

Gas Sorption and Permeation of Poly(γ -methyl Glutamate)

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Synopsis

Sorption, permeation, and diffusion behaviors of poly(γ -methyl glutamate) were examined in the light of superstructure including conformation. Highly crystalline PMG, cholesteric twisted structure, low crystalline PMG, which are all composed of α helix, and β form PMG were prepared using cast solvent of chloroform, dichloromethane–dimethylformamide, and dimethylformamide and treating by formic acid, respectively. The large amount sorbed and the sorption capacity were interpreted by an existence of a microvoid in PMG cast film from chloroform. On the other hand, β form PMG had small amount sorbed. The sorption behavior was remarkably influenced by superstructure as well as conformation, while the effect of only conformation on the permeation behavior was recognized. A peculiar permeation was detected around 100°C for all the samples.

INTRODUCTION

It has been researched that the permeation of small molecules through polypeptide membranes takes place in the side chain regions.¹⁻⁵ The permeation depends to a major extent upon the side chain structure such as arrangement and packing of the side chain. A different side chain structure might be, in part, caused by a different array of a helical rod.³⁻⁵ Thus, it is considered that permeation behavior depends also upon the helical array influencing the side chain structure. The permeability coefficients of the forms A and B of poly(γ -benzyl-L-glutamate) (PBLG),³ the racemic form of poly(γ -benzyl glutamate),⁵ and the α form of poly(β -benzyl-L-aspartate) (PBLAsp)⁴ show a remarkable change at the transition temperature where the breakdown of the benzene ring stacking occurs in the first two polypeptides and the formation of the benzene ring stacking in the last one. The spacing of the helical array of polypeptide described above is also changed as well as the side chain structure at the transition temperature. Furthermore, 2-dimensional array is different for various solid state modifications of polypeptides described above. Such a remarkable change in the permeability coefficient indicates the difference of not only the side chain structure but also the helical array.

It is well known that poly(γ -methyl glutamate) (PMG) is possible to form several superstructures with a different helical array, depending upon the kind of casting solvent.⁶⁻⁹ PMG cast from chloroform solution has a high crystallinity with 2-dimensional hexagonal array, and PMG from dichlo-

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romethane (DCM)-dimethyl formamide (DMF) mixed solution takes cholesteric twisted structure consisting of the α helix and its comparatively low crystallinity. Gellike structure with low crystallinity is cast from DMF solution. Three kinds of superstructure consist of the α helix. Finally, the β form of PMG is formed by formic acid treatment. Thus, one can easily prepare the several superstructures of PMG including the β form different from α helix conformation.

In the present paper, the permeation and sorption of carbon dioxide gas through and on PMG with several superstructures were studied in the light of helical array. The permeation behavior of PMG film consisting of the α helix was, in addition, compared with that of the PMG β form.

EXPERIMENTAL

Material

PMG of average molecular weight of 100,000 was kindly supplied from Ajinomoto Co., Ltd. Chloroform and DCM-DMF mixed solution of 3 wt % concentration were cast at room temperature for several days. DMF solution of 1.5 wt % concentration was similarly cast at 50-60°C for about 10 days, and subsequent casting at room temperature continued for about 1 month. Cast films obtained above were immersed into methanol and then dried under vacuum at room temperature for 2 days. PMG cast films obtained were designated as C, D-D, and D film, respectively, corresponding to used cast solvent. PMG cast from ethylene dichloride solution was treated in about 80% formic acid aqueous solution for 66 h and dried for 2 days after washing by water. The β form of PMG thus obtained was designated as β film.

Measurements

X-ray diffraction profile was taken with DX-GO-S goniometer manufactured by Japan Electron Optics Laboratory Co., Ltd.

Circular dichroism spectra were obtained in the wavelength range from 650 to 300 nm by ORD/UV-5 automatic spectropolarimeter (Japan Spectroscopic Co., Ltd.).

