

Synthesis and Characterization of Spinning Poly(acrylonitrile-co-silk fibroin peptide)s

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ABSTRACT: A novel spinning acrylic polymer containing silk protein was synthesized by copolymerization of acrylonitrile (AN) and silk fibroin peptide (SFP) modified by acryloyl chloride (AC) with vinyl groups. From results of the examination to the chemical compositions, we established that the modified SFP is more reactive than AN in the copolymerization. The intrinsic viscosity values of these copolymers showed that the copolymers have good spinnability, which were synthesized under the condition of adding a trace of metal ions into the synthesizing solvent. These copolymers exhibited good thermal property. The fiber based

on the poly(acrylonitrile-co-silk fibroin peptide) was prepared and characterized by SEM, FTIR measurement of its shell and core flakes, and moisture absorption. The fiber exhibited a smooth surface and could be assumed to have excellent adhesive property between SFP and PAN. Furthermore, these fibers showed a core-shell structure and excellent moisture absorption. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1540–1547, 2004

Key words: copolymerization; core-shell polymers; fibers; viscosity; FTIR

INTRODUCTION

As an important fiber material, polyacrylonitrile (PAN) is used in the textile industry in quantities not only because of its relatively cheap price and good mechanical properties, but also because acrylonitrile can be easily copolymerized with one or two comonomers by vinyl copolymerization to obtain various novel fiber materials. In recent years there has been increasing interest in the combination of AN-based polymers and silk protein.^{1–3} *Bombyx mori* silk fibroin (SF) fibers show excellent luster, tensility, handling, and moisture absorption, and can improve the defects of PAN homopolymer such as low dyeing affinity, uncomfortableness, and low moisture absorption. The synthetic strategies reported are mainly classified into two methods: (1) blending of SFs and AN-based polymers¹ and (2) graft-polymerization of acrylonitrile onto SFs.^{2,3} These polymers show very poor adhesive properties, and the mechanical properties are inferior to those of PAN homopolymer. For this reason, we synthesized a new acrylic polymer containing silk protein by vinyl copolymerization of AN and modified silk fibroin peptide (SFP). We previously reported some

of our earlier studies concerning this copolymer.⁴ In that article, mainly by comparing the solubility, thermal stability among the blend of SF fiber and PAN, graft-polymer of AN onto SFs, vinyl copolymer of SFP monomer and AN, we explained their structures, and it was assumed that the vinyl copolymers have a covalently crosslinking structure by the SFP segment. It was also indicated that the vinyl copolymers have excellent thermal stability and better moisture absorption. However, no specific data were obtained about the influence of composition ratio of SFP and PAN in the vinyl copolymers on the solid-state property of these copolymers, and the characterization of the fibers prepared by the vinyl copolymers was also not examined, both of which have important associations with application.

Herein, we report the synthesis of a series of poly(acrylonitrile-co-silk fibroin peptide)s (vinyl copolymers) from SFP monomer and AN in various compositions that can be used as spinning polymer intermediates. The chemical composition, intrinsic viscosity, and thermal properties were characterized. Furthermore, the characterizations of the fibers prepared by poly(acrylonitrile-co-silk fibroin peptide)s were examined in detail.

EXPERIMENTAL

Materials

Acrylonitrile was purified by distillation just before use. *N,N*-Dimethylformamide (DMF) was purified by the method of vacuum distillation. α -Chymotrypsin

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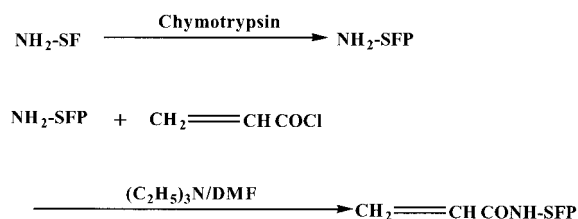


Figure 1 Monomer preparation.

and the other chemicals were of the highest commercial grade and used without further purification.

Preparation of silk monomer

Silk fibroin (SF) was obtained by removal of expendable components such as cocoon waxes, carbohydrates, lipids, and sericin from *Bombyx mori* cocoon shell. Cocoon waxes were removed by extraction with ether using a Soxhlet extractor for 48 h. Carbohydrates and lipids were extracted with ethyl alcohol. Sericin was removed by washing in boiling soapsuds. Pure SF powder was obtained by dialysis in a mixed solution of distilled water and methanol (1 : 5) containing LiBr (0.01 mol/L). SF powder (1.0 g) was then dispersed in distilled water (100 mL) at 80°C for 5 min. The solution was adjusted by a 25% ammonia solution to about pH 7.5. α -Chymotrypsin (0.1 g) was added and the solution was stirred at 37°C for 1 h. After the reaction was deactivated by cooling, the SFP was filtered, washed with distilled water, and dried. The average molecular weight of the SFP was about 25,000 (measured by electrophoresis).

