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(METHYL GLUTAMATE - GLUTAMIC ACID) COPOLYMER AND SURFACE SAPONIFIED POLY(METHYL GLUTAMATE) FIBERS

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Summary

Preparing of polypeptide fibers having the excellent characteristics of both poly(methyl glutamate) (PMG) and poly(glutamic acid) (PGA) fibers was examined, and the following results were obtained.

(1) By uniformly saponifying PMG fiber, a uniform (methyl glutamate - glutamic acid) copolymer fiber was obtained, and the water-sorptive capacity and the dyeability were improved without serious deterioration of mechanical properties. By surface saponifying PMG fiber, which yielded a continuous composite fiber of copolymer of surface part and PMG of core part, especially the wet strength and the wet modulus were much improved.

(2) The tensile strength of polypeptide fibers depended more on the content of β -form structure than on the degree of molecular orientation.

(3) The water vapor sorption of fiber was higher than that of membrane, because of the β -form structure of fiber.

(4) The water sorption process in the β -form structure may be described as follows: water molecules are sorbed on free polar groups of main chain at low relative vapor pressure, and hydrogen bonds between polar groups in the main chain are in some extent broken at the higher relative vapor pressure for water molecules to be absorbed on those parts.

INTRODUCTION

Synthetic polypeptide fibers have been an object of interest because they may be the model of natural protein fibers such as silk and wool, and because their characteristics may be changed widely by regulating the first and higher order structure of the molecules. Several homopolypeptide fibers,^{1,2)} especially, poly(methyl glutamate) (PMG)³⁾ and poly(glutamic acid) (PGA) fibers⁴⁾ have been studied in some detail. It has been elucidated that the PMG fiber is excellent in wet strength, heat stability and weathering property, while it has a defect in water sorbing and dyeing properties. Particularly, as for the mechanical properties of PMG in wet state, it has been shown that the modulus of PMG membrane in wet state is larger than that in dry state. This fact was clarified by free damping oscillation method in a closed system whose relative humidity was regu-

lated accurately.⁵⁾ On the other hand, PGA fiber is marked with excellent water sorptive capacity and dyeing properties, while its mechanical properties in wet state are not particularly good.

In the present study, two procedures were employed to examine the possibility of preparing polypeptide fibers having the excellent characteristics of both PMG and PGA fibers. One is the preparation of (methyl glutamate - glutamic acid) copolymer fiber by uniform saponification of PMG fiber, and the other is the preparation of surface saponified PMG fiber composed of peripheral (methyl glutamate - glutamic acid) copolymer part and non-saponified PMG core part. The latter fiber in particular is expected to retain the excellent water sorbing capacity as well as mechanical properties in wet state. The characteristics of surface saponified PMG fiber will be examined in comparison with those of copolymer fiber.

While polypeptide molecules in membrane take

usually α -helical conformation, those in fiber consist of both α -helical and β -pleated sheet conformations. To clarify the influence of β -form structure on water sorption behavior, the membrane composed mainly of β -form structure was prepared, and its water sorption capacity was compared with that of usual membrane of α -helical structure.

EXPERIMENTAL

Preparation of the Fibers and Membranes

(1) Spinning and Drawing of PMG Fiber

Poly(γ -methyl D-glutamate) (PMG) was supplied by Ajinomoto K.K. (Japan), and its viscosity-average degree of polymerization was 1150 as determined by the intrinsic viscosity in dichloroacetic acid at 25°C. Spinning dope was prepared by dissolving 5.5% PMG in mixed solvent of dichloromethane-dioxane (8:2 in volume ratio). Wet spinning was made according to Noguchi's method;¹⁾ i.e., the spinning dope was extruded by N₂ gas pressurized to 4 kg/cm² through glass nozzle of 0.18 mm ϕ (extrusion volume rate: 0.19 cc/min) into acetone coagulating bath (110 cm in length) at 27°C. The coagulated fiber was washed continuously in water bath (65 cm in length) at 27°C. Winding velocity at this stage was 10.4 m/min. Then, the fiber was drawn to 1.63 times in air. Wound PMG fiber was heat-treated in boiling water for one hour, and was air-dried. By this method, uniform PMG fiber of 4.4d was obtained.

