Polyion Complex Fiber and Capsule Formed by Self-Assembly of Poly-L-lysine and Gellan at Solution Interfaces

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Received 9 November 1999; accepted 18 March 2000

ABSTRACT: Different characteristic surface structures such as capsules, regularly spaced droplets, and fibers are formed by electrostatic interaction between poly-L-lysine (PLL) and gellan gum via polyion complex (PIC) formation. Spherical droplet PIC capsules of varying diameters form in solutions. Some dyes adsorb on the surface of the capsules, and other dyes penetrate into the capsules. The strong PIC fiber can be spinnable by gravity and by wet spinning in ethanol. This fiber possesses a counterion pairing structure and exhibits the nervation/veining pattern and hollow yarn. The tensile strength of the fiber is 27.8 kg/mm^2 [1.40 g/denier (d)] and the knotting strength is 9.98 kg/mm^2 (1.13 g/d). By using an organic crosslinking agent, epichlorohydrin, the tensile strength can be increased to 38.5 kg/mm^2 (2.46 g/d) and the knotting strength can be increased to 12.2 kg/mm^2 (1.99 g/d). The PIC fiber can be dyed by five different dyeing procedures such as direct and vat dyeings. The PLL PIC fiber is water insoluble and has potential as a new synthetic polypeptide fiber technology. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 437–446, 2001

Key words: interface self-assembly; polyion complex; fiber; capsule; poly-L-lysine; gellan

INTRODUCTION

Polyion complexes (PICs) are formed by the reaction of a polyelectrolyte with an oppositely charged polyelectrolyte in aqueous solution. Considering that almost all biopolymers are polyelectrolytes, the studies on PICs as models of complicated biological systems and as biodegradable material formulations are very important. PICs have been investigated for a long time from the standpoints of the polyacid–polybase interaction, stoichiometry, and self-assembly.[1–5] They also have numerous applications such as membranes, antistatic coatings, surfactants, and microcapsules.[6] The most promising system developed is the encapsulation of alginate beads coated with chitosan [(1 → 4)-2-amino-2-deoxy-β-D-glucan] with amino functional groups or its derivative.[7–9] Such polysaccharide PICs have been widely studied.[10,11] For example, the swelling properties of polylysine and chitosan-coated sodium alginate gel beads is reported.[12] Most recently, we have reported chitosan-gellan PIC capsule and fiber formed by self-assembly at solution interfaces.[13,14]

We studied the synthesis,[15] conformation,[16] potentiometric titration,[17] induced circular dichro-

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Contract grant sponsor: Grant-in-Aid for COE Research, Ministry of Education, Science, Sports and Culture of Japan; Contract grant number: 10CE2003.

Journal of Applied Polymer Science, Vol. 79, 437–446 (2001)

ism,[18] photochromism,[19] adhesion,[20] wettability,[21] biohydrogel,[22] and biodegradation[23] of poly-L-lysine (PLL) homologs and their derivatives for many years. During the course of our continuing work on PLL, we found that some of the interactions between anionic and cationic biopolymers can give characteristic structures at the interface in aqueous solutions. In this article we report different characteristic surface structures, such as capsules and fibers, formed by cationic PLL and anionic gellan gum with carboxyl functional groups,[24–26] which are composed of tetrasaccharide repeat units comprising 1,3-β-D-glucose, 1,4-β-D-glucuronic acid, 1,4-β-D-glucose, and 1,4-α-L-rhamnose, via PIC formation. The PLL–gellan PIC fiber structures were studied with microscopes, and the fiber characteristics are described here in detail.

EXPERIMENTAL

Materials

PLL was prepared according to the modified method as described in our earlier article.[16] The viscosity average molecular weights of PLL hydrobromide are 73,200 [degree of polymerization (DP) 350], 118,000 (DP 570), 418,000 (DP 2000), and 682,000 (DP 3260) from the viscosity equation $\log \mathrm{DP} = 1.47 \times \log[\eta] + 2.99$ for protected poly(ϵ-benzyloxycarbonyl-L-lysine).[27] The PLL samples were dissolved in the 1–8% range in water. Gellan gum [molecular weight (MW) 880,000–920,000] was a kind gift from San-Ei Gen F.F.I., Inc. It was dissolved in the 0.5–1.5% range in water at 50–60°C. The following dyes were purchased from Wako Pure Chemical Industries: Congo Red (CI 22120), Indigo (CI 73000), Alizarine Yellow GG (CI 14025), Orange IV (CI 13080), Fuchsin Acid (CI 42685), Methylene Blue (CI 52015), Rhodamine B (CI 45170), Crystal Violet (CI 42555), Methyl Red (CI 13020), Methyl Yellow (CI 11020), and New Coccine (CI 16255).

Silk and cotton were the two natural fibers used in the dyeing experiment for comparison with the PIC fiber. Raw silk [21 denier (d)] and sewing cotton (180 d) were commercial products.

Degree of Swelling

The degree of swelling (q_m) was determined from the ratios of $(d_s/d_0)^3$, where d_s is the diameter of the spherical swelled capsules after they reached equilibrium in the medium and d_0 is the initial diameter of the prepared capsules.