As shown in Figure 1, to a dry DMF solution of SFP (1.0 g) and triethylamine (10 mL), acryloyl chloride (3.0 mL) was slowly added on an ice bath with vigorous stirring. The resulting solution was stirred at room temperature for 1 h. The product was filtered, washed with distilled water, and dried in vacuum at 50°C for 24 h.

Polymerization

A series of copolymers were prepared in 60 wt % ZnCl_2 aqueous solution by vinyl copolymerization of modified SFP and AN in various molar fractions using ammonium persulfate as initiator (Fig. 2). A typical copolymerization was as follows: SFP-AC (0.1 g) was stirred in 60 wt % ZnCl_2 aqueous solution at room temperature for 48 h, and insoluble compounds were filtered off. To the filtrate, AN (10 g) and aqueous solution (5 mL) of ammonium persulfate (0.1 g) were added, and the mixed solution was heated at 55°C for 1 h with stirring. The resulting solution was poured into a dilute HCl aqueous solution and stirred constantly for 10 h. A white precipitate, obtained by fil-

tration, was washed with distilled water and acetone, and then dried in vacuum at 50°C overnight. The dried samples were then immersed in 9.5 mol L⁻¹ LiBr aqueous solution at room temperature for 10 h under constant stirring to dissolve out the unreacted SF without extracting the PAN homopolymer. Finally, the resulting polymer was filtered, washed, and dried.

Spinning

Poly(acrylonitrile-co-silk fibroin peptide)s were dissolved in DMF at room temperature under constant stirring. The concentration of this copolymer solution was made up to 10 wt %. The spinning solution was filtered and deaired. By using a wet-spinning apparatus, the spinning solution was extruded into a water coagulation bath. The obtained fiber was then washed thoroughly with distilled water and dried in a vacuum at 40°C for 24 h.

Measurements

A wet-spinning apparatus using the immersion method (Musasino, KS-18525) was used for spinning the fiber. Ultraviolet-visible spectra were recorded on a Jasco V-570 spectrophotometer (Jasco, Tokyo, Japan). SFP, PAN homopolymer, and their copolymers were determined from infrared (IR) spectra using a Jasco FS-420 spectrophotometer. Elementary analysis was carried out on Perkin-Elmer Series II CHNS/O analyzer 2400 (Perkin Elmer Cetus Instruments, Norwalk, CT).

The intrinsic viscosity $[\eta]$ of the synthesized copolymers was measured in DMF at 25°C using a Ubbelohde suspended-level capillary viscometer (Cannon-Ubbelohde, State College, PA). The relative and specific viscosities were measured at three concentra-

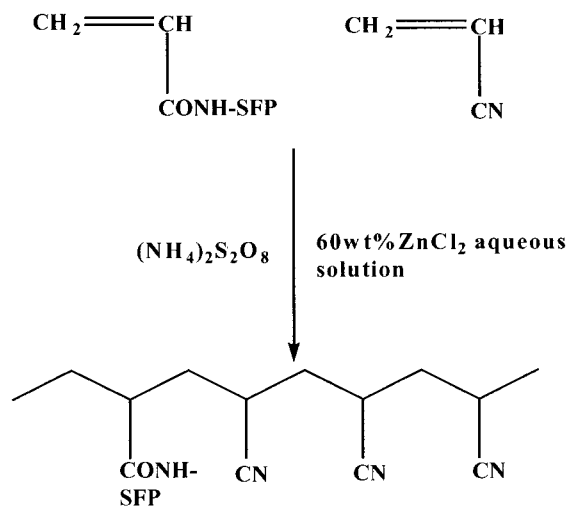


Figure 2 Copolymer synthesis.

tions in the range of 0.2–0.4 g/dL, and the value of $[\eta]$ was determined by extrapolating the reduced and inherent viscosities to infinite dilution.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a Seiko DSC 15200 instrument system (Seiko Instruments, Japan), consisting of thermogravimetric analysis, differential thermal analysis (TG/DTA 220), and differential scanning calorimetry (DSC 220). TG analysis was performed in the temperature range between 25 and 600°C under nitrogen atmosphere at a heating rate of 10°C/min.

We sliced a fiber to shell and core flakes (0.5 μm thick) by an RV-240 microtome (Yamato Kohki). The shell and core compositions of the fiber were measured, respectively, from infrared spectra using a Jasco FS-420 spectrophotometer equipped with an infrared microscope detector cooled by liquid nitrogen.

A Hitachi S-2380N scanning electron microscope (SEM; Hitachi, Osaka, Japan) was used to study the morphological structure of the fiber. All the samples were coated with gold under vacuum for microscopic inspection.