To examine the influences of orientation and of conformational change of PMG molecules on mechanical properties of the fiber, two drawing procedures were adopted. One is drawing at 150°C, where molecular orientation is mainly affected, and the other is drawing at 25°C, where molecular conformation is mainly affected. The fibers drawn

at 150°C were slowly cooled to room temperature, and those drawn at 25°C were left in that state for one hour. Those fibers of draw ratio 1.0 obtained as above were further drawn with draw velocity 4 mm/min up to predetermined draw ratio (1.0~1.8) by Tensilon.

(2) Preparation of Uniformly Saponified (methyl glutamate - glutamic acid) Copolymer Fiber

4.4d PMG fiber obtained by the above procedure was immersed in a mixed solution of NaOH aqueous solution (0.03N~0.05N), methyl alcohol and isopropyl alcohol (1:2:2 in volume ratio) for predetermined duration (21~48 hrs.) at 25°C. Then, the fiber was developed by 0.1N phosphoric acid solution for 24 hours at 25°C, washed with methyl alcohol and vacuum-dried. Relatively long reaction time with dilute NaOH solution was applied to attain the uniform saponification through cross section of the fiber. The saponification conditions and the corresponding degree of saponification are shown in Table 1. The degree of saponification is expressed in terms of the percent mole fraction of glutamic acid as determined by high resolution NMR. The saponified fiber, for example, with 12% glutamic acid content is designated as the fiber A-12.

(3) Preparation of Surface Saponified PMG Fiber

In order to saponify the peripheral surface region of a PMG fiber, relatively large denier PMG fiber was spun. That is, according to the procedure described in (1), the fiber which left the acetone coagulating bath was wound with the winding velocity of 3.6 m/min, washed, heat-treated in boiling water for one hour, and dried. By this method, 9.8 denier PMG fiber was obtained.

The similar procedure was applied for surface saponification as described in (2), where, however,

Table 1 Conditions for uniform saponification and degree of saponification

Fiber	Saponification conditions	Degree of saponification	Density
PMG	—	—	1.292
A-12	0.03N NaOH, 21 hr	12.0 %	1.297
A-30	0.04N NaOH, 48 hr	30.2 %	1.308
A-42	0.05N NaOH, 48 hr	41.8 %	1.316

Table 2 Conditions for surface and uniform saponifications, and degree of saponification

Fiber	Saponification conditions	Degree of saponification
surface A-1.8	1 N NaOH, 1 min.	1.8 % (Av.) (surface copolymer 6.0 %)
surface A-3.4	2 N NaOH, 1 min.	3.4 % (Av.) (surface copolymer 15.4 %)
uniform A-7	1 N NaOH, 15 min.	7.0 %
uniform A-8	0.04 N NaOH, 24 hr.	8.0 %

the NaOH concentration in mixed solution was higher (1~2N), and the saponification time was shorter (order of minute). The saponification conditions and the resultant degree of saponification are shown in Table 2. The surface saponification was confirmed with the Acridine Red (0.1 mol/l, 2 hrs, 25°C), a basic dye well capable to dye glutamic acid polymer, which dyes only the peripheral surface part of the cross section of the fiber. The surface saponified fiber with 1.8% glutamic acid content is designated as the surface A-1.8 fiber, where the glutamic acid content was determined by high resolution NMR and denotes the average value through the fiber cross section. From the average degree of saponification and cross sectional area of the surface saponified region, the degree of saponification of the surface copolymer is obtained as 6.0% and 15% for A-1.8 and A-3.4 fibers, respectively.

For the comparison of surface saponified fiber with uniformly saponified copolymer fiber, PMG fibers spun as above were saponified uniformly. The conditions of uniform saponification for A-7 and A-8 fibers are shown in Table 2.

