Gas Permeability and Side Chain Structure of Poly(γ-benzyl L-Glutamate)

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Synopsis

Three structural modifications of poly(γ-benzyl L-glutamate) (PBLG), forms A, B, and C, were prepared by varying the casting solvents and casting temperature. From x-ray analysis, infrared absorption spectroscopy, differential scanning calorimetry, and viscoelastic measurements, it is concluded that form A of PBLG is characterized by intramolecular stacking between the benzene rings in the side chain, form B exhibits intermolecular stacking, and form C has no stacking. The transition which corresponds to the breakdown of stacking of form A at 135°C is irreversible, while that of form B at 110°C is reversible. The degree of stacking is larger for form A than for form B. These structural features of the side chain region reflect the permeation and sorption behavior of carbon dioxide. Breakdown of stacking between benzene rings causes an abrupt increase in permeability in both form A and form B, and the permeation behavior for form A is not reversible, as is suggested from the irreversibility of the transition. The larger the degree of stacking, the lower is the amount of sorption. Although stacking is considered to affect the sorption site (solubility) and molecular motion, its influence on solubility is more evident in the temperature range up to about 50°C.

INTRODUCTION

It has been shown that the sorption and diffusion of small-molecule substances in various polypeptides take place in the side chain region between helices. This result has been obtained using various penetrants and a number of polypeptides of different chemical structure.[1]

In the present paper, using the polymer poly(γ-benzyl L-glutamate) (PBLG), the influence of the higher-order structure of the side chain region to the gas permeability is studied. The structure of the side chain region is markedly affected by the casting method (solvent and temperature). This is revealed by x-ray diffraction, infrared absorption, differential scanning calorimetry, and viscoelastic properties. The permeation and sorption of carbon dioxide gas through and in the PBLG membrane were examined in relation to the higher-order structure of the side chain.

EXPERIMENTAL

Materials

Poly(γ-benzyl L-glutamate) (PBLG) was prepared by the polymerization of γ-benzyl L-glutamate N-carboxyanhydride (NCA) by triethylamine as an initiator. The viscosity-average molecular weight is 2.7×10^5.

Three principal PBLG modifications were prepared by changes in casting

conditions (solvent and temperature) (Table I). Form A was cast at 45°C from 3% PBLG solution in benzene. Form B was cast at 60°C from the same solution. Form C was cast from 3% PBLG solution in ethylene dichloride at room temperature. The casting solutions were aged for one day before casting. Casting was then carried out by air drying for five to six days at the indicated constant temperature. After casting was almost accomplished as deduced by visual inspection, the membrane was washed with methanol and vacuum dried for several days. Samples designated as form A (H.T.) and form B (H.T.) were prepared as for forms A and B and subjected to heat treatment at 140°C for several hours (duration of permeation experiment).

All of the membranes described above have α-helical structures, which is confirmed by the amide V band (620–610 cm^{-1}) in the infrared absorption spectroscopy.

Though the above "forms" are in some ways similar to those obtained by Tobolsky et al.[2] or Tsujita and Uematsu[3] by variations in casting temperature or solvent, they are different in details as is clear from the following structural observations. Purification of the carbon dioxide used for sorption and permeation experiments is described in detail elsewhere.[4]

Apparatus

Structural observations were made by an x-ray diffractometer (Rotor Unit of Rigaku Denki K. K., Japan), an infrared absorption spectrometer (IRA-II Type of Japan Spectroscopic Co., Ltd.), a differential scanning calorimeter (DSC Standard Type of Rigaku Denki K.K., Japan, heating rate 10°C/min), and a Vibron DDV-II (Toyo Baldwin Co., Ltd., Japan, frequency 110 Hz).

Permeation experiments were performed with a Rouse-type[5] apparatus in which the carbon dioxide that permeated through membranes was trapped by liquid nitrogen, so the pressure on the delivery side was essentially zero. The pressure on the feed side was about 10 cm Hg at room temperature and was decreased at higher temperature to prevent membrane rupture. The bath temperature of the cell section was controlled by a silicone oil bath; measurements up to 150°C were possible within 1°C. Because the permeation curve (amount of permeant-vs-time relationship) was strictly linear in the stationary state at any temperature, the accuracy of permeability measurements was quite high and the standard deviation was less than a few percent.