The moisture absorption experiments were performed using an Enviro KCL-1000 (Eyela) environmental chamber. Polymer samples (dried at 50°C for 1 week) were allowed to stand in an environmental chamber that was thermostated at 20°C and humidistated at 65% of relative humidity for 1 week. The moisture absorption (%) of these polymers was defined by the following equation:

$$\text{Moisture absorption (\%)} = \frac{W_i - W}{W} \times 100 \quad (1)$$

where W and W_i represent the weight of the dried sample and the moisture-absorbed sample, respectively.

RESULTS AND DISCUSSION

Preparation of SFP monomer

As shown in Figure 1, after hydrolyzing SF protein by α -chymotrypsin, SFP monomer was prepared by acylation of SF peptide (SFP) with acryloyl chloride in DMF. In fact, this experiment is a chemical modification process of silk protein; with general proteins, the steric hindrance of SF protein molecular may contribute to interfering with the effect of the modifications.⁵ Thus we had to use α -chymotrypsin because the α -chymotrypsin preferentially catalyzes the hydrolysis of peptide bonds at the carboxyl groups of tyrosine, and is very useful for hydrolyzing silk fibroins containing about 5% tyrosine by weight.⁶ Furthermore, it was previously reported that the acylation of protein

can be performed completely with the use of α -chymotrypsin.⁷

The resulting monomer was confirmed by the change of solubility in the good solvent for SFP and that of UV–visible spectra of SFP before and after acylation. The unmodified SFP shows good solubility in the mixture of H₂O and methanol (1 : 5) containing LiBr (0.01 mol/L). Dissolving the SFP modified by AC into the same solvent is not only time-consuming but also necessarily induces swelling. This result indicates that the conformation of silk protein varied. A comparison of the visible spectra of unmodified and modified SFP, as shown in Figure 3, shows that the absorbance at 278 nm decreased after acylation, attributed to the acylation of tyrosyl residues. From this result, it could also be assumed that considerable amino already has been modified by AC because amino, compared to tyrosyl residues, can be easily and effectively acylated (in the preparation procedure, we used a large excess of AC).^{8,9} These results are in good agreement with those of the literature.¹⁰

Polymerization

The compositions of the copolymers were determined from elementary analysis. The results, summarized in Table I, show that every copolymer contains a molar fraction of SFP that is larger than the feed fraction of this component used in the copolymerization. Furthermore, the molar ratio of SFP in copolymer increased with increasing the feed fractions of this component, which indicates that modified SFP is more reactive than AN in the copolymerization. This behavior might be attributable to the steric hindrance caused by SFP segments. Moreover, it suggests the possibility that so long as a small amount of SFP is loaded in the copolymerization, the copolymer appears to have characteristics similar to those of silk protein.

As shown in Table I, the intrinsic viscosity $[\eta]$ of copolymers was determined. The $[\eta]$ values of polymers 1 and 2 are 4.90 and 9.50 dL/g in DMF at 25°C, respectively, indicative of their relatively high molecular weights. No intrinsic viscosity value of polymer 3 was obtained because polymer 3 could not sufficiently dissolve in DMF, although it probably has a large molecular weight (MW). On the other hand, after adding a trace of metal ions into the synthesizing solvent (i.e., 60 wt % ZnCl₂ aqueous solution), the copolymerization was also performed under the same synthesis conditions as those of polymers 1, 2, and 3, after which polymers 1-M, 2-M, and 3-M were obtained. Their $[\eta]$ values were measured and it was found that the $[\eta]$ decreased to about 1.64, 1.70, and 2.20 dL/g in DMF at 25°C, respectively. This phenomenon is attributed to the decrease of copolymer MW. In this study, Cu(II) and Fe(II), as chain transfer agents, were added to the synthesizing solvent. They hindered the propagation