Strength of Fiber

The tensile and knotting strengths of the PIC fibers were measured by a tensile testing machine at a rate of 10 mm/min (PS-5K, Imada Co.). The strengths per fiber (kg/mm^2) were calculated from the average strengths of 10 independent measurements using bundles of three threads and the average cross-sectional areas of the fibers.

Microscopy

A Jeol JSM-840F scanning electron microscope (SEM) was used to observe the surface topography and fracture surfaces of the fibers. Fibers were examined using an accelerating voltage of 5 kV. The diameter of the fibers was measured by optical micrographs and the SEM.

Dyeing

Three meters of each (10–12 mg) of the PIC fibers was dyed.[28] There were five different methods of dyeing.

Direct Dyeing

The fibers were dyed in a 3 wt % Congo Red solution with an added salt of Na_2SO_4 (20 wt % in wt %/PIC fiber) for 1 h at 50°C.

Vat Dyeing

In this method a stock vat was prepared with a mix of zinc dust (4 g in 0.5 mL of methanol) and powdered Indigo (4 g in 0.5 mL of methanol) in 50 mL of hot water (60°C), and then 10 g of calcium hydroxide was added into 0.5 mL of methanol. After 6 h the stock vat was diluted to be 60 wt % of dye for a fiber with a solution containing 0.1 g of zinc dust and 0.2 g of calcium hydroxide in 200 mL of water. The PIC fiber was dyed in the diluted vat solution for 1 h at 50°C, air oxidized for 10 min, and immersed in 1% AcOH for 10 s.

Acid Dyeing

Fibers were acid dyed in 6 mg (60 wt %) of Fuchsin Acid in 60 mL of water with 1 mg of Na_2SO_4 (10 wt %) for 1 h at 50°C.

Basic Dyeing

In basic dyeing the fibers were dyed in 6 mg (60 wt %) of Methylene Blue or Rhodamine B in 60 mL of water with 0.1 mg of AcOH (1 wt %) for 30 min at 50°C and then immersed in 0.5% AcOH for 10 min.

Acid Mordant Dyeing

According to the metachrome process, the fibers were dyed in 6 mg (60 wt %) of Alizarine Yellow GG in 60 mL of water containing 1 mg of Na_2SO_4 (10 wt %), potassium bichromate (1.5 wt %), and ammonium acetate (3 wt %) for 20 min at room temperature and then for 1 h at 60°C. After adding AcOH (2%), they were dyed for 15 min at room temperature.

RESULTS AND DISCUSSION

Microbial polysaccharide gellan gum is produced by *Pseudomonas elodea* and is a linear anionic polymer consisting of the [(3)-β-D-glucose-(1,4)-β-D-glucuronic acid-(1,4)-β-D-glucose-(1,4)-α-L-rhamnose-(1)] repeating unit,[29,30] and a carboxyl group in the glucuronic acid as a fourth component is responsible for the interaction with an amino group in the PLL. The native gellan is reported to contain 3–6% by weight of *O*-acetyl groups and the exact location of the *O*-acetyl groups is uncertain.[11,24,29] The counterion of gellan gum supplied by San-Ei Gen F.F.I., Inc. is mostly monovalent potassium salt (79%) and sodium salt (10%). The carboxyl and amino interaction between the polysaccharide and polypeptide causes the PIC capsule and fiber formation by self-assembling of their counterions.

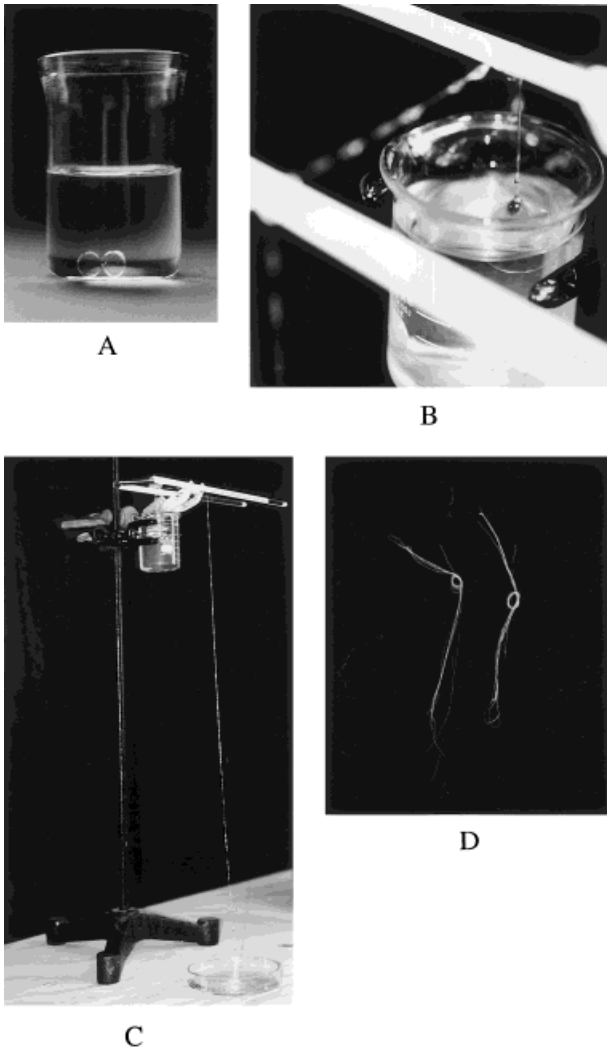


Figure 1 Characteristic polyion complex capsule and fiber formation via polyion complex formation: (A) the spherical capsules formed, (B) the continuous reaction at the interface, (C) the continuous formation and removal of a polyion complex fiber by gravity, and (D) the fiber after drying.