(4) Preparation of β -form Membrane

5% PMG solution in trifluoroacetic acid was cast in a flat Petri dish, under the reduced pressure using an aspirator for half a day. The resultant membrane was washed by methanol, and vacuum-dried. The PMG membrane consists mainly of α -helix at this stage. The membrane was immersed in 50% formic acid aqueous solution for three weeks, in 80% formic acid solution for nine days, and then in 100% formic acid for two weeks in succession. As the result, the transformation of

α -helix to β -form and the simultaneous hydrolysis of side chains occurred, and the β -form copolymer membrane of 48% glutamic acid content was obtained.

Structure Analysis

The glutamic acid content of copolymer was determined by high resolution NMR apparatus (Hitachi Seisakusho, Model R-24) from the proton decrease of the end $-\text{CH}_3$ group of methyl glutamate side chain using 5% trifluoroacetic acid solution.

The IR spectra ($4000 \sim 400 \text{ cm}^{-1}$) were taken for the conformational analysis by the transmission method with the diffraction grating type IR Spectrometer (Nippon Bunko K.K. Model IRA-2).

As for the conformation and orientation of the polypeptide molecules, X-ray analysis was made by X-ray diffraction apparatus (Nihon Denshi K.K. JDX-5P) and counter. Wide angle X-ray photograph was obtained by plate camera method using X-ray generation apparatus (Rigaku Denki Kogyo K.K., Model RL-3H).

Measurement of Mechanical Properties

Using Tensilon (Toyo Baldwin Co. Ltd.), single fiber of 1 cm length was extended with extension velocity 4 mm/min at 20°C under 65% humidity, and the breaking strength (g/d), breaking elongation (%) and Young's modulus (g/d) were estimated from the resultant stress-strain curve, vacuum-dried fibers were used to examine the dry properties, whereas the fibers soaked in water for 24 hours at 25°C were used for the wet property test.

Sorption of Dyestuff

Acridine Red, which dyes glutamic acid polymer, but not methyl glutamate polymer, was used to

examine the dyeability of PMG and uniformly saponified copolymer fibers. Sample fibers of known weight were immersed in 50cc of 0.1 mol/l Acridine Red aqueous solution at 25°C, and the electric conductivity of the solution was measured by the electroconductometer (Toa Denpa Kogyo K.K., Model CN-5B) as a function of time. The sorption equilibrium was attained after two days. Dye concentration at sorption equilibrium was determined from the conductivity using the calibration curve between electroconductivity and dye concentration of the aqueous solution. The difference between the initial and the equilibrium concentration amounts to the dye sorption into fiber at equilibrium state.

RESULTS AND DISCUSSION

PMG and Uniformly Saponified (Uniform Copolymer) Fibers

(1) Structure of Fiber

X-ray diffraction diagrams of PMG and uniform copolymer (A-30) fibers are shown in Fig. 1. Diffractions due to α -helix ($2\theta=8^\circ 30'$, $10\bar{1}0$ spacing) and β -form ($2\theta=19^\circ$, 110 spacing) are observed, and from the diffraction intensity the content of β -form is comparable with that of α -helix. This result is consistent with that of Sakamoto et al.³⁾ The saponification does not cause any conformational change. The X-ray diffraction photograph also showed the same result.

The orientation degree of the fiber may be

Fig. 1 Intensity of X-ray diffraction of PMG (—) and A-30 (---) fibers

expressed in terms of the ratio of the diffraction intensity at $2\theta=8^\circ 30'$ of the equatorial direction to that of the meridian direction. The degrees for PMG and copolymer fibers were almost identical and estimated as 90%. The result confirms no change of the orientation degree with saponification.

(2) Mechanical properties

The results of the Tensilon observation are summarized in Table 3.

The dry as well as the wet strength and the ratio of wet to dry strength decreased with the increase of the degree of saponification. While elongation decreased, wet elongation and the ratio of wet to dry elongations increased remarkably with the increase of glutamic acid content. The interactions between carboxylic acid groups may reduce the elongation, whereas the breaking of the interactions and plasticization by hydration of the side chain may increase the elongation.