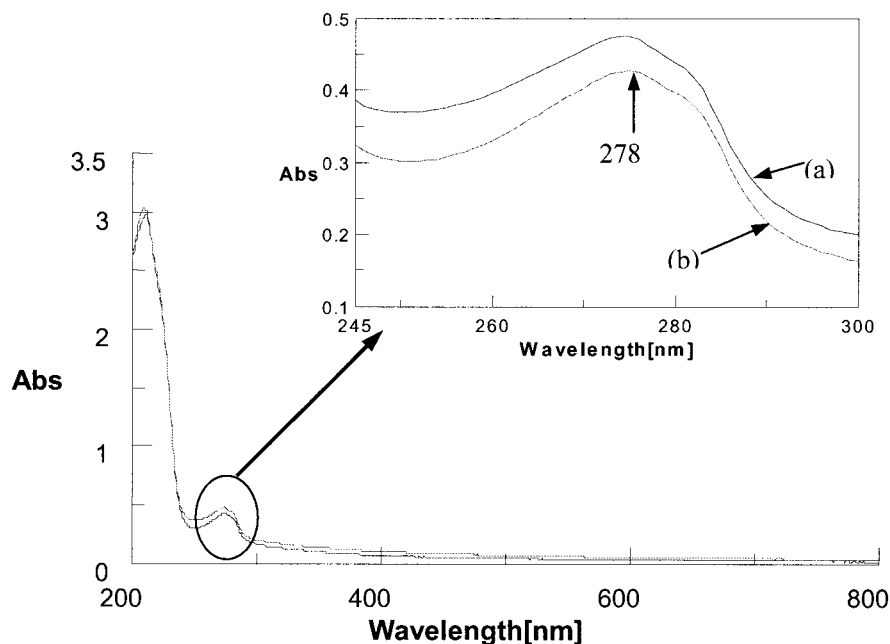


Figure 3 UV-visible spectra of (a) SFP unmodified and (b) SFP modified with acryloyl chloride (AC).

of copolymer chains by trapping free radicals during the copolymerization under the presence of ammonium persulfate as initiator and decreased copolymer MW. The way that Cu(II) and Fe(II) trap free radicals is the same as that of using an initiator for polymerization of AN or copolymerization of AN and other vinyl monomers.^{11–13} On the other hand, the intrinsic viscosities of polymers 1-M, 2-M, and 3-M are lower than those of copolymers 1, 2, and 3, but are always higher than 1.5 dL/g. The study about the connection between the viscosity of acrylic polymer solution and its spinnability was conducted.¹⁴ Generally speaking, if the intrinsic viscosity of the spinning acrylic polymer solution is too low ($\sim <1.5$ dL/g), the fiber could not be obtained. If the intrinsic viscosity of the spinning polymer solution is too high, it is necessary to lower the concentration of the spinning solution; then

the fibers, of the appropriate intensity, also could not be obtained. Thus, we considered that polymers 1, 2, and 3 have poor spinnabilities and polymers 1-M, 2-M, and 3-M have good spinnabilities. This result agrees well with our experimental observation in spinning.

The homopolymers and copolymers were characterized using FTIR spectroscopy. Figures 4 and 5 show the IR spectra of PAN, SFP, and their copolymers. The IR spectrum of SFP [Fig. 4(e)] shows peaks at 1653 cm^{-1} ($\nu\text{C=O}$, amide I), 1534 cm^{-1} ($\delta\text{N-H}$, amide II), 1239 cm^{-1} (δ , amide III), and that of the PAN [Fig. 4(a)] shows peaks at 2243 cm^{-1} ($\nu\text{C}\equiv\text{N}$), 1454 cm^{-1} (δCH_2), and 1252 cm^{-1} ($\gamma_{\omega}\text{CH}$). The spectra of copolymers 1, 2, and 3 are very similar, respectively, displaying vibrational peaks at $1681, 1675, 1675\text{ cm}^{-1}$ ($\nu\text{C=O}$, amide I); $1532, 1538, 1539\text{ cm}^{-1}$ ($\delta\text{N-H}$, amide II), typical of SFP; and at 2243

TABLE I
Copolymers: Monomer Feed Ratio in Copolymerization, Copolymer Composition, Yield, and Viscosity

Copolymer	Monomer feed ratio in copolymerization		Concentration of metal ion added in solvent		Copolymer composition ^a			
	AN (f)	SF-AC (1-f)	[Cu ²⁺] (ppm)	[Fe ²⁺] (ppm)	AN (F)	SF (1-F)	Yield (%)	[η] (dL/g)
1	0.995	0.005	0	0	0.950	0.040	96	4.90
2	0.990	0.010	0	0	0.958	0.042	95	9.50
3	0.980	0.020	0	0	0.935	0.065	93	—
1-M	0.995	0.005	0.3	2	0.906	0.034	94	1.64
2-M	0.990	0.010	0.3	2	0.959	0.041	95	1.70
3-M	0.980	0.020	0.3	2	0.952	0.048	96	2.20

^a The data were obtained by elementary analysis.