The method of sorption⁴ and permeation⁵ measurements is described in detail elsewhere. The permeation measurement was performed over a temperature range from -5 to 200°C. The upstream pressure was 11-6 cm Hg for C film, 8-6 cm Hg for D-D film, 10-5 cm Hg for D film, and 12-8 cm Hg for β film. There appeared a very slight pressure dependence of the permeability coefficient at 25°C of PMG cast from ethylenedichloride and independence at -30°C.¹⁰ Therefore, it is likely to be pressure-independent in the upstream pressure range obtained above.

RESULTS AND DISCUSSION

Film Characterization

X-ray diffraction profiles of C, D, and β film of PMG were shown in Figure 1. C film exhibits high crystallinity while D film is low crystallinity, as

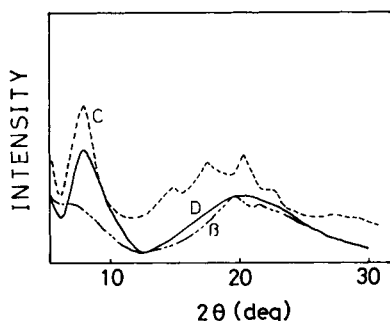


Fig. 1. X-ray diffraction profiles of C, D, and β films of poly(γ -methyl glutamate).

shown in the figure. These two films which are confirmed to take the α helix conformation by IR amide bands show the characteristic spacing of α helical array observed around $2\theta \simeq 8^\circ$. Crystallinity of D-D film was almost the same as that of D film, although not shown in the figure. The characteristic spacing corresponding to the direction of hydrogen bond appears around $2\theta \simeq 19^\circ$ for the β film, indicative of β form conformation.

Figure 2 shows circular dichroism spectrum of D-D film. One can see the peak of selective reflection ascribed to cholesteric twisted structure at wave length of 510 nm. The selective reflection was not observed at all for the other films. Therefore, it was found that only D-D film of PMG could form cholesteric twisted structure with cholesteric pitch of approximately 510 nm.

Sorption

Sorption isotherms of carbon dioxide gas at various temperatures are shown in Figure 3; the volume at the standard state of carbon dioxide gas sorbed per residue of PMG is plotted against the fugacity ratio f_2/f_2^0 , i.e., activity.¹¹ For a gas with low critical temperature like carbon dioxide (31.0°C), it is adequate to utilize the fugacity ratio f_2/f_2^0 as the activity.¹² The value of f_2^0 is obtained to be 47.3 atm for carbon dioxide by the corresponding state principle.¹³ The value of f_2 may be almost equivalent to the pressure itself at the low pressure range used in the present experiment. The sorption isotherms at each temperature where it is above the glasslike transition due to the side chain motion were reduced to a single curve. This behavior was observed above glasslike transition for various forms of PBLG,³ racemic form of PBG,⁵ and PBLAsp.⁴ The volume sorbed was in the order:

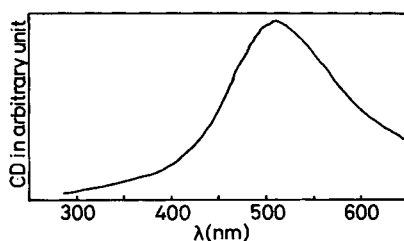


Fig. 2. Circular dichroism spectrum of selective reflection for D-D film of poly(γ -methyl glutamate).

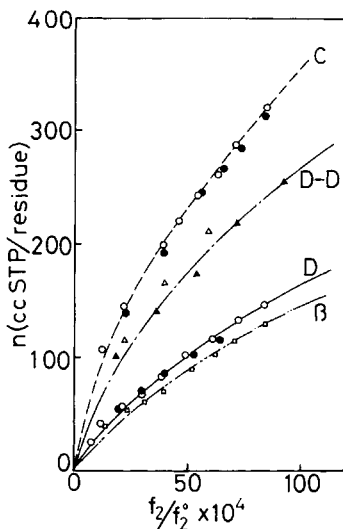


Fig. 3. Sorption isotherms of C (○,●), D-D (△,▲), D (○,●), and β (□) films of poly(γ -methyl glutamate)-carbon dioxide gas system at various temperatures ($^{\circ}$ C): (○,△,□) 25; (●,▲) 35.

