3

Obtained by the copolymerization using potassium persulfate as the initiator.

^a The value of PMMA/silk can be calculated by using an assumed value of 330,000 for molecular weight of silk fibroin.

Table II Effect of Weight Gain on the Molecular Weight of the MMA Polymer Separated from the MMA-Grafted Silk Fiber

Weight Gain (%)	Molecular Weight		PMMA/Silk (mol ratio)
	Heavy Chain	Light Chain	
40	336,000	—	0.4
489	637,000	825	2.5
582	816,000	829	2.4
480	782,000	869	2.1
428	564,000	897	2.5

Obtained by the copolymerization using tri-*n*-butylborane as the initiator.

molecular weight values ranging from 336 to 816 kD, while the latter attains a maximum value of 200 kD for the sample with a weight gain of 82%. From the quantitative point of view, the relative amount of heavy and light components is different between the two groups of samples examined. The poly-MMA obtained by using the KPS system shows a higher amount of light component compared to the polymer separated from silk grafted with TBB as initiator. These data suggest the effect of grafting parameters, i.e., concentration of monomer, type and concentration of initiator, temperature, time, reaction medium, on the molecular weight and molecular weight distribution of poly-MMA grafted onto silk. At the same time, they contribute useful information to better understand the different physical properties of the two kinds of grafted silk fibers already reported in previous papers.^{1,11} The poly-MMA light component has an average molecular weight lower than 1,000 *D* and its presence should be related to the MMA oligomers observed by SEM analysis on the surface of the fibers grafted using KPS as initiator. This hypothesis has been confirmed by the GPC analysis of the MMA polymer separated from the grafted silk fiber after acetone extraction, which revealed that the light component almost completely disappeared from the GPC elution pattern (these results will be reported elsewhere). The GPC data also confirm the presence of MMA oligomers on silk fibers grafted by the TBB initiator system. Their molecular weight distribution is similar to that of the corresponding component obtained using KPS as initiator for the graft-copolymerization reaction.

The molar ratio between poly-MMA chains and silk fibroin in the copolymerized polymer has been calculated on the basis of GPC data and assuming a value of 330 kD for the molecular weight of silk

fibroin. It is important to note that as the weight gain increases the poly-MMA/silk ratio attains a constant value that seems to be specific for a certain reaction system. This observation is quite interesting, suggesting that after the initial stages of the copolymerization reaction the growth of poly-MMA chains already reacted with the silk fiber plays the most important role in enhancing the graft yield.

The type and number of active sites formed during MMA grafting of silk fibers, as well as the physical and chemical interactions between the growing poly-MMA chains and the substrate, have not been clearly elucidated yet. For this reason, the interpretation of the constant value attained by the poly-MMA/silk molar ratio as a sort of "saturation" value requires further investigations. Nevertheless, it is of interest to note that these results may contribute new tools to improve our knowledge of the graft copolymerization reaction between MMA and silk fiber.

As summarized in Tables I and II, it is obvious that there is a straight correlation between the weight gain and the average molecular weight corresponding to the heavy component of the poly-MMA separated from grafted silk fiber prepared in the KPS system (Fig. 5) and in the TBB system. This observation is important not only from the fundamental point of view but also because it provides useful information for better control of grafting processes. In fact, the physical properties and the textile performances of the grafted silk fibers depend on the extent of grafting as well as on the average molecular weight and molecular weight distribution of the grafted polymer chains.

The results reported in this article draw our attention to different important aspects related to the

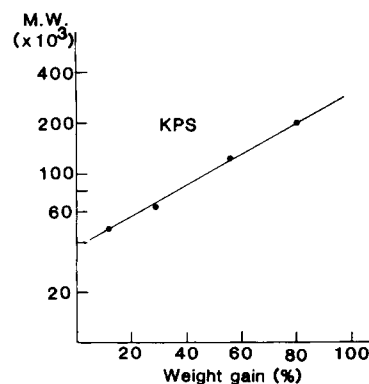


Figure 5 Relationship between the values of weight gain and the average molecular weight of the poly-MMA chains separated from silk fibers grafted in the KPS reaction system.

copolymerization reaction of MMA with silk fibers. First, we should emphasize the importance of the selection of the initiator and the composition of the reaction system in determining the rate and extent of grafting, as well as the molecular weight distribution of the grafted MMA polymer. The KPS system permits a good control of the weight gain at a relatively low extent of grafting by varying the reaction time, while the TBB system enables us to attain a very high weight gain, especially after pretreatment with FeCl_3 .^{11,12} In addition, the TBB system is safer as concerns the mechanical properties of silk because the copolymerization reaction is carried out at a very low temperature (37°C) and for a short time.

Besides the type of initiator, there are other parameters related to the composition of the reaction medium whose effect on the activation of fibrous substrate and on the growth of MMA polymer chains should be further investigated. We refer to the extent of fiber swelling, which influences the penetration and diffusion of MMA monomer and initiator, as well as to the contribution of the solvent system to the stages of activation and/or termination of the copolymerization reaction.

Another important aspect emerging from our results relates to the MMA oligomers detected by GPC analysis in poly-MMA chains separated from silk grafted either by the KPS or TBB initiator system, even if the former shows more evidence of this phenomenon. MMA oligomers begin to appear on the fiber surface only after that a certain weight gain has been attained (usually 40–50%) and are easily removed by acetone extraction. This behaviour gives evidence that MMA oligomers are not chemically bonded to the silk fiber but only adsorbed to its surface and that the copolymerization reaction takes

place preferably inside the fiber. Only when the space inside the fiber, namely in the amorphous regions, has been almost completely filled by the growing poly-MMA chains do oligomers start forming also in the solution medium and are physically attached to the boundary layer of silk fiber.

REFERENCES

1. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
2. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 2133 (1988).
3. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **39**, 1289 (1990).
4. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
5. S. Kobayashi, M. Sugiyama, and H. Yoshida, *Report Tokyo Metro. Textile Res. Inst.*, **15**, 137 (1979).
6. P. L. Nayak and S. Lenka, *Proc. Int. Meet. Graft. Proc. Polym. Fibers Surf.: Sci. Techn. Aspects*, Milano, Italy, Nov. 30 and Dec. 1, 1990, suppl. 85, Ricerca Scientifica ed Educazione Permanente, Universita' degli Studi di Milano, 1990, p. 243.
7. S. N. Bhattacharyya and D. Maldas, *J. Appl. Polym. Sci.*, **31**, 1671 (1986).
8. N. Kuramoto, K. Suda, and K. Nagai, *J. Appl. Polym. Sci.*, **27**, 1713 (1989).
9. M. D. Fernandez, M. J. Fernandez, and G. M. Guzman, *J. Appl. Polym. Sci.*, **27**, 3439 (1989).
10. K. Kojima, T. Suzuki, S. Iwabuchi, and J. Tarumi, *Nippon Kagaku Kaishi*, **10**, 1943 (1972).
11. M. Tsukada, T. Yamamoto, N. Nakabayashi, H. Ishikawa, and G. Freddi, *J. Appl. Polym. Sci.*, to appear.
12. T. Yamamoto and N. Nakabayashi, *J. Jpn. Soc. Dental Mat. Devices*, **8**, 375 (1989).
13. T. Miyazawa and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 712 (1961).

Received February 18, 1991

Accepted July 11, 1991