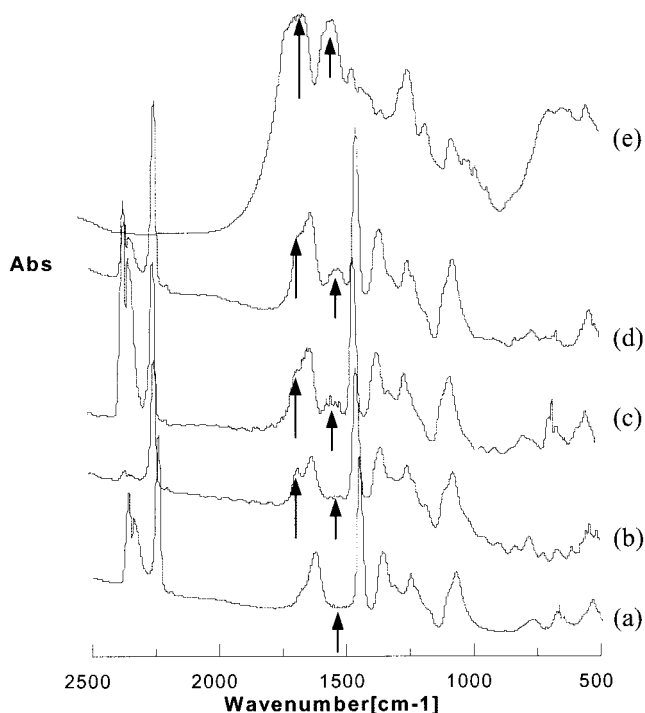


Figure 4 FTIR spectra in the range of 500 to 2500 cm^{-1} of (a) PAN; (b) copolymer 1; (c) copolymer 2; (d) copolymer 3; (e) SFP.

($\nu\text{C}\equiv\text{N}$), 1454 (δCH_2), and 1252 cm^{-1} ($\gamma_{\omega}\text{CH}$), identical with those of PAN. This result indicates that these copolymers consist of SFP and AN. Another thing worth noting about the FTIR spectrum of the copolymers is that the amide I and amide III bands of pure SFP are at 1653 and 1239 cm^{-1} ; however, in the copolymers, the amide I band shifted to about 1675 cm^{-1} and the amide III band disappeared, phenomena attributed to the conformation changes of SFP induced by copolymerization. In Figures 4 and 5, it was also observed that the intensities of the absorption band at about 1535 cm^{-1} are related to the weight ratios of PAN and SFP in the copolymers.

Thermal analysis

Figure 6 depicts the thermogravimetric analysis (TGA) thermograms measured from the PAN, SFP, and their copolymers. The TG curve of SFP showed that the first weight loss appears at around 80°C, a loss associated with the removal of water. The second weight loss began above 250°C, mainly resulting from the thermal decomposition of silk fibroin with changed β -form. On the other hand, PAN exhibited two-stage weight-loss behavior. The first stage of weight loss of PAN occurred at over 300°C; this loss was attributed primarily to the degradation of the polymer backbone. The second stage of weight loss of PAN occurred at 370 to 420°C, resulting from the cyclization of PAN.

The copolymers exhibited three-stage weight-loss behavior. The first weight loss appeared at around 80°C and was caused by removal of water, the same behavior as that observed for SFP. The second stage of weight loss of polymers 1-M, 2-M, and 3-M occurred at over 290, 289, and 285°C (shown in Table II), respectively, attributed to the degradation of the copolymer backbone. The degradation behaviors of these copolymer backbones occurred at a lower temperature compared with that of PAN homopolymer; furthermore, these temperatures decreased with increase of the weight ratio of SFP in the copolymers, but always higher than that of SFP. The third stage of weight loss of copolymers appeared at the range of 390 to 450°C, caused by the cyclization between AN segments, such as that of PAN homopolymer. It is interesting to note that the weight residue of the resulting copolymers at 560°C varied from 68 to 73%, showing a trend to increase with decrease of the weight ratio of SFP in the copolymers, and are higher than that of PAN homopolymer (67%) (as shown in Table II). This result suggests that the copolymers have good thermal stabilities as with PAN homopolymer.

The phase transitions and melting points of the PAN, SFP, and their copolymers investigated by DSC in nitrogen atmosphere are also listed in Table II. We can see from Table II that the glass-transition temperature for copolymers decreases with increases of the feed fraction of SFP, and that of copolymer 1-M is about 77°C higher than that of PAN homopolymer ($\sim 70^\circ\text{C}$) and that of copolymer 3-M is about 39°C, a value similar to that of SFP ($\sim 40^\circ\text{C}$). On the other hand, it is apparent that, although the melting temperature for copolymers also decreased with increases

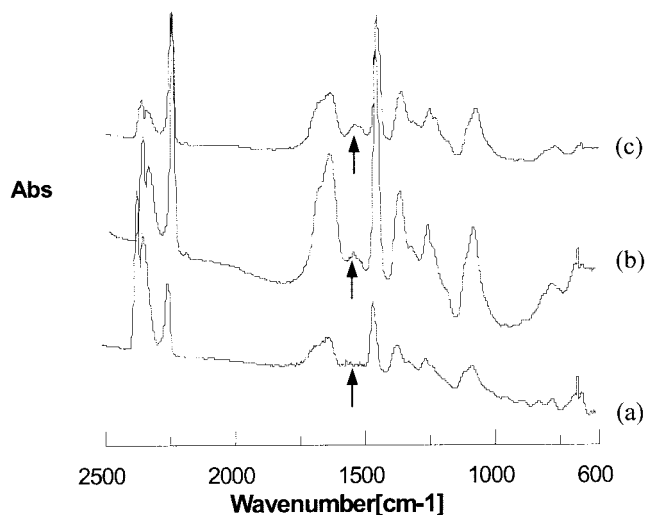


Figure 5 FTIR spectra in the range of 500 to 2500 cm^{-1} of (a) copolymer 1-M; (b) copolymer 2-M; (c) copolymer 3-M (copolymers 1-M, 2-M, and 3-M were synthesized after adding a trace amount of metal ions to the synthesizing solvent).

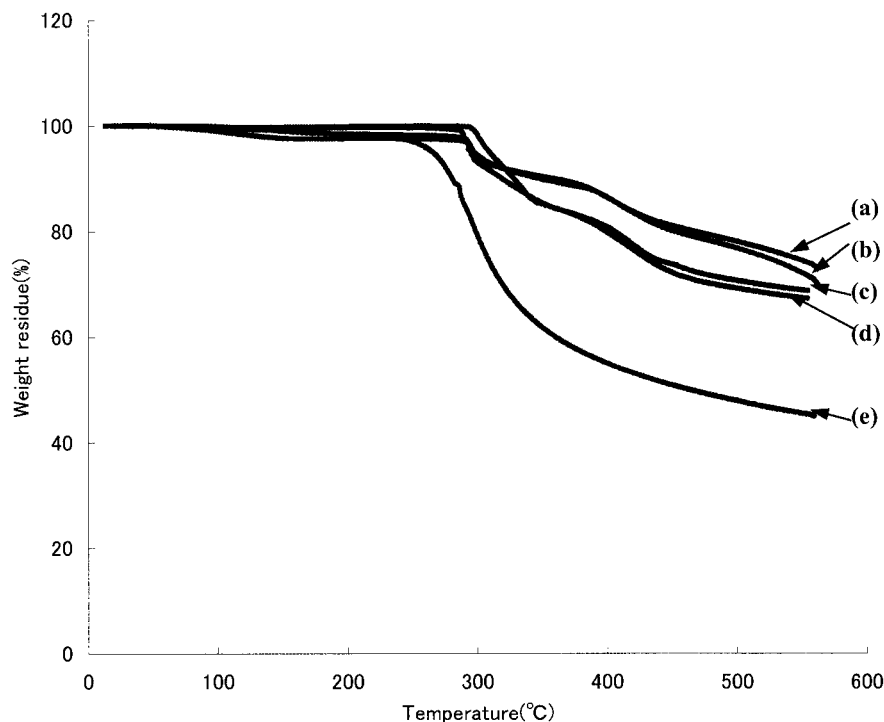


Figure 6 TG curves of (a) copolymer 1-M; (b) copolymer 2-M; (c) copolymer 3-M; (d) PAN; (e) SFP.

of the feed fraction of SFP (from 196 to 176°C), the melting point of copolymer 3-M is about 176°C, much higher than that of SFP (~ 97°C) and similar to that of the PAN homopolymer. It probably is attributed to the presence of the carbon-carbon chain in the copolymer backbone; that is, considering the preparation procedure of these copolymers, SFP molecular is only grafted onto the carbon-carbon backbone of the copolymers.

Structural characterization of fiber

In this study, the spinning poly(acrylonitrile-*co*-silk fibroin peptide)s were synthesized by vinyl copolymerization. Considering the process of the synthesis, we can establish that the copolymer backbones

possess pendent large molecular weight SFPs; in other words, the copolymer backbone is covered in SFPs. Thus we considered that the fibers spun from the copolymers have a core-shell structure. To verify the core-shell structure of the fibers, we sliced the fiber obtained from copolymer 2-M to shell and core flakes, and measured by FTIR using an infrared microscope detector cooled by liquid nitrogen. The results, as shown in Figure 7(1), of the IR spectrum of the shell portions appeared at 1658 cm^{-1} ($\nu\text{C}=\text{O}$, amide I) and 1545 cm^{-1} ($\delta\text{N}-\text{H}$, amide II), although no peak appeared at 2243 cm^{-1} (i.e., no $\nu\text{C}\equiv\text{N}$ was observed); in contrast, as shown in the IR spectrum of the cores [Fig. 7(2)], the vibrational peaks at 1680 ($\nu\text{C}=\text{O}$, amide I), 1570 ($\delta\text{N}-\text{H}$, amide II), and 2243 cm^{-1} ($\nu\text{C}\equiv\text{N}$) were displayed, respectively. The shift of the vibrational peaks of $\nu\text{C}=\text{O}$ and $\delta\text{N}-\text{H}$ is attributed to the change of the silk peptide conformation. From these results, it is considered that the fibers are characterized by a core-shell structure and the cores consist of PAN and SFP segments and the shells consist of SFP segments. Therefore, it is expected that the fibers are able to carry the excellent surface properties such as those of silk fibers (e.g., luster, handling, and moisture absorption), a result that is verifiable by the test of moisture absorption. We can also presume that the dyeability of the copolymers is better than that of the PAN homopolymer. Moreover, because of the presence of the carbon-carbon chain in the polymer backbones,

TABLE II
Thermal Properties of PAN Homopolymer, SFP, and Their Copolymers

Polymer and copolymer	Phase transition ^a		Thermal stability ^b	
	T_g (°C)	T_m (°C)	T_d (°C)	R_{560} (%)
PAN	70	186	300	67
1-M	77	196	290	73
2-M	67	181	289	70
3-M	39	176	285	68
SFP	40	97	250	47

^a Phase transition was determined by DSC.