C film of PMG > D-D film of PMG > D film of PMG > β film of PMG. The high volume sorbed of C film of PMG was explained by sorption of carbon dioxide gas into a microvoid contained in C film irrespective of high crystallinity. The volume sorbed of β form of PMG is, as a whole, lower than that of the α helix of PMG, indicating a small amount of sorption site of the β form.

It was found that we could empirically apply the Langmuir equation to sorption isotherm obtained here. The Langmuir constants a (sorption energy factor) and b (sorption capacity) estimated were tabulated in Table I. The b value was in the order: C film of PMG > D-D film of PMG > D film of PMG \geq β film of PMG. A large b value suggests that a microvoid contained in C film of PMG was utilized as valuable sorption sites. The b value of

TABLE I
Langmuir Constants a and b of Poly(γ -methyl Glutamate)-Carbon Dioxide Gas System at 25° C

Conformation	Conditions of Preparation	a (cm Hg $^{-1}$)	b (cm 3 STP/residue)
α helix	CHCl $_3$	0.036	660
	CHCl $_3$ annealed at 65° C	0.034	705
	CHCl $_3$ annealed at 80° C	0.025	815
	CHCl $_3$ annealed at 125° C	0.027	696
	DMF ^a	0.022	370
	DCM ^b -DMF	0.035	480
β form	Formic acid	0.018	371

^a DMF = dimethyl formamide.

^b DCM = dichloro methane.

PMG was, as a whole, found to be several times higher than that of the solid state modification of PBLG and PBLAsp. This indicates a much more sorptive site of C=O group in the side chain of PMG.

Figure 4 shows sorption isotherms of C film annealed at 65, 80, and 125°C. The sorbed volume of C film annealed at 65 to 80°C was slightly high. Langmuir constants a and b of the annealed sample are also demonstrated in Table I. The b value of C film annealed at 65 and 80°C became comparatively high, indicative of slight development of a microvoid by annealing.

Permeation

The steady state permeability coefficient (\bar{P}) of C film, D-D film, D film, and β film of PMG is shown against reciprocal of temperature in Figure 5. The permeability coefficient of the β form is lower than that of various PMG films of the α helix over a whole temperature range. One can suppose an existence of a sheet structure of β form, perpendicular to permeation direction. Although the permeability coefficient increased with temperature, a considerable decrease of the permeability coefficient was observed for all the samples studied here around 100°C. The \bar{P} of 2.11×10^{-8} cc STP/cm s cm Hg at 80°C decreased to 1.95×10^{-8} cc STP/cm s cm Hg at 95°C for D-D film, 1.43×10^{-8} cc STP/cm s cm Hg at 81°C to 1.13×10^{-8} cc STP/cm s cm Hg at 100°C for C film, 1.11×10^{-8} cc STP/cm s cm Hg at 70°C to 8.27×10^{-9} cc STP/cm s cm Hg at 80°C for D film and 1.02×10^{-8} cc STP/cm s cm Hg at 100°C to 9.17×10^{-9} cc STP/cm s cm Hg at 120°C for β film. There appeared no characteristic behavior by another method such as thermal analysis, X-ray diffraction, and viscoelasticity, which corresponds to the peculiar permeation behavior around 100°C. We could not detect such a permeation behavior for various solid state modifications of PBLG and PBLAsp.³⁻⁵ Although one cannot make the behavior clear, this is the characteristic for PMG film. It might be likely to assign the peculiar permeation behavior to molecular motion of the backbone α helix chain.

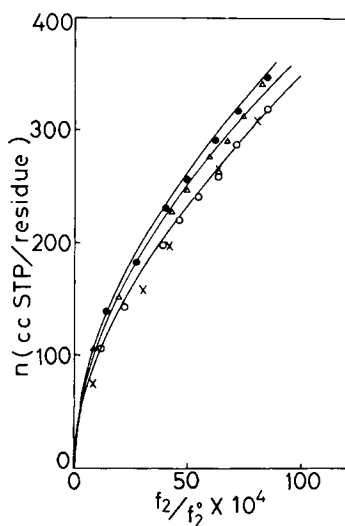


Fig. 4. Sorption isotherms of poly (γ -methyl glutamate) C film annealed at 25°C (O), 65°C (●), 80°C (Δ), and 125°C (×).