PIC Capsule

PIC Capsule Formation

A 1–8% PLL solution at pH 5–5.5 and 50°C (after being adjusted) is added dropwise into a 0.75% gellan aqueous solution (at pH 6 and 60°C) causing spherical droplets to form in the gellan solution [Fig. 1(A)] under the conditions listed in Table I. The spherical droplets, whose inside is PLL and outside surface is gellan, are stable enough for finger pinching or magnetic stirring in distilled water. After reacting for 5–45 min, this procedure gives the true spherical droplet structures with various diameters. The droplets thus formed are stable when washed with water and 80% ethanol to rinse extra gellan off the outside surfaces of the droplets. The soft droplet capsule is acid resistant, alkaline resistant, and mostly boiling water resistant.

The swelling degree and strength of the droplet capsule depend on both the PLL concentration and the reaction time between the PLL and gellan. For example, when a 1% PLL (DP 3260) solution and a 0.75% gellan solution react for 5 min, the swelling degee q_m of the capsule placed

Table I PLL–Gellan PIC Capsule Forming Conditions

Concn of PLL Solution (w/v %)	Degree of Polymerization			
	350	570	2000	3260
1	DNF	DNF	DNF	FC
2	DNF	DNF	FC	C
3	DNF	DNF	C	SC
5	DNF	DNF	SC	DNF
8	DNF	DNF	DNF	DNF

The concentration of the gellan solution was 0.75%. DNF, did not form; FC, fragile capsule; C, capsule; SC, strong capsule.

in distilled water is 1.81 after 1 h and 1.60 after 24 h. When the PLL concentrations are increased to 2, 3, and 4%, the q_m in distilled water changes to 1.36, 1.05, and 1.00 after 1 h and 0.97, 0.86, and 0.86 after 24 h, respectively. In case lower DP PLL samples are used, the smaller q_m values are obtained. Conversely, when a 0.5% gellan solution and a 3% PLL (DP 3260) solution react for 5 min, the q_m of the capsule in distilled water is 1.64 after 1 h. When the gellan concentrations are increased to 0.75 and 1%, the q_m in distilled water decreases to a constant value of 1.05. As for the reaction time to prepare the PIC capsule, when a 3% PLL (DP 3260) solution and a 0.75% gellan solution are allowed to react, the q_m values of the capsule in distilled water are 1.05 after reacting for 5 min, 1.12 after 15 min, 1.24 after 30 min, and 1.33 after 45 min. The longer reaction time gives capsules with larger degrees of swelling. When the pH of the PLL solution is changed from 2.6 to 6.0, the largest qm value of 1.32 is obtained at pH 5 and the smaller qm values of 1.05, 1.28, 1.26, and 1.20 are obtained at pH 2.6, 4.1, 6.0, and 7.2, respectively. Thus, the optimal pH to prepare the PLL–gellan PIC capsule is around 5.

Capsule Properties

In water–ethanol mixed solvents, the PIC capsules shrink to white turbid solid particles at 75% ethanol (Fig. 2). When the NaCl concentration is increased to sink the PIC capsule (1% PLL, DP 3260, and 0.75% gellan after 24 h), the qm values of 1.60, 1.47, 1.44, 1.28, and 1.10 are obtained at 0, 0.5, 1.0, 2.0, and 4.0M, respectively. Thus, the PIC capsule shrinks in ethanol and concentrated NaCl solution.

The true spherical capsules prepared according to the above conditions (PLL, DP 3260 at pH 5) were immersed in the dye solutions for 30 min. A disperse dye (Methyl Red), two basic dyes (Crystal Violet and Methylene Blue), a direct dye (Congo Red), an acid dye (Orange IV), and a food dye (New Coccine) distinctly dyed the capsules. Then in the next step the six kinds of dyed capsules were immersed in the distilled water. The capsules dyed by the disperse dye and the basic dyes were decolorized after 2 h; the capsules dyed by Congo Red, Orange IV, and New Coccine exhibited no decolorization, even overnight. From the results it can be expected that the controlled adsorption and release using these PIC capsules and aromatic chemical and medicine systems changed the counterion densities of the capsules and the bulk watery conditions.

