Low Pressure CO_2 Sorption in Poly(vinyl Cyclohexane-carboxylate)

TAKUJI HIROSE, KEISHIN MIZOGUCHI, and YOSHINORI KAMIYA, *Packaging Materials Division, Industrial Products Research Institute, 1-1-4 Higashi, Yatabe-Machi, Tsukuba-Gun, Ibaraki, Japan, 305*

Synopsis

A gravimetric method was applied to determine the solubility of CO_2 in poly(vinyl cyclohexanecarboxylate) below 1 atm. The temperatures were varied from 5 to 85°C, above and below the glass transition temperature. The sorption isotherms were concave to the pressure axis below T_g and they were tentatively analyzed by the dual-mode sorption model. Above T_g, the isotherms were linear and described by the Henry's law. Below 75°C, the diffusion coefficients of CO_2 were also obtained from the half-time of the sorption process.

INTRODUCTION

Gas sorption isotherms in glassy polymers are usually known to be concave to the pressure axis and this characteristic is admitted to be related to the nonequilibrium state of polymers.[1-10] That is, according to the dual-mode sorption model, the isotherm is mathematically represented as a sum of a Henry's law dissolution contribution, C_D, and a Langmuir contribution, C_H:

$$C = C_D + C_H$$

$$= k_D p + \frac{C'_H b p}{1 + bp} \tag{1}$$

where C is the total concentration of gas, k_D is the Henry's law dissolution parameter, C'_H is the concentration in the unrelaxed volume or microvoids at saturation, and b is the hole affinity constant. The model, Eq. (1), has described the nonlinear sorption isotherms of glassy polymer–gas systems very well. But recently it has been shown that the model cannot be applied for the CO_2-poly(vinyl benzoate) (PVB) system at all, because sorbed CO_2 plasticizes the polymer to a rubbery state at high pressures.[11] For the analysis of such a system, the effect of plasticization on sorption isotherms should be estimated. For this purpose, it is of value to measure sorption isotherms accurately at low pressures, where plasticizing effect of sorbed gas is small enough to be neglected.

For the gas sorption measurement at high pressures, we have recently developed a gravimetric method with an electromicrobalance.[11,12] This method has worked well to reveal the hysteretic behavior of sorption data in some CO_2–polymer systems for the first time. The volumetric method has also been

CCC 0021-8995/87/041657-09$04.00

often used to measure gas solubilities at low pressures[2,13–15] as well as at high pressures. But the gravimetric method is expected to be easier operatively and more accurate compared to the volumetric method, especially at low pressures. The gravimetric method was used at low pressures by Barrie et al.[16,17] and Berens[18,19] to study the sorption and diffusion on some vapor-polymer systems. This method has not been applied to determine sorption isotherms of gases probably because gas solubility is much less than organic vapors but the solubility of CO_2 is rather large and comparable to that of C_2H_6.[12,13] In this work, the gravimetric method was attempted to measure the solubility of CO_2 in poly(vinyl cyclohexanecarboxylate) (PVCH) at low pressures below 1 atm. Following earlier analyses,[2,3,10,14,15] the results were analyzed by the dual-mode sorption model and the sorption parameters were presented. At the same time, the diffusion coefficient, D, was also obtained by Eq. (2):

$$D = 0.04919 \, l^2/t_{1/2} \tag{2}$$

where $t_{1/2}$ is the half-time of a sorption or desorption process and l is the film thickness.[20]

As this polymer has a proper glass transition temperature, T_g, for the sorption apparatus, the behavior of both the glassy and rubbery states was observed. Gas sorption behavior in a polymer is very important to understand the mechanism of permeation of gases. Considering the results obtained here, the permeation of some gases in PVCH will be discussed in the following paper.[21]

EXPERIMENTAL

Materials

PVCH was prepared from poly(vinyl alcohol) (PVA) and cyclohexane-carboxylic acid chloride just as PVB reported previously.[22] To the suspension of 5 g of PVA in 100 mL of anhydrous pyridine, 25 g of cyclohexanecarboxylic acid chloride was added slowly at 90°C. The mixture was cooled to 50°C, kept for 4 h and allowed to cool to room temperature. After the solution was diluted with 400 mL of acetone and the white precipitate was filtered, the product was obtained by pouring the mixture into water. The polymer was purified by repeated reprecipitations from tetrahydrofuran (THF) with a mixture of water and methanol. From the elemental analysis for carbon, hydrogen, and nitrogen, the degree of esterification was more than 97% and nitrogen was not detected.

PVA (polymerization degree n = 2000, 80% hydrolyzed) was obtained from Wako Pure Chemicals Co., Ltd. Cyclohexanecarboxylic acid chloride was also obtained from Wako Pure Chemicals Co., Ltd. and distilled from calcium chloride before use.

The molecular weight of PVCH measured by gel permeation chromatography in THF on a Shimazu 830 Liquid Chromatograph was about 270,000 on the basis of a polystyrene calibration.

Films of PVCH were prepared by casting on a glass plate on mercury from a 10% solution of benzene. The solvent was allowed to evaporate slowly and

then the films were dried under vacuum at 60°C for several days as reported in the previous paper.[22] The sample films were, however, exposed to 50 atm of CO$_2$ atmosphere before the sorption experiments at low pressures. They were transparent and the density (1.119 g/cm^3) was determined with an Anton Paar K.G. Density Meter and a KI aqueous solution at 25°C.

CO$_2$ gas was at least greater than 99.99% pure and no further purification was performed.

The specific volume-temperature relationship on PVCH film was measured as reported previously.[22]

T_g determined by differential scanning calorimetry (DSC) was 55–56°C with the heating rate of 10 K/min on a Du Pont 9900 Thermal Analyzer. This polymer was amorphous from the DSC and dilatometry results.

Apparatus and Procedure

The sorption isotherms were determined gravimetrically using a Cahn RG electromicrobalance, which was mounted in a glass vacuum chamber such as Berens developed.[18, 19] The whole apparatus could be evacuated by rotary and diffusion pumps and could be filled with CO$_2$ through a reservoir at an intended pressure. A sample with a buoyancy compensator (Au wire) and a counterbalance (Al rod of 3 mm diameter) were threaded on Nichrome wires and were suspended from a microbalance in glass tubes immersed in constant temperature water baths controlled by a thermoregulator. The total volume of the sample film and the compensator was adjusted to that of the counter-balance to eliminate the difference of the buoyancy between the arms of the microbalance. Pressures were measured with a "Baratron" pressure trans-ducer (227A). The sample weight was about 200 mg and the weight of the Au wire was about 400 mg. The standard procedure was to evacuate the sample on the balance to constant weight at first, then to operate to determine CO$_2$ solubilities at various pressures.

In this study, two types of sorption experiment were performed. One is that each experiment started after the concentration of penetrant in the polymer was reduced to zero. The other is that gas pressure was changed stepwise upto 1 atm and then reduced to zero. The equilibrium state was confirmed before each new measurement and no difference in gas solubility was observed between the measurements of two types. Sorption and desorption caused little change in pressures after each operation because of the small sample size, large gas volume, and low gas solubility.

RESULTS AND DISCUSSION

Sorption data for CO$_2$ in PVCH are presented in Figures 1 and 2. Below 35°C, the isotherms show the nonlinear character well known for glassy polymers in the pressure range of below 1 atm. Above 45°C the isotherms are linear in this pressure range. The dilatometry results of this polymer are presented in Figure 3 and reveal the glass transition at 52.3°C. As mentioned in the Experimental section, the T_g determined by DSC was 55–56°C. These values seem to correspond fairly well to the temperature, at which the nonlinearity of sorption isotherms disappears. The nonlinear isotherms are surely characteristic of the glassy state as mentioned by many workers and
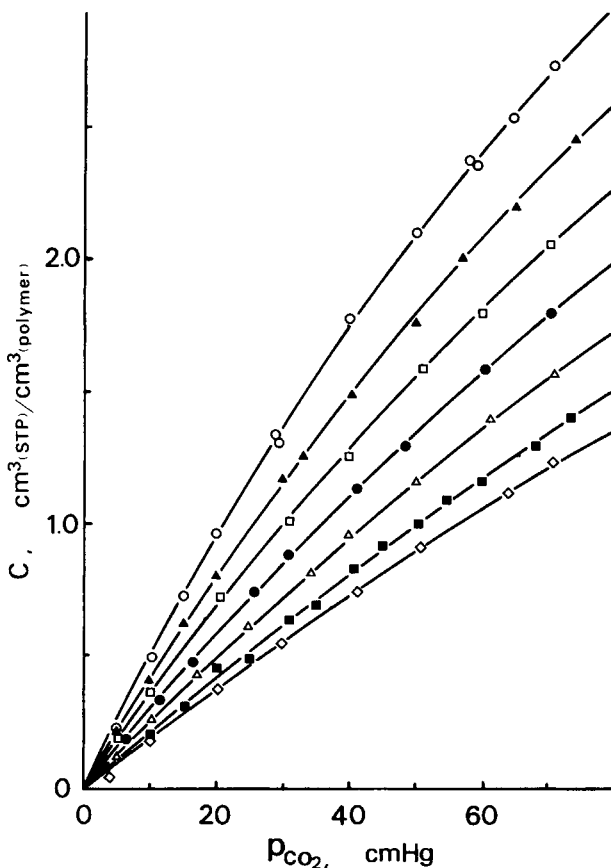
Fig. 1. Sorption Isotherms of CO_2 in PVCH between 5 and 35°C. (○) 5°C; (▲) 10°C; (□) 15°C; (●) 20°C; (△) 25°C; (■) 30°C; (◇) 35°C.

disappearance of nonlinearity from the isotherms is also observed for other gas-polymer systems near Tg.[7,11]

For analysis of the sorption isotherms of glassy polymers, the dual-mode sorption model is very often used as has been mentioned. At high pressures the plasticizing effect of sorbed CO_2 could be serious,[11] however, at low pressures, for example below 1 atm, the effect should be negligible. In fact, the hysteretic behavior, which is also expected to be caused by plasticization of polymer,[11,12] was not observed in this system. On the other hand, the dual-mode sorption model has also been applied to the low-pressure range by some researchers.[2,10,14,15] In the present study, the analysis was performed by this model with a little modification for the increase of accuracy as follows. From the isotherms above T_g, not only k_D but also the heat of solution, ΔHs, which is -3.35 kcal/mol, can be obtained. The parameters are shown in Table I. They were used for the dual-mode analysis of the sorption isotherms below T_g. With the aid of these data, k_D above T_g and ΔHs, k_D below T_g were estimated at first and then the other two parameters, C'_H and b, were determined by the nonlinear regression technique and the results are shown in
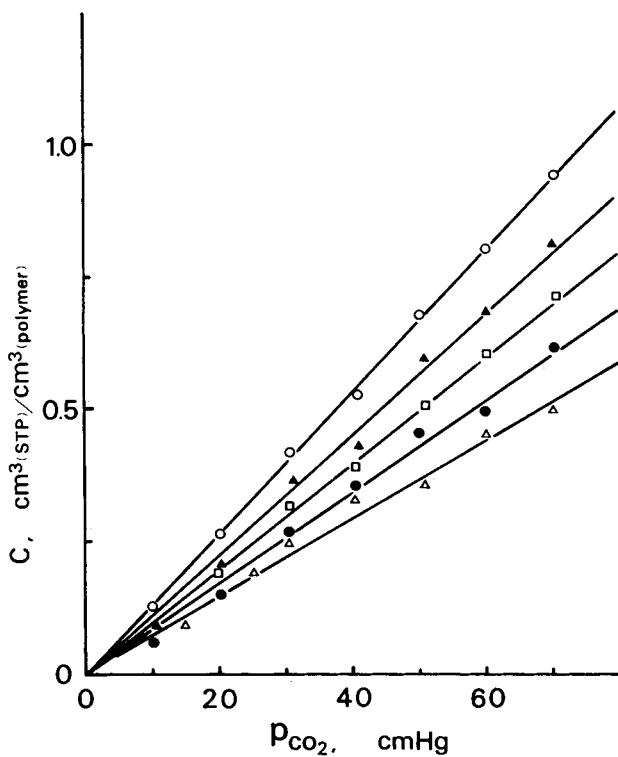
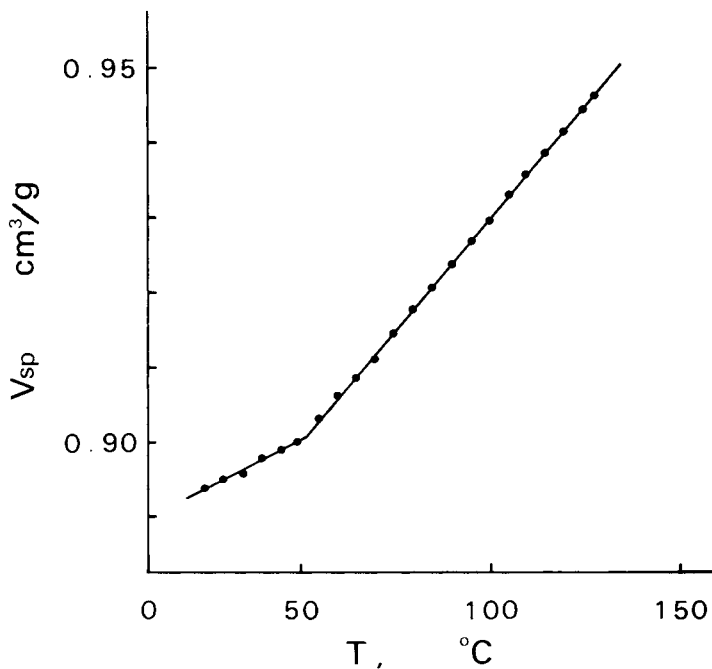Fig. 2. Sorption Isotherms of CO_2 in PVCH between 45 and 85°C. (○) 45°C; (▲) 55°C; (□) 65°C; (●) 75°C; (△) 85°C.

Fig. 3. