Influence of Side Chain Structure on Sorption of Xenon and Carbon Dioxide Gas by Polypeptide Membranes

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Synopsis

The influence of side chain structure on sorption of xenon and carbon dioxide gas by polypeptides is examined in two ways: chemical structure of side chain and higher order structure of the side chain region. Sorption of xenon gas increases progressively with increase in side chain length of poly(n-alkyl L-glutamates). The sorption isotherms of a polymer at various temperatures are reduced to one curve when the data are arranged in the form of sorption per residue versus fugacity ratio (as activity). The sorption of carbon dioxide gas shows a minimum at an intermediate length of side chains, corresponding to poly(n-propyl or n-butyl glutamate). The behavior is considered the result of overlapping influences of looseness of the side chain region and density of polar groups. The Langmuir constants and the enthalpy and entropy of sorption explain this quantitatively. Sorption of carbon dioxide gas is influenced by the higher-order structure of poly(γ-benzyl L-glutamate). In this polymer, the benzyl ester part is the main sorption site, and it was confirmed that the stacking between side-chain benzene rings significantly reduces the extent of sorption.

INTRODUCTION

Sorption and diffusion of various small molecular substances in polypeptide membranes take place in the side chain region between the helices.[1,2] Therefore, the side chain structure would have a considerable influence on the sorption behavior of polypeptide membranes.

In order to clarify this relationship, it is desirable to use nearly nonpolar, small molecules as the penetrant, to avoid the influence of highly polar substance such as water, which has a clustering tendency.

In the present paper, the influence of the side chain structure on the sorption of xenon or carbon dioxide gas by polypeptide is examined in two ways. First, the gases are sorbed by a series of poly(n-alkyl L-glutamate) (where alkyl = methyl, propyl, butyl, amyl, and octyl) which demonstrates the influence of side chain length or the first-order structure of the side chain. Secondly, the sorption behavior of carbon dioxide gas by various poly(γ-benzyl L-glutamate) membranes is studied. The higher-order structure of the side chain region of these membranes is changed by using different casting methods.

EXPERIMENTAL

Poly(γ-methyl L-glutamate) (PMLG) and poly(γ-ethyl L-glutamate) (PELG), supplied by Kyowa Hakko K.K. and Ajinomoto K.K. (Japan), were obtained by polymerization of N-carboxyamino acid. The viscosity-average degree of polymerization of both polymers is approximately 1150, determined by the intrinsic

TABLE I
Casting Conditions of PBLG Membranes

Membrane	Solvent	Casting temperature, °C
Form A	benzene	45
Form A (H.T.)[a]	benzene	45
Form B	benzene	60
Form B (H.T.)[a]	benzene	60
Form C	ethylene dichloride	25

[a] Heat treated at 140°C for several hours.

viscosity of dichloroacetic acid solution at 25°C. Other poly(n-alkyl L-gluta-mates) are prepared by the ester exchange method; details have been explained elsewhere.[1] When n-alkyl is propyl, butyl, amyl, or octyl, the polymer is abbreviated PPrLG, PBuLG, PAmLG, and POcLG, respectively.

The poly(n-alkyl L-glutamate) membranes are prepared by dissolving about 5% polymer in dichloroethane and air drying the thin layer of the solution on a mercury surface for two days, and finally vacuum drying at 50°C for one day. The thickness is 0.10–0.20 mm. All of the membranes prepared have α-helical structures as confirmed by infrared absorption spectra.

Poly(γ-benzyl L-glutamate) (PBLG) is prepared by benzylation of L-glutamic acid, supplied by Ajinomoto K.K., and polymerization of NCA of the benzyl L-glutamate. The preparation conditions of various PBLG membranes are shown[3] in Table I.

The membranes were prepared by air drying of 3% PBLG solution in the indicated solvent at the indicated temperature for several days, washing with methanol, and then vacuum drying for one day. The degree of polymerization of the membrane was about 1200 for form A and form B, and about 550 for form C.