The result of Young's modulus is quite interesting. Wet Young's modulus was higher than the dry one about 8% in PMG fiber and decreased eventually to the smaller value than the dry value, when the degree of saponification was increased. The mechanism of this phenomenon was already clarified using PMG and copolymer membranes.⁵⁾

The influence of drawing on mechanical properties of PMG fiber are summarized in Fig. 2(a) and (b). It is known that the orientation of α -helix change without causing serious change in conformation when the drawing is made at 150°C, while the mainly conformational change occur when the drawing is made at room temperature. The degree of orientation increased from 75% of undrawn

Table 3 Mechanical properties of PMG, A-30 and A-42 fibers

Fiber		PMG	A-30	A-42
Tensile strength (g/d)	dry	2.61	2.25	2.06
	wet	2.43	1.86	1.73
	ratio	0.93	0.83	0.84
Tensile elongation (%)	dry	19.8	19.5	18.9
	wet	22.7	32.0	33.4
	ratio	1.15	1.64	1.77
Young's modulus (g/d)	dry	28.9	27.4	27.3
	wet	31.3	25.6	24.1
	ratio	1.08	0.93	0.88

Fig. 2 Influences of drawing on degree of orientation, fraction of β -form and mechanical properties of PMG fiber: (a) drawing at 150°C, (b) drawing at room temperature

fiber to 93.6% of 1.5 times drawn fiber in the case of the drawing at 150°C. This increase of the degree of orientation resulted in the increases of the fiber strength and its Young's modulus and the decrease of elongation. When drawn at room temperature, the degree of orientation increased only from 75% (undrawn) to 82% (1.9 times), while the β -form content increased from 30% (undrawn) to 41% (1.9 times) so as to decrease the α -helical content from 36% to 30%. Increases of strength and Young's modulus and decrease of elongation in this case were more remarkable than in the case of drawing at 150°C. That is, the influence of α - β transformation on mechanical properties was more effective than that of the simple orientation of α -helix.

(3) Water vapor sorption

Water vapor sorption isotherms at 25°C of PMG fibers, uniformly saponified copolymer fibers (A-12 and A-30), PMG membranes are summarized in Fig. 3. With a similar glutamic acid content,

Fig. 3 Water vapor sorption isotherms (amount sorbed n vs. relative vapor pressure p/p_0) for fibers (solid line, (○) PMG; (△) A-12; (□) A-30) and membranes (broken line, (●) PMG; (▲) A-17; (■) A-45)

fiber absorbed more water than membrane, and this tendency was more pronounced in low relative vapor pressure region.

The standard chemical potential difference $\Delta\mu^\circ$ of water between in polymer phase (fiber or membrane) and in vapor phase is obtained by the following equation.⁶⁾

$$\Delta\mu^\circ = \mu_p^\circ - \mu_v^\circ = RT [\ln(p/p_0) - \ln(\gamma x)] \quad (1)$$

where μ_p° and μ_v° are the standard chemical potentials of water in polymer and in vapor phases, respectively, p/p_0 is the relative vapor pressure, x is the mole fraction of water in polymer phase with respect to polymer repeating unit, and γ is the activity coefficient of water in polymer, which may be approximated to be unity because the water content in polymer is low. $\Delta\mu^\circ$ is the free energy required to transfer 1 mol water from vapor phase to polymer phase. The calculated values for fibers and membranes are shown in Fig. 4 using the x value corresponding to $p/p_0 = 0.9$. $\Delta\mu^\circ$ decreased rapidly and the water sorption tendency became pronounced with the glutamic acid content.