PIC Fiber

PIC Fiber Formation

When the film of a PIC at the interface of both cationic and anionic solutions is removed without stirring, it is instantly and continuously replaced [Fig. 1(B)] under the conditions listed in Table II. When this PIC film is withdrawn from a liquid interface and hung over a glass rod, regularly spaced droplets form along the fiber line in the wet states as reported in our earlier articles.[13,14] These regularly spaced droplets look like a stretched capture thread of the garden cross spider (*Araneus diadementus*) suspended in air.[31]

When the intact wet droplet fiber is dried in air, a strong fiber forms [Fig. 1(D)]. The inside of the fiber is PLL (1–8%), and its outside is coated with gellan (0.75%). The fiber is spinnable by hand. This fiber is a kind of PIC structure: the outside layer is gellan, the inside layer is PLL, and the methods capable of producing the fiber are dry and wet spinnings. Likewise, a strong fiber made in a similar way as previously described but whose outside layer is PLL with DPs of 2000 and 3260 (2–3%) and inside layer is gellan (0.75%) is spinnable. The diameters of the fiber are about 40–200 μm. However, a fiber whose combination is gellan (0.75%) and PLL (DP 3260) over 8% concentration is less spinnable, exhibiting no continuous fiber formation.

The fiber can be made self-propelled by passing the film prepared from the middle area of the vessel over a glass rod and then out and down

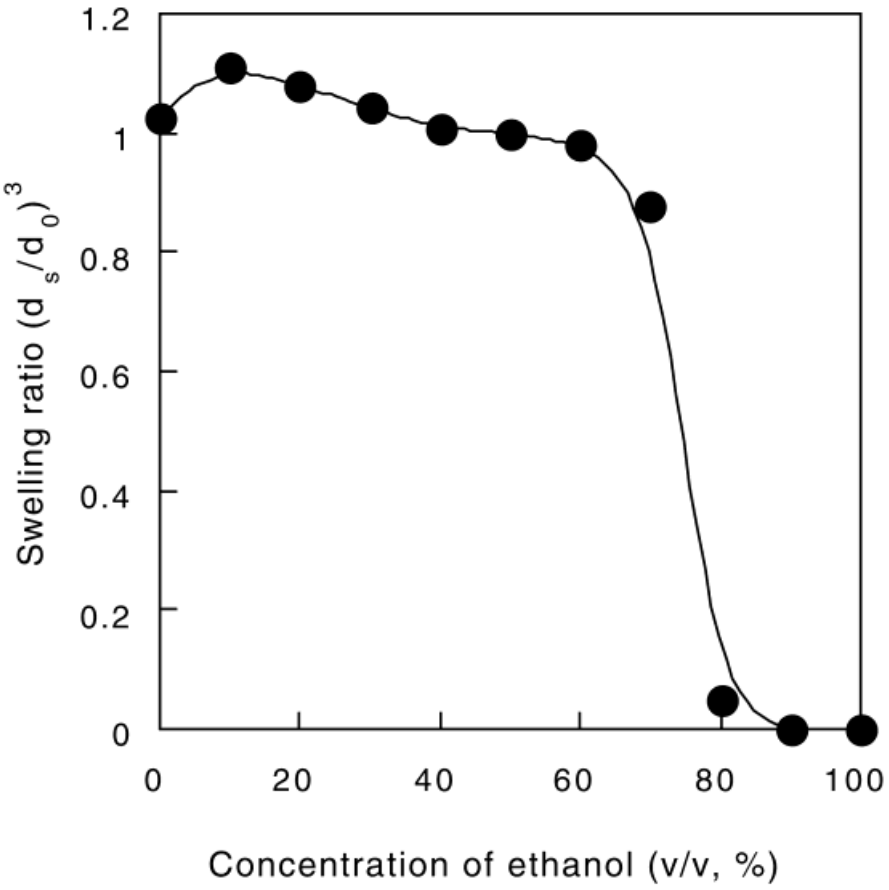


Figure 2 The swelling ratios of the PIC capsule in water–ethanol mixed solvents.

over a second rod by gravity [see Fig. 1(C)], as in the case of interfacial polycondensation.[32,33] These simple methods to prepare the capsule and fiber are particularly well suited for a lecture demonstration [Fig. 1(B,C)].

Table II PLL–Gellan PIC Fiber Spinnable Conditions

Concn of PLL Solution (w/v %)	Degree of Polymerization			
	350	570	2000	3260
1	NS	NS	TWF	F
2	NS	TWF	F	SF
3	NS	TWF	SF	F
5	NS	F	F	F
8	NS	F	F	NS

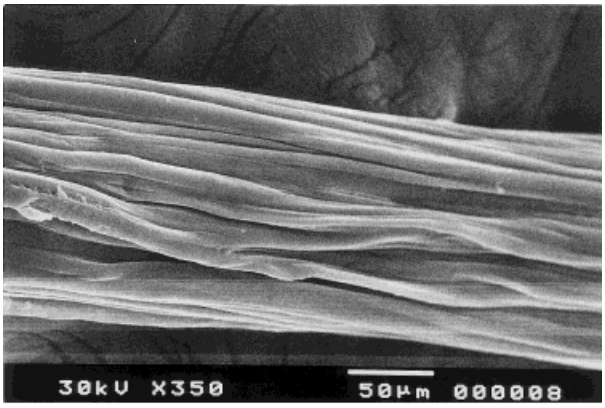
The concentration of the gellan solution was 0.75%. NS, not spinaable; TWF, thin and weak fiber; F, fiber; SF, strong fiber.