Sorption of the carbon dioxide was determined with a Cahn Electromicrobalance (Cahn Inc., accuracy ±10 μg).

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] Subjected to heat treatment at 140°C for several hours.

RESULTS AND DISCUSSION

Side Chain Structure

X-Ray determination of the three modifications is summarized in Table II. The values in parentheses are for heat-treated samples. The (110) spacing for form A, the (100) spacing for form B, and the (110) spacing for form C correspond to each other[6,7] and are in the order form A >form B >form C. In form A, the reflection of 5.08 Å, which is assigned to the axial translation of benzene rings stacked in the pseudohelical structure of PBLG,[7] is evident. For this structure, therefore, intramolecular stacking between benzene rings is clearly present. Furthermore, referring to the infrared absorption spectrum at 1360 cm^{-1} (Fig. 1), which shows the existence of stacking in form A and also in form B,[8] the above order of the spacing indicates that stacking in any form would prevent the mutual approach of the helices. In other words, in form C, which has no stacking as described later and apparent from infrared absorption measurements,[9] the free conformation of each side chain would make the spacing small. It is interesting to note that heat treatment has no effect on form B but decreases the spacing for form A. The latter indicates that an irreversible structural change occurs by heat treatment in form A.

The DSC thermogram is shown in Figure 2. The endothermic peak of form A at about 135°C is due mainly to the breakdown of intramolecular stacking of benzene rings, which conforms to the result of Tsujita and Uematsu.[3] In comparison with the thermogram for form A (H.T.), it is clear that this endothermic transition is irreversible. With form B a broad endothermic peak appears at about 110°C, and this transition is reversible as is evident from the thermogram for form B (H.T.). This transition is attributed to the breakdown of intermolecular stacking of benzene rings, as explained more fully below. The transition enthalpy for form A, 2.2 cal/g, is larger than that for form B, 1.2 cal/mole. This suggests that stacking occurs more in form A than in form B. In form C there is no endothermic peak, considering the curved baseline in this case, and it is safe to assume that there is neither intramolecular nor intermolecular stacking between benzene rings.

The dynamic viscoelastic measurements are summarized in Figure 3. Two tan δ peaks are observed. The peak around room temperature (lower temper-

TABLE II
X-Ray Spacings of PBLG

(hkl)		Spacing (A)	
		Form A	
(110)		14.54	(13.55)[a]
		5.08	
		Form B	
(100)		14.00	(14.13)
(110)			(7.42)
(120)	(320)	4.59	(4.51)
(130)	(330)	4.13	(4.10)
		5.20	(5.19)
		Form C	
(110)		13.84	

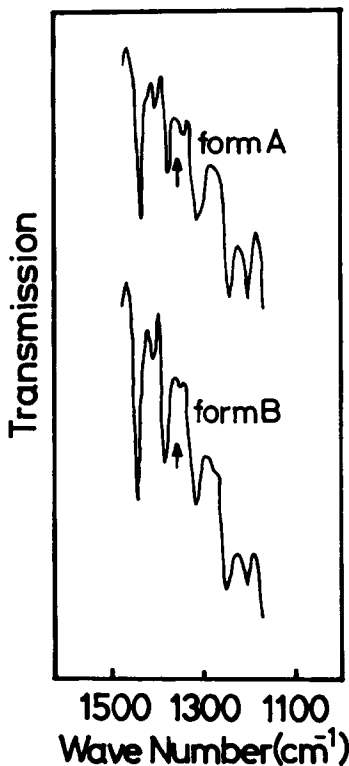[a] Heat-treated samples (140°C for several hours).