It was confirmed by DSC, viscoelastic properties, and x-ray observation that for form A, the benzene rings of the side chain are stacked in an intramolecular manner as described by Elliott.[4] This is explained by the endothermic peak at 135°C in DSC observations, and by the decrease in modulus near this transition temperature in viscoelastic observations. The transition at 135°C is irreversible, and the heat treatment of form A breaks away almost all the intramolecular stacking. Thus, there is little intramolecular stacking of side chain benzene rings in the form A (H.T.) membrane. In the form B membrane, there is intermolecular stacking between the benzene rings which is broken reversibly at 110°C. Therefore, the form B (H.T.) membrane has the same side chain structure as the form B membrane. The stacking content of form B is about 1/5 that of form A, judging from the ΔH values of DSC observation. In the form C sample, there is neither intra- nor inter-molecular stackings. The details of structural observation were given in the preceding paper.[3]

Xenon gas used as the sorbate was supplied by Takachiho Kagaku K.K. (Japan) in ampoule form, of 99.999% purity. The ampoule is directly connected to a vacuum line.

As for the carbon dioxide gas, Dry Ice is placed in the vacuum line, and the gas is purified by the method described below.

Sorption Experiment

The sorption experiment of the gases were performed with a Cahn electromicrobalance (Cahn Instrument Co., California). The vacuum line apparatus is shown in Figure 1. The sample film (50–100 mg) was hung at one side of the arm of the electromicrobalance and dried under vacuum at less than 10^{-3} mm Hg for three days, which was enough to obtain constant weight.

Purification of carbon dioxide gas was performed as follows. Dry Ice is placed in a flask in the vacuum line, and the path from the flask to the next trap is cooled with a Dry Ice–methanol mixture. Impure water is removed from the carbon dioxide gas during the cooling process. The carbon dioxide gas is then collected by a trap cooled with liquid nitrogen, and nitrogen and oxygen are removed by evacuation. The purified carbon dioxide gas is then introduced into the sorption chamber of the electromicrobalance.

Pressure range of the experiment is 5–37 cm Hg for xenon gas and 5–40 cm Hg for carbon dioxide gas. The pressure is observed directly by a mercury manometer. The temperature range is 20–35°C, at 5°C ingervals, and the temperature of the sorption chamber is controlled to ±0.5°C by circulating water to the jacket. The weight accuracy of the apparatus is ±10 μg.

RESULTS AND DISCUSSION

Effect of Side Chain Length of Poly(n-alkyl L-Glutamates) on Sorption of Gases

The sorption isotherms of xenon gas on PMLG, PELG, PPrLG, PBuLG, and PAmLG at 25°C are summarized in Figure 2. The ordinate of the figure is the sorption amount expressed by cc (S.T.P.)/cm^3, which is directly related to the numbers of molecules sorbed. The abscissa records pressure (cm Hg) directly. Except for PMLG, the sorption increases with increase in side chain length, which shows the looseness of the side chain region, as revealed by density determina-
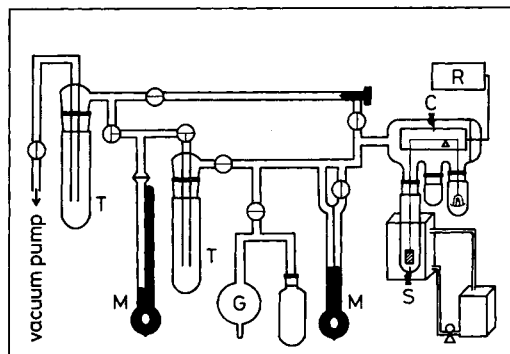

Fig. 1. Schematic diagram of sorption apparatus: (T) trap; (M) manometer; (G) gas reservoir; (C) Cahn electrobalance; (R) recorder; (S) sample.
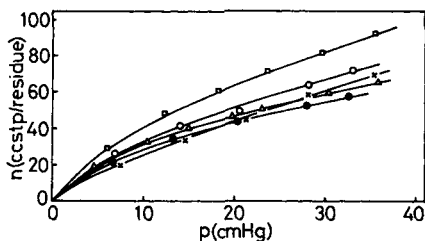
Fig. 2. Sorption isotherms of poly(n-alkyl L-glutamate)–xenon gas systems at 25°C: (□) PAmLG; (○) PBuLG; (▲) PPrLG; (●) PELG; (×) PMLG.

tions.[1] The curious behavior of the sorption by PMLG will be discussed later.