PIC Fiber Spinning

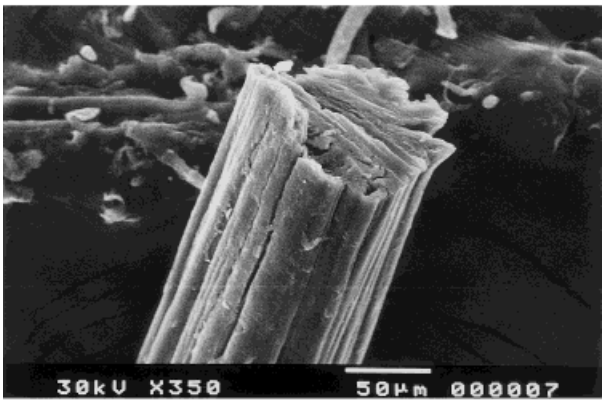
A simple wet-spinning apparatus accompanied by a roller was used as reported in our earlier article.[14] The PLL–gellan PIC fiber can be spun continuously in ethanol. The spinning method is the simplest. A 0.75% gellan solution in water kept at 60°C was slowly added onto a 2–5% PLL (DPs 2000 and 3260) solution in water kept at 60°C and adjusted to pH 5–5.3. The interface was immediately drawn by a pincette at a rate of 2 cm/s. The thread formed was passed through a 3-L ethanol bath (150 cm long and 3.5 cm deep in a commercial semicylindrical rain conduit) and rolled up at a rate of 40 cm/min by air drying (20 cm) at 40°C.

PIC Fiber Structures

The fiber structures were partly described above (see PIC Fiber Formation). Although the diameter of the PIC fiber shown in Figure 3 is about 120 μm, the diameter of the fiber can be changed from



A



B

Figure 3 SEM photographs of the PIC fiber: (A) the nervation/veining pattern, and (B) a cross section of the fiber.

40 to 200 μm by changing the spinning roll-up speed and the concentration of the PLL solution. Figure 3 shows the SEM photographs of the PIC fiber. The fiber exhibited the "nervation/veining pattern" on the lateral surface [Fig. 3(A)] as described by Fambri et al.[34] in poly(L-lactic acid) fibers and chitosan-gellan PIC fibers.[14] Because the fiber break was performed in liquid nitrogen, the fracture surface showed a sharp cross section with little plastic deformation for the fiber [Fig. 3(B)].

A short hollow yarn can be prepared by a special technique. First a 10-cm nylon monofilament (370 μm) was sunk in a 0.75% gellan solution at 60°C. Then a 3% PLL solution at pH 5.3 was poured into the gellan solution, and the nylon fiber was drawn up into air and dried. Finally, the 10-cm nylon filament covered with a PIC fiber was immersed in a mixed phenol–ethanol solvent (70:30, v/v) for 5 h at room temperature and dried intact in air. Figure 4 shows the microscopic photograph of the hollow yarn of the gellan (outside)–PLL (inside).

PIC Fiber Properties

The gellan solutions at 60°C were added dropwise into the PLL solutions at pH 5.3 to spin the PIC fibers. The relationship between the fiber tensile strength and molecular weight and the concentration of the PLL is shown in Figure 5. The fiber strength exhibited the optimal concentration at 5%, and the PLL with the highest molecular weight (DP 3260) had greater strength than those with lower molecular weights (Table II). Alternatively, when 0.5, 0.75, and 1% gellan solutions were added into the PLL solution, the optimal concentration of gellan was 0.75%. The 1% gellan was less spinnable, forming short and thick fibers. At gellan concentrations higher than 1.25%, it was difficult to spin the PIC fibers. The relationship between the pH of the PLL solution and the fiber strength is shown in Figure 6. The optimal condition to spin the PIC fiber was at pH 5–5.3. In order to enhance the tensile strengths of the PIC fiber, organic crosslinking reagents, such as glutaraldehyde, epichlorohydrin (ECH), ethyl-

Figure 4 An optical micrograph of the PIC hollow yarn structure.

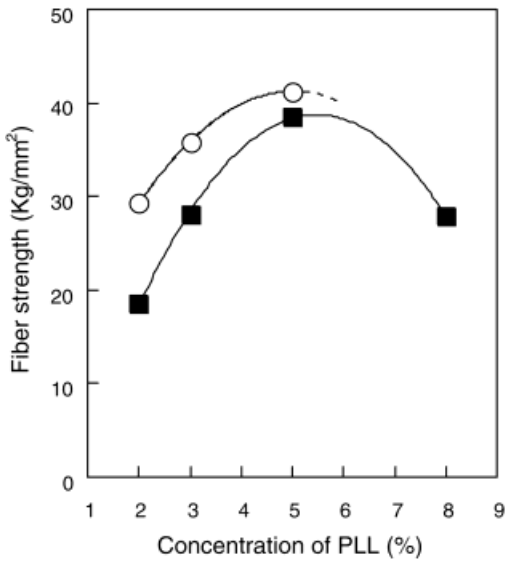


Figure 5 The relationship between the tensile strengths of the PIC fiber and the concentrations of PLL. PLL DP = (○) 3260 and (■) 2000.