In the following, the water amount absorbed in the glutamic acid part was analysed to explain the difference between sorption behaviors of fiber and that of membrane. It is assumed that the water sorption of the copolymer fiber or membrane

corresponds to the sum of water absorbed in the glutamic acid part and in the methyl glutamate part. The water absorbed on the methyl glutamate residue is equivalent to that absorbed in PMG. That is, the water sorption in the glutamic acid part N is expressed as follows:⁷⁾

$$N = (G - 143 f_m \cdot M) \times 6.02 \times 10^{23} \quad (2)$$

(molecules/g)

Here, G is the sorption amount in copolymer (fiber or membrane) (mol/g), M is the sorption in PMG (fiber or membrane) (mol/g), f_m is the fraction of the methyl glutamate residue of the copolymer (mol/g) and 143 denotes the molecular weight of the methyl glutamate residue. As for G and M , (1) unimolecular adsorption value (mol/g) of BET plot which shows straight line in the p/p_0 range from 0.05 ~ 0.4 in this case, and (2) sorption amount (mol/g) at $p/p_0 = 0.9$ are adopted. Eq. (2) yields thus the water sorption in the glutamic acid side chain, where the consistent values (either for fiber or for membrane) should be used for G and M . The water sorption as calculated by Eq. (2) are shown in Fig. 5 as a function of the stoichiometric number of carboxylic acid per gram polymer. The unimolecular adsorption number becomes to level off at high $-\text{COOH}$ numbers, indicating that the interaction between $-\text{COOH}$ groups prevents the water sorption in the carboxylic acid group. The absorbed water molecules at $p/p_0 = 0.9$ is approximately equivalent to stoichiometric carboxylic acid number. It should be emphasized that regardless of fiber or membrane, the glutamic acid side chain

Fig. 4 Standard chemical potential difference $\Delta\mu^\circ$ calculated from water vapor sorption isotherms for fibers and membranes

Fig. 5 Relationships between number of water molecules sorbed on glutamic acid portion N in Eq. (2) and stoichiometric number of glutamic acid residue. Lower line corresponds to unimolecular adsorption value of BET plot and upper line corresponds to sorption amount at $p/p_0 = 0.9$. $\triangle, \blacktriangle$; A-12 fiber, $\square, \blacksquare$; A-30 fiber, $\circ, \bullet$; various membranes

absorbs the same number of water molecules. The larger water sorption in fiber than in membrane is due to the conformational difference of the main chain. In the α -helical structure, the polar groups in main chain can not contribute to the water sorption, while in the case of β -form structure the free polar groups in the disordered region of the main chain seems to provide sorption sites for water. More detailed discussion will be found in the section of the water sorption in β -form membrane.

(4) Dyeability

Equilibrium dye sorptions of Acridine Red by PMG and uniformly saponified copolymer fibers are shown in Fig. 6. The dyeability of copolymer fibers with about 40% glutamic acid was one order higher than that of PMG fiber.

The standard chemical potential difference $\Delta\mu_d^\circ$ is given by the following equation.

$$\Delta\mu_d^\circ = -RT \ln(c_i/c_0) \quad (3)$$

Here, c_i and c_0 are the dye concentrations in fiber and in dyeing solution, and the latter is 0.01 mol/l. $\Delta\mu_d^\circ$ takes the negative value when the glutamic acid content exceeds 15% (Fig. 6), indicating that the dye affinity to fiber becomes exceedingly good.

Fig. 6 Equilibrium dye sorption and standard chemical potential difference $\Delta\mu_d^\circ$ in Eq. (3) vs. glutamic acid content of uniformly saponified copolymer fiber. Closed circle corresponds to PMG membrane

Summarizing, the uniform saponification of PMG fiber improved the water sorption capacity and dyeability remarkably, while the mechanical properties slightly deteriorated.

Surface Saponified Fiber

(1) Structure of Fiber

The photographs of the optical microscope observation ($\times 400$) show that the cross section of PMG fiber is dyed in pale yellow while that of uniformly saponified fiber is dyed in dark red. In contrast to these uniform fibers, the surface saponified fiber dyes only in the peripheral surface region. Thus the outer region is considered to

Fig. 7 Infrared spectra of surface saponified A-1.8 (—) and uniformly saponified A-7 (---) fibers

consist of (MG-GA) copolymer and the core region to be made of the unchanged PMG.