For the same polymer and the same pressure, sorption decreases with increase in temperature, which demonstrates the usual exothermic sorption even in the case of nonpolar xenon gas. For a gas of low critical temperature like xenon (16.6°C), it is adequate to use the fugacity ratio f_2/f_2^0 as the activity a.[5] The value of f_2^0 is obtained by the corresponding state principle.[6] The value of f_2 may be almost equivalent to the pressure itself at the low pressure range used in the present experiment. Therefore,

$$a = f_2/f_2^0 \tag{1}$$

The experimental results for the temperature dependence are shown by this method in Figures 3 and 4 for PMLG and PELG, respectively.

Except for PMLG, the sorption isotherms (amount of sorption versus activity) are reduced to only one curve. This result resembles the sorption behavior when the sorption isotherm of water on a relatively hydrophobic polymer is arranged
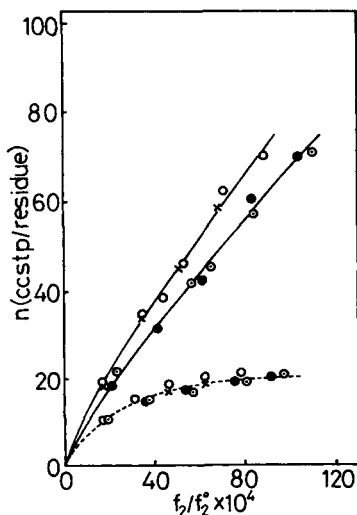

Fig. 3. Sorption isotherms of poly(γ-methyl L-glutamate)–xenon gas system at various temperatures. Broken line represents heat-treated sample. Abscissa is the fugacity ratio f_2/f_2^0 of xenon gas. Temperature (°C): (⊚) 20; (●) 25; (○) 30; (×) 35.
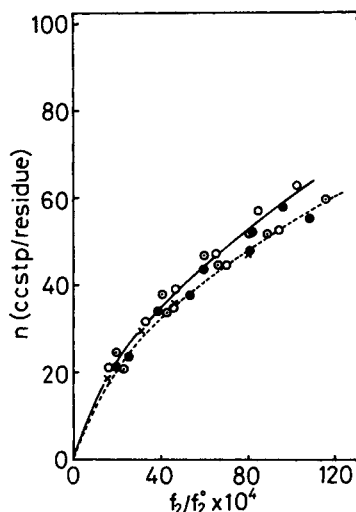
Fig. 4. Sorption isotherms of poly(γ-ethyl L-glutamate)–xenon gas system at various temperatures. Broken line represents heat-treated sample; f_2/f_2^0 is fugacity ratio Temperature (°C): (⊙) 20; (●) 25; (○) 30; (×) 35.

in a sorption-versus-relative vapor pressure relationship, and this result is quite useful for the prediction of sorption behavior.

In the case of original PMLG (solid lines in Fig. 3), though the isotherm may be divided into two parts, there is no systematic temperature dependence between the successive temperatures. Considering that the second-order transition temperature of the side chain for PMLG is 28°C, this behavior may due to the structural change at the transition temperature. It is known that the regularity of the molecular orientation of PMLG depends on the casting method, and this orientation is low compared with that of the other polyglutamates for the same
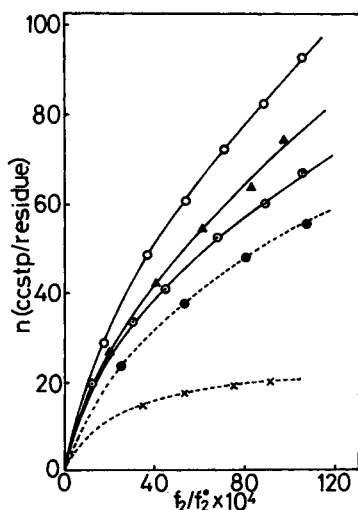