ene glycol diglycidyl ether, and hexamethylene diisocyanate (HMDI), were used. The organic crosslinking reagents were added into the PLL solution at pH 5.3, and the mixed solutions were stirred for 5 h. The gellan solutions were then poured into the PLL mixture solutions. The greatest effect in enhancing the tensile strength [from 27.8 kg/mm^2 (1.40 g/d) to 38.6 kg/mm^2 (2.46 g/d)] of the PIC fibers was obtained when ECH was used as a crosslinking reagent. The effects of adding the crosslinking reagents are listed in Table III. The tensile properties of the PLL–gellan PIC fibers are summarized in Table III, together with those of chitosan–gellan fibers reported in our earlier article.[14]

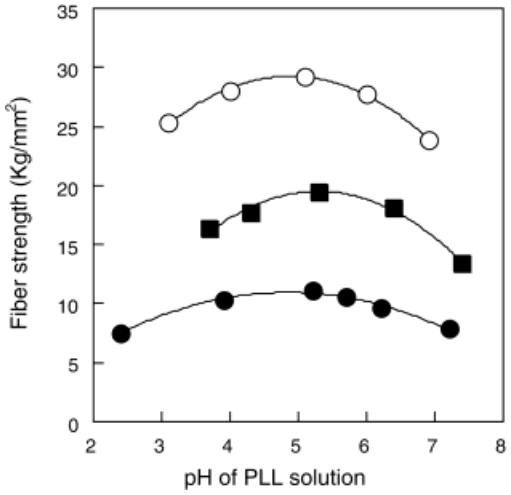


Figure 6 The relationship between the tensile strengths of the PIC fiber and the pH of PLL. PLL DP = (○) 3260, (■) 2000, and (●) 570.

Table III Tensile Strengths of Crosslinked PLL–Gellan PIC Fibers

Samples	Crosslinker	Equiv Mol	Tensile Strength kg/mm^2	Tensile Strength g/d
PIC fiber[a]	None		27.8	1.40
	GA	0.005	30.1	
		0.010	33.5	
		0.013	34.6	
		0.017	35.6	2.10
		0.020	31.6	
		0.025	23.4	
	ECH	0.010	32.9	
		0.020	37.2	
		0.025	38.6	2.46
		0.040	35.0	
		0.050	28.3	
	EGDE	0.010	31.3	
		0.020	34.7	
		0.025–0.033	35.7	2.10
		0.040	30.5	
		0.050	26.9	
	HMDI	0.005	31.7	
		0.010	33.9	
		0.020	36.1	2.74
		0.033	31.0	
		0.040	27.0	
CG–PIC fiber[b]	None		18.4	2.42
	ECH	0.50	24.6	2.64
	HMDI	0.10	36.0	3.99
Cotton[b]			27.3	3.69
Raw silk[b]			96.3	7.62

g/d, grams per denier; GA, glutaraldehyde; EGDE, ethylene glycol diglycidyl ether.

[a] The present work.

[b] The tensile strengths of the chitosan–gellan (CG) PIC fiber are from our previous study.[14]

The knotting strengths of PLL–gellan fibers and crosslinked PLL–gellan fibers are also summarized in Table IV. The knot strength is one of the major defects when one prepares a new fiber. In the present PLL–gellan PIC fiber, the knot strength of the untreated PIC fiber was 9.98 kg/mm^2 (1.13 g/d), and ECH crosslinked PIC fiber

Table IV Knot Strengths of Crosslinked PLL–Gellan Fibers

			Knot Strength	
			kg/mm^2	g/d
PIC fiber[a]	None		9.98	1.13
	GA	0.017	11.9	1.66
	ECH	0.025	12.2	1.99
	EGDE	0.025	12.1	1.27
	HMDI	0.020	11.4	1.45
CG–PIC fiber[b]	None		2.98	0.40
	ECH	0.50	5.17	0.55
	HMDI	0.10	9.24	1.07
Cotton[b]			6.03	1.86
Raw silk[b]			17.7	2.94

[a] The present work.
[b] The knot strengths of chitosan–gellan PIC fiber.[14]

was enhanced to 12.2 kg/mm^2 (1.99 g/d). The knot strength (kg/mm^2) of the crosslinked PLL–gellan PIC fiber was greater than the chitosan–gellan PIC fiber [untreated: 2.98 kg/mm^2 (0.40 g/d); HMDI crosslinked: 9.24 kg/mm^2 (1.07 g/d)] and cotton (6.03 kg/mm^2, 1.86 g/d) but lower than raw silk (17.7 kg/mm^2, 2.94 g/d).[14]

PIC Fiber Dyeing

Judging from the facile and cheap fiber preparative methods described above, the strong PLL–gellan PIC fiber gives some practical applications as a biodegradable artificial biopolmer fiber. The dyeing problem is very important for practical use. From such a standpoint, the following dyeing experiments were carried out using two representative natural fibers: an animal fiber silk and a plant fiber cotton.

The results of the dyeing of PIC fibers are photographically shown in Figure 7. The dyeing by a direct dye, Congo Red, dyed the PIC fiber well; the dyeing order was PIC fiber > silk > cotton. Likewise, the dyeing by a vat dye, Indigo, also dyed the PIC fiber well; the dyeing order was PIC fiber > silk > cotton. However, the strength of the PIC fiber and silk were weakened. The dyeing by an acid mordant dye, Alizarine Yellow GG, dyed the PIC fiber well and scarcely dyed the silk and cotton; the dyeing order was PIC fiber ⩾ silk > cotton. The dyeing by acid dyes, Orange IV and Fuchsin Acid, dyed the PIC fiber and silk well and scarcely dyed the cotton; the dyeing order was PIC fiber ≈ silk ⩾ cotton. The dyeing by basic dyes, Methylene Blue and Rhodamine B, exhibited a characteristic dyeing property for the three fibers; the dyeing order was PIC fiber > silk > cotton with Methylene Blue and silk > cotton > PIC fiber with Rhodamine B. Thus, on the whole, the PLL–gellan PIC fiber dyes well in many colors (Fig. 7), and especially the dyeing of PLL–gellan PIC fiber by the coordination bond is more intense than the typical silk and cotton natural fibers.

Finally, as an additional remark, as early as 1945–1970s, synthetic polypeptide fibers such as poly-L-alanine and poly(γ-methyl-l-glutamate) were studied from industrial standpoints in the United States, the United Kingdom, and Japan.[35,36] All synthetic polypeptide fibers at that time were spun from the polypeptides dissolved in organic solvents such as dichloroacetic acid, benzene, and dichloromethane. No attempt succeeded in spinning water-soluble polypeptides to change them into water-insoluble fibers. The present PLL–gellan fiber was prepared via interfacial complex formation, not a pure PLL fiber. However, this was the first synthetic PLL fiber spun from the aqueous solution. The present results may offer some clues toward synthetic polypeptide fiber science, together with the formulation design and selection of polyelectrolytes in composite materials.

CONCLUSIONS

When the concentrations of anionic and cationic biological macromolecules are both increased to

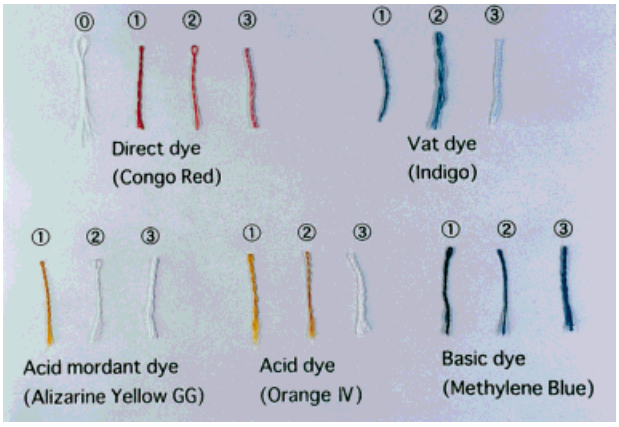


Figure 7 The dyeing properties of the PIC fibers by the five different dyeing methods: (0) the PIC fiber before dyeing, (1) dyed PIC fiber, (2) dyed raw silk, and (3) dyed cotton.

the percent order in water, characteristic water-insoluble PIC structures are formed. The spherical capsules and the strong fibers that have the nervation/veining pattern and hollow yarn can be easily prepared by the PIC between PLL and gellan at aqueous solution intefaces. The PIC structures are molecular weight dependent and concentration dependent. The PIC structures themselves are scientifically interesting and might offer some clues to understanding the biological counterion interaction such as blood and extracellular material systems, as well as understanding its biomimesis, which undoubtedly includes the protein and polysaccharide interaction process, along with biodegradation by microorganisms and enzymes involved in keeping both land and sea ecology clean.[23,37–39]

These findings expand the earlier results of polysaccharide interpolyelectrolyte association.[40,41] Besides, they may also have the prospect of developing new biodegradable biohydrogel materials with very high water content. As we have reported, given the selective adsorption ability of anionic molecules such as benzoic acid and acidic amino acids in the cationic model protein gel matrices,[42,43] it may be possible to adsorb anionic medicines and chemicals into the capsule and onto the fiber. When the capsules and fibers are biodegraded, the digested polylysine fragments are expected to exhibit chemotherapeutic possibility as reported earlier.[44,45] Simultaneously, the medicines or agricultural chemicals released from within the capsules and fibers are also expected to be effective in curing injured tissues of animal organisms or in exterminating pests. Thus, the PIC capsules and fibers look very promising in their diverse medical, agricultural, and fiber industrial applications.

We thank San-Ei Gen F.F.I., Inc. for the gellan.