Two IR spectra of the surface saponified fiber A-1.8 and of the uniformly saponified fiber A-7 are compared in Fig. 7, where the absorption at 1630 cm^{-1} of Amide I band (β -form) and 620 cm^{-1} (α -helix) of Amide V band are similar for both fibers. That is, both the α -helical and β -form conformations are present in these fibers. The α and β fractions (38 and 29% in average, respectively) for various fibers estimated from Amide V band indicate that no conformational difference is observed in PMG and any saponified fiber.

(2) Fiber Properties

Mechanical properties of various fibers are summarized in Table 4. The dry and wet tensile strengths decreased with the degree of saponification for both type of fibers. However, the ratio of wet to dry strength did not change in the case of surface saponification. This behavior is one of the

Table 4 Mechanical properties of PMG, surface saponified A-1.8, A-3.4, uniformly saponified A-7 and A-8 fibers

Fiber		PMG	surface		uniform	
			A-1.8	A-3.4	A-7	A-8
Tensile strength (g/d)	dry	0.73	0.60	0.60	0.50	0.49
	wet	0.73	0.60	0.60	0.49	0.48
	ratio	1.00	1.00	1.00	0.96	0.98
Tensile elongation (%)	dry	112.0	106.4	106.0	96.0	93.8
	wet	116.8	118.4	120.0	126.0	127.0
	ratio	1.04	1.11	1.13	1.31	1.35
Young's modulus (g/d)	dry	21.1	20.0	19.8	19.5	19.5
	wet	27.3	24.9	23.7	17.7	17.6
	ratio	1.29	1.25	1.20	0.91	0.90
Degree of hydration (%)		4.19	4.88	5.32	6.13	7.55

characteristic features of surface saponification. The dry elongation decreased and the wet elongation increased with the degree of saponification. The ratio of wet to dry elongation was smaller in the surface saponified fibers than in the uniformly saponified fibers, indicating that the PMG core part supported the mechanical property of the whole fiber. The characteristic that the wet mechanical properties of surface saponified fibers are excellent is also reflected on Young's modulus of the surface saponified fiber.

The water sorptive capacities for various fibers are listed in Table 4 in terms of the degree of hydration. The degree of hydration is lower for the surface saponified fiber than for the uniformly saponified fiber as expected. However, the sorptive capacity of the copolymer part does not depend on the saponification method. From the view point of clothes, which requires the sorption and release of water, only the surface layer of the fiber is required to be water-sorptive. That is, the low degree of hydration should not be regarded as the defect of the surface saponified fiber.

Structure of β -form Membrane and Its Water Sorption

The IR spectrum of the β -form membrane A-48 treated with formic acid shows the strong absorption at about 700 cm^{-1} , so this membrane consists mainly of the β -form structure. In Fig. 8 the X-ray diffraction photograph of the β -form membrane (a) is compared with that of the α -helical PMG membrane (b). The former shows two diffraction rings at $2\theta=18^\circ50'$ ($d=4.7\text{\AA}$) and

Fig. 8 X-ray diffraction photographs of (a) β -form A-48 and (b) α -helical PMG membranes

$2\theta=23^\circ5'$ ($d=3.9\text{\AA}$), but lacks the diffraction of α -helical structure at $2\theta=8^\circ30'$ ($10\bar{1}0$ spacing). This X-ray results reconfirm that the structure of the β -form membrane A-48 is nearly the perfect β -form. The diffractions corresponding to $d=4.7\text{\AA}$ and $3.9\text{\AA}$ are those of (110) and (021) spacings of the orthorhombic system of the β -form structure.³⁾ The molecular distance in the direction of hydrogen bond is thus $4.7\text{\AA}$, and the distance between sheets is $7.8\text{\AA}$. Those distances are large enough compared with the size of water molecule.