Fig. 5. Reduced sorption isotherms of poly(n-alkyl L-glutamate)–xenon gas systems. Abscissa is the fugacity ratio f_2/f_2^0 of xenon gas: (○) PAmLG; (△) PBuLG; (⊙) PPrLG. Broken lines are isotherms of heat-treated PMLG (×) and PELG (●).

(a)
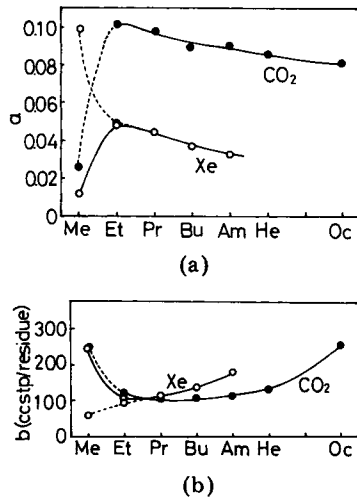

(b)

Fig. 6. (a) Langmuir constant a for various poly(n-alkyl L-glutamates)–xenon gas (●) and –CO$_2$ gas (●) systems at 25°C. Broken lines represent heat-treated samples. (b) Langmuir constant b for various poly(n-alkyl L-glutamate)-xenon gas (○) and –CO$_2$ gas (●) systems at 25°C. Broken lines represent heat-treated samples.

casting method.[7,8] Therefore, the influence of heat treatment (250°C, 10 min), which is expected to improve the molecular order of PMLG, was studied. At the same time, the influence on PELG was also examined for comparison. The sorption isotherms after heat treatment for PMLG and PELG are also shown by broken lines in Figures 3 and 4, respectively. The decrease in sorption after heat treatment is considerable for PMLG and rather small for PELG. Furthermore, the effect of the transition temperature is not clear for heat-treated PMLG.

Using the results for heat-treated PMLG and PELG, the reduced isotherms are summarized in Figure 5. In general, the sorption increases systematically with increase in side chain length.

Since all the isotherms show a simple Langmuir-type sorption curve, analysis by the equation

$$p/n = (1/ab) + (p/b) \qquad (2)$$

is applied, where n is the sorption amount for pressure p, b is the saturation value of n, and a is the energy factor. Though the above equation was designed originally for sorption by a localized sorption site, in this case, b denotes the sorption
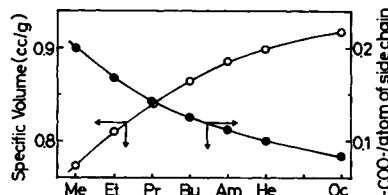

Fig. 7. Specific volume and polarity of side chain (ester group/atoms of side chain back bone) vs. side chain length.
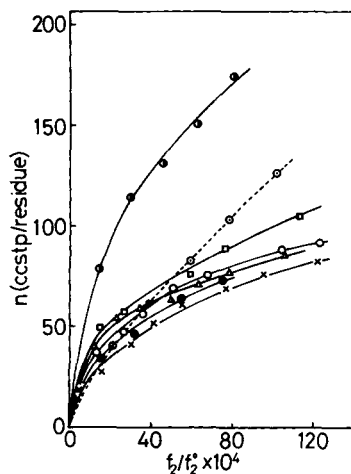
Fig. 8. Sorption isotherms of poly(n-alkyl L-glutamate)–CO_2 gas systems at 25°C. Abscissa is the fugacity ratio f_2/f_2^0 of CO_2 gas;)●) POcLG; (□) PHeLG; (△) PAmLG; (×) PBuLG; (●) PPrLG; (○) PELG; (◉) heat-treated PMLG.