REFERENCES

1. Noguchi, J.; Saito, T.; Hayakawa, T.; Tokuyama, H.; Harada, T.; Nishi, H.; Ikeda, S.; Yamashita, T.; Isemura, T.; Hiraoka, T. Nippon Kagaku Zasshi 1961, 82, 597.
2. Goddard, E. G. Colloids Surfaces 1986, 19, 255.
3. Staikos, G.; Bokias, G.; Tsitsilianis, C. J Appl Polym Sci 1993, 48, 215.
4. Lysenko, E. A.; Bronich, T. K.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. Macromolecules 1998, 31, 4511.
5. Bronich, T. K.; Cherry, T.; Vinogradov, S. V.; Eisenberg, A.; Kabonov, V. A.; Kabanov, A. V. Langmuir 1998, 14, 6101.
6. Kondo, T. Microcapsules [in Japanese]; Nihon Kikaku Kyokai Press: Tokyo, 1991.
7. Yabuki, M. Applications of Chitin and Chitosan [in Japanese]; Gihoudo Press: Tokyo, 1990.
8. Lee, K. Y.; Park, W. H.; Ha, W. S. J Appl Polym Sci 1997, 63, 425.
9. Roberts, G. A. F.; Domszy, J. Int J Biol Macromol 1982, 4, 374.
10. Chilvers, G. R.; Morris, V. J. Carbohydr Polym 1987, 7, 111.
11. Shinoda, K.; Hayashi, T.; Nakajima, A. Polymer J 1976, 8, 216.
12. Ottøy, M. H.; Smidsrød, O. Polym Gel Networks 1997, 5, 307.
13. Amaike, M.; Senoo, Y.; Yamamoto, H. Macromol Rapid Commun 1998, 19, 287.
14. Yamamoto, H.; Senoo, Y. Makromol Chem Phys, to appear.
15. Yamamoto, H.; Hayakawa, T. Biopolymers 1982, 21, 1137.
16. Yamamoto, H.; Yang, J. T. Biopolymers 1974, 13, 1109.
17. Yamamoto, H.; Yang, J. T. Biopolymers 1974, 13, 1093.
18. Yamamoto, H. Makromol Chem 1983, 184, 1479.
19. Yamamoto, H. Macromolecules 1986, 19, 2472.
20. Yamamoto, H.; Ohara, S.; Tanisho, H.; Ohkawa, K.; Nishida, A. J Colloid Interface Sci 1993, 156, 515.
21. Yamamoto, H.; Ogawa, T.; Nishida, A. J Colloid Interface Sci 1995, 176, 105.
22. Yamamoto, H.; Kitsuki, T.; Nishida, A.; Asada, K.; Ohkawa, K. Macromolecules 1999, 32, 1055.
23. Yamamoto, H.; Hirata, Y. Macromolecules 1995, 28, 6701.
24. Kang, K.; Veeder, G.; Mirrasoul, P.; Kaneko, T.; Cottrell, I. Appl Environ Microbiol 1982, 43, 1086.
25. Sanderson, G. R. In Food Gels; Harris, P., Ed.; Elsevier Applied Science: London, 1990; p 201.
26. Gibson, W. In Thickening and Gelling Agents for Food; Imeson, A., Ed.; Chapman & Hall: London, 1992; p 227.
27. Hatano, M.; Yoneyama, M. J Am Chem Soc 1970, 92, 1392.
28. Giles, C. H. A Laboratory Course in Dying; Society of Dyers and Colourists, Chorley & Pickersgill Ltd.: Leeds, UK, 1974.
29. Upstill, C.; Atkins, E. D. T.; Attwool, P. T. Int J Biol Macromol 1986, 8, 275.
30. Ogawa, E. Macromolecules 1996, 29, 5178.
31. Vollrath, F.; Edmonds, D. T. Nature 1989, 340, 305.

32. Wittbecker, E. L.; Morgan, P. W. J Polym Sci 1959, XL, 289.
33. Morgan, P. W.; Kwolek, S. L. J Polym Sci 1959, XL, 299.
34. Fambri, L.; Pegoretti, A.; Fenner, R.; Incardora, S. D.; Migliaresi, C. Polymer 1997, 38, 79.
35. Bamford, C. H.; Elliott, A.; Hanby, W. E. Synthetic Polypeptides; Academic: New York, 1956.
36. Noguchi, J.; Tokura, S.; Nishi, N. Angew Makromol Chem 1972, 22, 107.
37. Yamamoto, H.; Amaike, M.; Saitoh, H. Biomimetics 1995, 3, 123.
38. Yamamoto, H.; Amaike, M. Macromolecules 1997, 30, 3936.
39. Yamamoto, H. In Biotechnology General Engineering Review; Tomb, M. P., Ed.; Intercept: Andover, MA, 1996; Vol. 13, p 133.
40. Kikuchi, Y.; Fukuda, H. Makromol Chem 1974, 175, 3593.
41. Fukuda, H. Bull Chem Soc Jpn 1980, 53, 837.
42. Yamamoto, H.; Tanisho, H. Mater Sci Eng 1993, 1, 45.
43. Yamamoto, H.; Hirata, Y. Polym Gel Networks 1995, 3, 71.
44. Stahmann, M. A. In Polyamino Acids, Polypeptides and Proteins; Stahmann, M. A., Ed.; University of Wisconsin Press: Madison, WI, 1962; p 329.
45. Sela, M.; Katchalski, E. Adv Protein Chem 1959, 14, 391.