Fig. 1. Infrared absorption spectrum of PBLG, forms A and B.
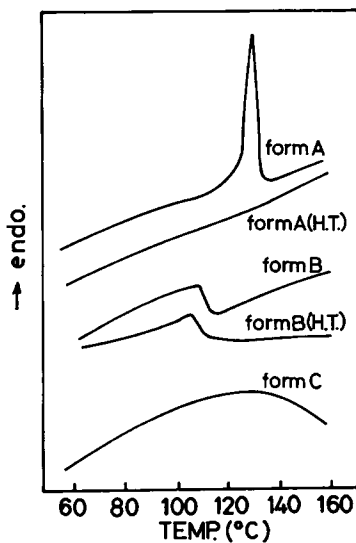

Fig. 2. DSC thermograms for PBLG.

ature) is known as the side chain dispersion[10] and is correlated with the inflection in plots of diffusion coefficient versus reciprocal temperature.[1]   As for the higher temperature dispersion, there has been no definite explanation, but it has no direct relation to transition of stacking, considering that form C shows the same
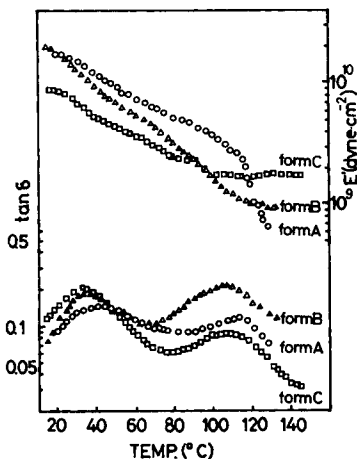
Fig. 3. Dynamic viscoelasticity of PBLG, forms A, B, and C (frequency 110 Hz).

dispersion. Examination of the temperature dependence of the modulus reveals that for form A the relatively high modulus falls considerably at a temperature corresponding to the endothermic peak of the DSC thermogram. This is due to the breakdown of stacking which bears the stress. The same behavior is seen for form B at about 110°C, corresponding to the breakdown of intermolecular stacking. For form C, the modulus is generally low, and there is no fall of modulus at this temperature range, which is consistent with the absence of distinct intramolecular or intermolecular stacking.

Considering the reversible transition at 110°C for form B observed in the DSC thermogram, the corresponding marked fall of elastic modulus in viscoelastic measurement, the reproducibility of x-ray data independent of heat treatment, the presence of stackings deduced from the IR spectrum, and also the fact that the transition from pseudohexagonal packing to pure hexagonal packing of helices occurs at 110°C,[2] the transition at 110°C for form B may be identified with the transition resulting from formation or breakdown of the intermolecular stacking of benzene rings.

Figure 4 shows that the temperature dependence of the dynamic viscoelasticity of form A (H.T.) is distinctly different from that of form A. The decrease in the modulus for form A (H.T.) around 110°C is due to the breakdown of intermolecular stacking and the transition from pseudohexagonal to pure hexagonal packing, which is analogous to the case of form B. The behavior of form B (H.T.) is similar to that of form B.

The structural observations on the higher-order structure of the side chain of the various forms of PBLG can now be summarized. In form A, stacking is principally of the intramolecular type, which breaks up at 135°C irreversibly. In form B, intermolecular stacking occurs with a transition temperature at about 110°C. The degree of stacking is much higher in form A than in form B. In form C, neither intramolecular nor intermolecular stacking between benzene rings is present.
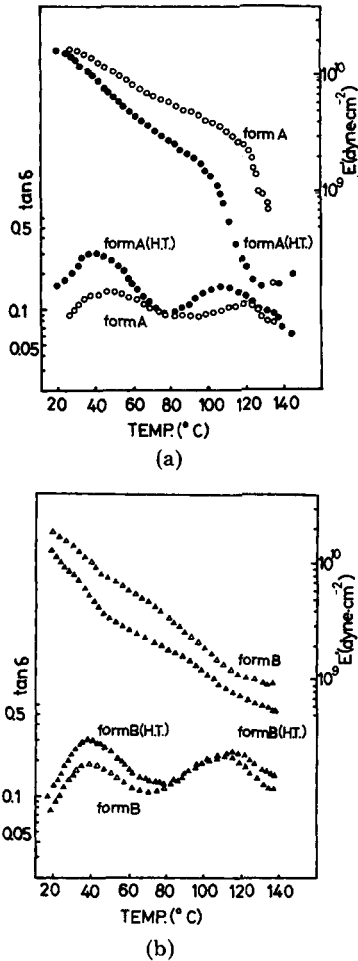
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Fig. 4. Influence of heat treatment on the dynamic elasticity of form A (a) and form B (b).

Permeation and Sorption of Carbon Dioxide in Three Modifications of Poly(γ-benzyl L-Glutamate)

The temperature dependence of the steady-state permeability $\bar{P}$ of carbon dioxide through the three kinds of PBLG membranes is shown in Figure 5. Firstly, a comparison of form A with form B is made. It is seen that generally $\bar{P}$ for form B is larger than that of form A, which reflects the degree of stacking corresponding to the transition enthalpy observed in the DSC thermogram. The $\bar{P}$ values coincide above 135°C. In form A, in conformity with the endothermic peak at 135°C in the DSC and the decrease of modulus, an abrupt increase of $\bar{P}$ is observed at about 130°–135°C, which may be due to breakdown of stacking of benzene rings.

Between 110° and 130°C, the increase in $\bar{P}$ slows down to some degree, reflecting stack formation near the transition temperature. This behavior is analogous to high-temperature crystallization at temperatures near the melting temperature. In form B, a sudden increase in $\bar{P}$ is seen at about 110°C, which
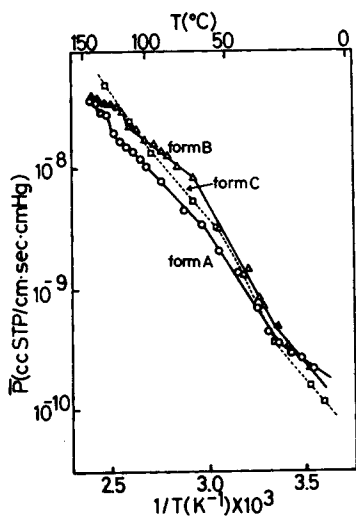
Fig. 5. Steady-state permeability coefficient $\bar{P}$ of carbon dioxide in membranes of PBLG, forms A, B, and C.

is attributed to breakdown of intermolecular stacking. All the above results show clearly that the disruption of stacking increases the number of sorption sites or molecular motion in the side chain region, and that carbon dioxide evidently diffuses through the side chain region between helices. In form C, which is included in Figure 5, the absence of an abrupt change of $\bar{P}$ in the high-temperature region reflects the absence of stacking of benzene rings.

In order to examine the influence of thermal history on form A, a membrane which had been heated to 150°C during the permeation experiment was subsequently cooled and its permeability measured as a function of decreasing temperature. As shown in Figure 6, with decreasing temperature there is no abrupt
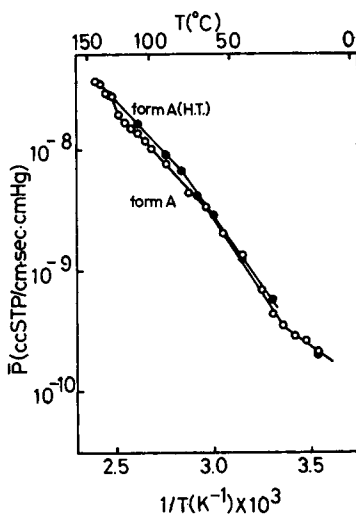

Fig. 6. Influence of thermal history on permeability $\bar{P}$ of carbon dioxide gas through PBLG form A membrane. Open and filled circles correspond respectively to experiments with increasing and decreasing temperature.

fall in $\overline{P}$ around 135°C, and it is concluded that the transition at 135°C is also irreversible from the permeation experiment, in conformity with the irreversibility of the structural aspects.