^b Thermal stability was determined by TGA.

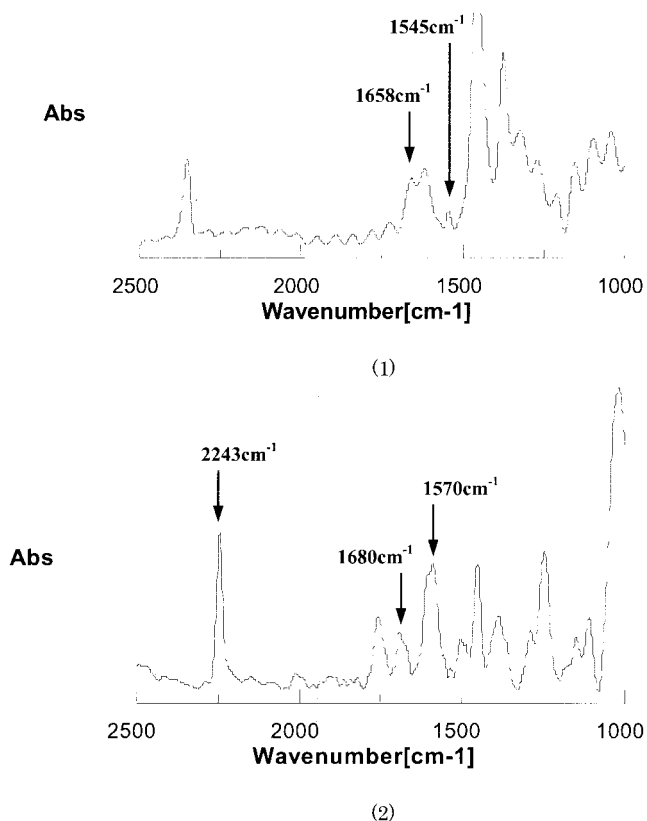


Figure 7 FTIR curves of (1) the shells (2) the cores of the fiber based on copolymer 2-M.

the fibers would be considered to have better mechanical properties, similar to those of PAN.

Scanning electron microscopy analysis

In a previous article, the study about the blend of SF and PAN was described,³ reporting that gross cracks were observed by SEM micrographs of longitudinal

direction of the blend fiber. That failure was thought to be attributable to cracking or slipping of the heterogeneous fibril structure, along the planes close to the fiber surface, thus indicating the poor adhesion between SF and PAN. In contrast, from Figure 8(1) we can see that the longitudinal section of fiber 2-M has a smooth surface with few microstripes and no fractured structure; that is, no shear of the heterogeneous fibril structure occurred. Figure 8(2) shows the cross section of the 2-M fiber. The fiber has a circular cross section, and no cracking was observed, whereas some holes were found. These holes are believed to result from the wet-spinning process because the wet-spinning process was used in this study, the spinning solution was prepared by dissolving the copolymers into DMF, and the coagulation bath used water. Because water is not a good coagulation bath against use of DMF solvent, the fiber structure tended to be characterized by porosity or to lose transparency. The study about the proper fiber-forming conditions for poly(acrylonitrile-*co*-silk fibroin peptide)s will be investigated in future studies.

Moisture absorption

Figure 9 shows the moisture absorption dependency of SFP monomer feed ratio in copolymerization. As shown in Figure 9, the moisture absorptions of the copolymers and their fibers increase with increasing the SFP monomer feed ratio. More remarkable is that, at the same feed ratio of the modified SFP, the moisture absorptions of the fibers based on the copolymers are much higher than those of the copolymer powders, which is explained by the fibers having a large surface area and the presence of SFP covering the fibers' surface. However, when the SFP monomer feed ratio in copolymerization increased and reached 2 wt %, the moisture absorption of the fibers was main-

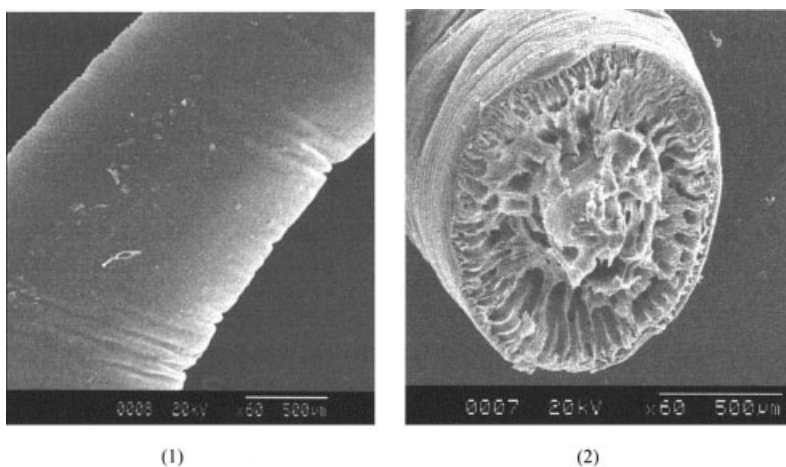


Figure 8 SEM micrographs of fiber based on the copolymer 2-M: (1) longitudinal section and (2) cross section.

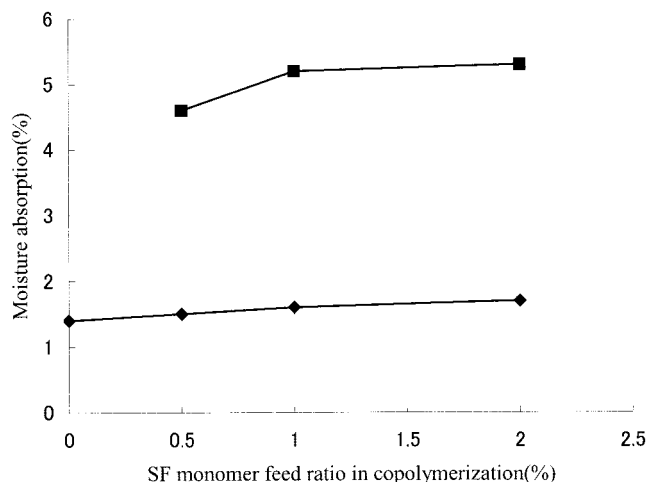


Figure 9 Moisture absorption dependency of SF monomer feed ratio in copolymerization: (◆) copolymer powders and (■) their fibers.

tained at constant levels, about the range of 5 to 6 wt %. Given that moisture absorption of the pure SF is about 8.0 wt %, and that of PAN fiber is about 1.0 wt %, we can consider that the moisture absorption of PAN fibers is improved significantly by being combined with SF protein.

CONCLUSIONS

In this study, a silk fibroin peptide monomer was prepared by a two-step procedure, which was used to synthesize a new acrylic polymer containing silk protein with acrylonitrile by vinyl polymerization. Their chemical compositions were determined. In the copolymerization, the SFP monomer was found to be more reactive than acrylonitrile monomer, and thus it was considered that if a small amount of SFP is loaded in the copolymerization, the copolymer would be characterized by the same excellent properties as those of silk protein. From the results of intrinsic viscosity measurements, the copolymers 1-M, 2-M, and 3-M, synthesized after the addition of a trace amount of metal ions into the synthesizing solvent, were concluded to have good spinnability.

Spectroscopic analysis showed that poly(acrylonitrile-*co*-silk fibroin peptide)s constitute a copolymer consisting of SFP and AN, and the conformation of SFP changed as a result of copolymerization.

We investigated the thermal property of the spun copolymers. The T_g values of the copolymers varied from 39 to 77°C, and the melting temperature ranged from 196 to 176°C, depending on the composition. From TG curves, we found that the copolymers un-

derwent a three-step degradation, and the degradation behavior of these copolymer backbones occurred at about 285 to 290°C. These degradation temperatures were lower than that of PAN homopolymer, but always higher than that of SFP. At about 400°C, cyclization between AN segments occurred. The TG curves suggest that the copolymers have high weight residue. From these results, it was thought that these copolymers have good thermal stability.

Then by using a simple wet-spinning method, a continuous fiber based on copolymers was obtained. It was confirmed that the fiber has a core-shell structure by spectroscopic analysis of the shell and core flakes of the fiber with FTIR using an infrared microscope detector. From SEM micrographs of the fiber, we confirmed that the fiber has a smooth surface with a few microstripes and no fractured structure. Because of the lack of a fractured structure, it was assumed that the poly(acrylonitrile-*co*-silk fibroin peptide)s have good adhesion between SFP and PAN.

The result of the moisture absorption showed the moisture absorption of the fibers based on the copolymers is much higher than that of the copolymer powders, and depended on the molar ratio of SFP in the copolymers, which is explained by the fibers having a large surface area and the presence of SFP covering the fibers' surface. Consequently, we established that these fibers are characterized by excellent moisture absorption approaching that of silk protein.

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