capacity more generally and a is considered the polymer–gas interaction energy. Furthermore, since the change in membrane surface area does not affect the sorption amount (expressed in cc (S.T.P.)/residue), a and b are considered to relate the bulk sorption behavior. The a and b values are plotted against the side chain length (carbon atoms in ester part) in Figures 6a and 6b. Including heat-treated PMLG, the capacity b increases and parameter a decreases with increase in side chain length. This may be understood by considering the specific volume of the polymer and the polarity of the side chains (Fig. 7).[1] Xenon gas is not polar, and sorption may occur mainly by induced dipole moment interaction and dispersion force. With regard to the dipole interaction, it is adequate to consider that the density of polar group may reflect.
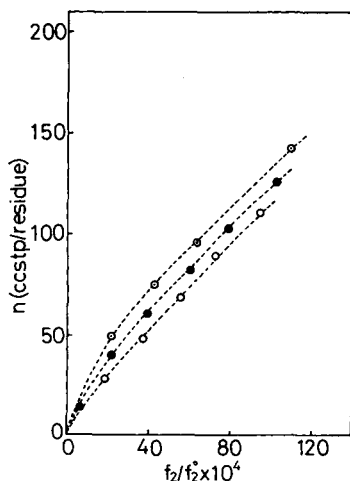

Fig. 9. Sorption isotherms at various temperatures of heat-treated poly(γ-methyl L-glutamate)–CO_2 gas system. Temperature: (◉) 20°C; (●) 25°C; (○) 30°C.
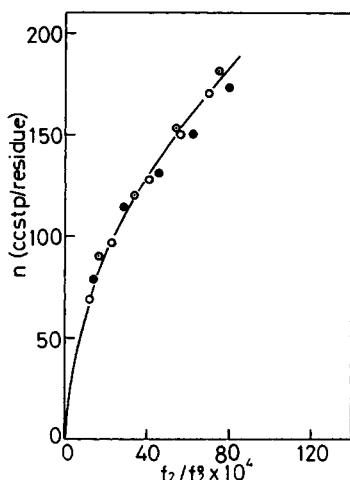
Fig. 10. Sorption isotherms of poly(γ-octyl L-glutamate)–CO_2 gas system at various temperatures: ($\odot$) 20°C; ($\bullet$) 25°C; ($\circ$) 30°C.

The sorption of carbon dioxide gas (which may show more polarity than xenon gas) on the poly(n-alkyl L-glutamates) was examined, and the sorption isotherms at 25°C are shown in Figure 7. As for PMLG, heat-treated sample is used. In this case, too, the fugacity ratio is used as the abscissa. Generally, the amount of sorption is about 1.5 times that of xenon. As for the side chain length, minimum sorption is observed in the region of PPrLG or PBuLG. The Langmuir constant b shows this clearly (Fig. 6). This behavior can be explained by the overlapping effect of polarity density (decreasing with side chain length) and specific volume (increasing with side chain length). The energy constant a decreases with side chain length (except for PMLG) and is larger than in the case of xenon, which shows that sorption of carbon dioxide gas is affected strongly by the polarity of the side chains (Fig. 7).

The temperature dependence of the sorption isotherms of PMLG and POcLG is shown in Figures 9 and 10. When the side chain length is short, sorption at low temperature is high and shows more exothermic tendency than in the case of xenon gas. It is interesting to note that in the case of POcLG, whose polarity

TABLE II
Enthalpy and Entropy of Sorption Obtained by Temperature Dependence of Sorption

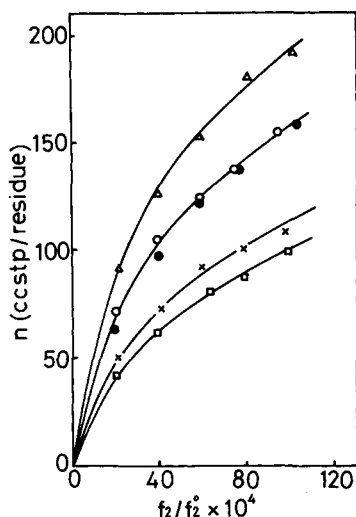| | Xe | | CO_2 | |
Membrane	$\Delta \bar{H}$, kcal/mole	$\Delta \bar{S} \times 10^3$, kcal/mole·deg	$\Delta \bar{H}$, kcal/mole	$\Delta \bar{S} \times 10^3$, kcal/mole·deg
PMLG	−3.2	−10.8		
PMLG (H.T.)	−5.5	−18.6	−9.0	−30.4
PELG	−4.9	−16.6		
PELG (H.T.)	−3.9	−13.6		
PPrLG	−3.5	−12.0		
PBuLG	−3.1	−10.6	−9.3	−31.3
PAmLG	−2.9	−9.8		
POcLG			−0.5	−1.8

Fig. 11. Sorption isotherms of five kinds of PBLG–CO_2 gas systems at 25°C. (□) form A; (×) form A (H.T); (○) form B; (●) form B (H.T); (△) form C. (H.T.) indicates heat treatment at 250°C for 10 min.

is relatively low, the sorption behavior approaches that in the case of nonpolar xenon gas.

The influence of heat treatment (250°C, 10 min) of PMLG is not so remarkable compared with the case of xenon. More severe heat treatment would make the relation more clear, because the molecular size is smaller for carbon dioxide gas than for xenon. However, since the present experiment imparts a light-brownish color to the sample, further examination is not pursued here.

From the experimental temperature dependence of sorption isotherms of various polymer–gas systems, the enthalpy ($\Delta\overline{H}$) and entropy ($\Delta\overline{S}$) of the sorption are calculated by the usual method:

$$\Delta\overline{H} = R(\ln P_1 - \ln P_2)/[(1/T_1) - (1/T_2)] \tag{3}$$

$$\Delta\overline{S} = \Delta\overline{H}/T \tag{4}$$

where T_1 and T_2 are 20°C and 25°C, respectively, and the pressures P_1 and P_2 are obtained at the constant sorption n (50 cc (S.T.P.)/residue). The result is shown in Table II. Both $\Delta\overline{H}$ and $\Delta\overline{S}$ are larger for carbon dioxide gas than for xenon. Furthermore, $\Delta\overline{H}$ and $\Delta\overline{S}$ decrease with increase in side chain length

TABLE III
Langmuir Constants a and b for Various Poly(γ-benzyl L-Glutamate)–CO_2 Gas Systems at 25°C

Membrane	a	b, cc(S.T.P.)/residue
Form A	0.052	148
Form A (H.T.)	0.056	162
Form B	0.056	225
Form B (H.T.)	0.059	232
Form C	0.066	264

(referring to heat-treated PMLG).   These results show clearly the effects of the polarity of sorbate gas and side chain length.

Effect of Higher-Order Structure of Side Chain on Sorption of Carbon Dioxide Gas by Poly(γ-benzyl L-Glutamate)

The sorption isotherms at 25°C of carbon dioxide gas by five kinds of PBLG membranes are shown in Figure 11.   Sorption increases in the order of

form A < form A (H.T.) < form B ≈ form B (H.T.) < form C

and the Langmuir constants a and b (Table III) systematically show this tendency.   From this result and referring to the $\Delta \overline{H}$ value of the DSC observation,[3] it is apparent that the sorption of carbon dioxide gas is markedly influenced by the side chain structure, namely, the stacking of benzene rings.   In other words, carbon dioxide gas is sorbed mainly on the benzyl ester parts of the side chains. The heat treatment (140°C, several hours) of form A, which causes the breaking of intramolecular stacking, increases the sorption ability irreversibly, and that of form B has no effect on sorption.   This also directly reflects structural changes of side chains.

The temperature independence of the sorption isotherms for various membrane forms is the same as in the case of poly(n-alkyl L-glutamates).

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