Water vapor sorption isotherms of the β -form membrane A-48, α -helical PMG, A-45 and polyglutamic acid (PGA) membranes are shown in Fig. 9. The β -form membrane absorbs more water than α -helical PGA membrane and the α -helical membrane A-45 which has the similar glutamic acid content of the β -form membrane. The standard chemical potential differences Δu° calculated by Eq. (1) are 371, 413, 578 and 821 cal/mol for β -form A-48, α -helical PGA, α -helical A-45 and α -helical PMG membranes, respectively.

Water sorption amounts (the BET monolayer value and the value at $p/p_0=0.9$) due to the glutamic acid residue were calculated from Eq. (2),

Fig. 9 Water vapor sorption isotherms of β -form A-48 (●), α -helical PMG (○), A-45 (□) and PGA (△) membranes at 25°C

Fig. 10 Relationships between number of water molecules sorbed on glutamic acid portion N in Eq. (2) and stoichiometric number of glutamic acid residue. Lower line corresponds to unimolecular adsorption value of BET plot and upper line corresponds to sorption amount at $p/p_0=0.9$. $\circ, \bullet$; β -form A-48, $\square, \blacksquare$; α -helical A-45, $\triangle, \blacktriangle$; PGA membranes

and the results are shown in Fig. 10 (c.f. Fig. 5). Though the water sorption amounts of the α -helical membranes increase in proportion to the acid content, that of the β -form A-48 membrane deviates to the larger value with respect to the same acid content. This deviation is due to the contribution of the polar groups of the main chain. If we assume that each $=NH$ or $-CO$ group in the main chain contributes to the sorption of one water molecule, it is calculated that the deviation of the water sorption amount of β -form membrane from that of α -helical membrane in Fig. 10 corresponds to 2.8% of the number of polar groups ($=NH$ and $-CO$) in the main chain for the BET monolayer value (lower curve in Fig. 10) and 18.4% for $p/p_0=0.9$ (upper curve). Namely, in the case of the β -form membrane, the water molecules may be sorbed on free (not hydrogen bonded) polar groups at low pressure range, while with the progress of water sorption, hydrogen bonds between $=NH$ and $-CO$ which support the β -form structure may break and the water molecules may be sorbed on those points.

To confirm this problem, the IR spectra and X-ray diffraction diagrams of the β -form A-48 membrane in dry state and water sorbed state under the saturated water vapor at 25°C are shown in Fig. 11 and Fig. 12, respectively. Both

Fig. 11 Infrared spectra of dry (—) and β -form A-48 (---) membranes

Fig. 12 Intensity of X-ray diffraction of dry (—) and wet (---) β -form A-48 membranes

the adsorption of amide V band (Fig. 11) and the diffraction intensity at $2\theta=19^\circ$ (Fig. 12) decrease in the water sorbed state, indicating that the intermolecular hydrogen bonds of β -form are in some extent broken according to the progress of water sorption.

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(methyl glutamate-glutamic acid)共重合体繊維および
Poly(methyl glutamate)表面鹼化繊維の研究

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Poly(methyl glutamate)(PMG)およびPoly(glutamic acid)(PGA)繊維の両方の優れた特性をもつポリペプチド繊維の調製について検討し、次の結果を得た。

(1) PMG繊維の均一鹼化で得られる(methyl glutamate-glutamic acid)共重合体繊維は、力学的性質をあまり害わずに、良い吸湿性と染色性を示す。PMG繊維の表面鹼化により、円周部分が共重合体、芯部がPMGの繊維が得られ、特に湿潤強度、湿潤弾性率が優れている。

(2) ポリペプチド繊維の引張強度は、分子の配向度よりも、 β -型構造の含有率に強く依存する。

(3) 繊維の吸湿性が皮膜のそれより高いのは、繊維中の β -型構造のせいである。

(4) β -型構造での吸湿は、低湿度では主鎖の自由な極性基に水分子が収着されるが、高湿度では、更に主鎖極性基間相互作用がこわれ、この部分に水分子がつくことが示された。