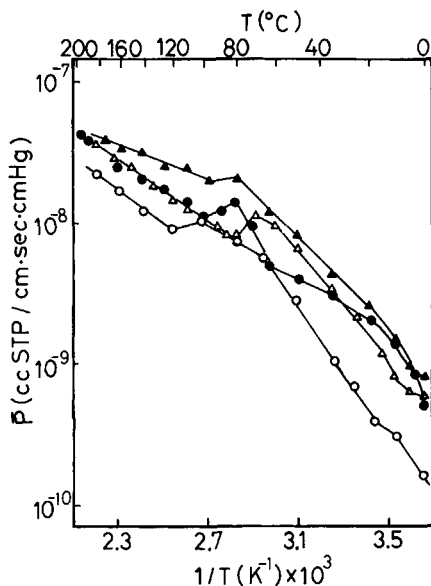


Fig. 5. Arrhenius plot of permeability coefficient of carbon dioxide gas through C (●), D-D (▲), D (Δ), and β (○) films of poly(γ -methyl glutamate).

It was found that the permeability coefficient of PMG was very sensitive to the structural change which was not detected by usual structural analysis. The permeability coefficient of C film increased at the temperature range from 60 to 80°C and decreased at the temperature range from 80 to 100°C, corresponding to the increase of the sorption capacity b observed for annealed C film.

An inflection in the Arrhenius plot of the permeability coefficient was seen around about 0°C for PMG film of the α helix and 20°C for the PMG β form. This is ascribable to the side chain motion.

Diffusion

One can evaluate the diffusion coefficient (\bar{D}) using $\bar{P} = \bar{D}S$, where S is the solubility coefficient obtained from sorption experiment. We got the diffusion coefficient only at 25°C, since many errors are expected to obtain the solubility coefficient at higher temperature by simply extrapolating the solubility coefficient from 25 to 40°C to a higher temperature range. The diffusion coefficient of various PMG films is shown in Table II. The \bar{D} value is in the following order: D film of PMG > D-D film of PMG > C film of PMG > β film of PMG.

The diffusion coefficient of D film of PMG was approximately twice high as that of C film, reflecting the gellike structure and low crystallinity of D film of PMG. The \bar{D} of D-D film of PMG was the intermediate value between D and C film, likely to be due to a rather regular structure of the cholesteric liquid crystal. The \bar{D} value of C film was depressed by high crystallinity, and the microvoid did not influence too much the \bar{D} value. Hence, the diffusion coefficient of various PMG films consisting of the α helix was a reverse order, compared to the order of volume sorbed and b value.

TABLE II
Diffusion Coefficient \bar{D} of Carbon Dioxide Gas through Poly(γ -methyl Glutamate) at 25°C

Conformation	Condition of preparation	\bar{D} (cm ² /s)
α helix	CHCl ₃	1.85×10^{-8}
	DCM ^a -DMF ^b	2.39×10^{-8}
	DMF	3.61×10^{-8}
β form	Formic acid	1.17×10^{-8}

^a DCM = dichloro methane.

^b DMF = dimethyl formamide.

CONCLUSION

The different sorption isotherm was obtained depending upon a helical array. The amount sorbed and the sorption capacity b of C film were much more as expected by an existence of a microvoid in the C film of PMG. The amount sorbed was lesser for the β form of PMG. Sorption behavior was remarkably influenced by conformation and superstructure of PMG.

We could not recognize a considerable difference of the permeability coefficient of various PMG films of the α helix over the temperature range measured. On the other hand, the β form of PMG exhibited a lower value of permeability coefficient. The decrease of the permeability coefficient was peculiarly observed around 100°C for all the PMG samples. A corresponding behavior by the other method was not detected at all. This behavior will be studied subsequently as a further problem of molecular motion of the backbone α helix chain.

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