In the three membranes, forms A, B, and C, the plot of $\overline{P}$ versus reciprocal temperature shows inflections at 20°–30°C. These are due to the side chain dispersion, and the results conform to those reported previously.[1] As for the inflections around 70°C (forms A and B) and 60°C (form C), further investigation will be necessary.

Sorption isotherms of carbon dioxide for three kinds of PBLG membranes are shown in Figure 7. In the figure the effect of heat treatment of forms A and B is also depicted. On the abscissa, the fugacity ratio is used as activity.[4] In this representation, sorption isotherms at various temperatures reduce to a single curve if no structural change occurs during the experiment. The amount sorbed for the various forms is in the order form C >form B = form B (H.T.) >form A (H.T.)>form A. This order corresponds to the side-chain structure and suggests that unstacked benzene rings are the effective sorption site. The large difference between sorption by form A and form B is a consequence of stacking content corresponding to the transition enthalpy.

Usually, when both the permeability coefficient $\overline{P}$ and the solubility coefficient S (from the sorption isotherm) are obtained, the steady-state diffusion coefficient $\overline{D}$ should be calculated as the ratio $\overline{P}/S$. However, the temperature independence of the sorption isotherms of each form is limited to temperatures at which structural change does not occur. Furthermore, determination of the sorption isotherm in the high-temperature region is difficult experimentally. Therefore, the comparison of $\overline{D}$ for different forms was made in the range from room temperature to about 50°C, as shown in Figure 8. In this case, the values of S are 2.6×10^{-2}, 4.0×10^{-2}, and 4.9×10^{-2} cc(S.T.P.)/cm³·cm Hg at 25°C for forms A, B, and C, respectively. The inflection in each plot of $\overline{D}$ versus reciprocal temperature is evident at the transition temperature due to side chain motion and is observed in the viscoelastic behavior (Fig. 3). Furthermore, $\overline{D}$ for form
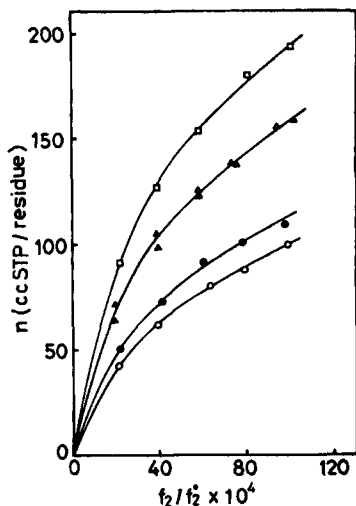

Fig. 7. Sorption isotherms of PBLG–CO₂ gas system at various temperatures. Abscissa is the fugacity ratio of CO₂ gas, and ordinate is the amount sorbed (cc S.T.P.) per one mole of repeating unit of PBLG: (O) form A; (●) form A (H.T.); (△) form B; (▲) form B (H.T.); (□) form C.
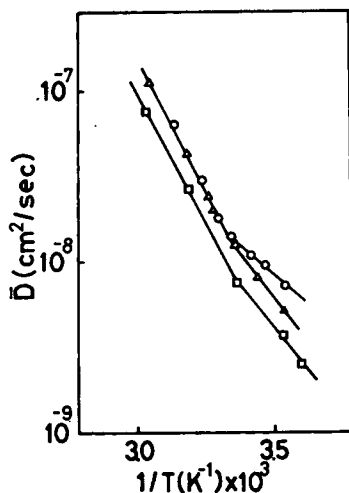
Fig. 8. Steady-state diffusion coefficient $\overline{D}$ of carbon dioxide near the transition temperature: (O) form A; ($\triangle$) form B; ($\square$) form C.

C is somewhat lower than for form A or form B.   Since x-ray analysis shows that the spacing in form C is the smallest, this result is understandable.

In conclusion, the stacking between benzene rings is considered to affect the sorption sites (solubility) and molecular motion in the side chain region. However, from the results of sorption and of the $\overline{D}$ value for form C, at least in the low-temperature range up to 50°C, the influence of stacking on solubility is more evident than on molecular motion.

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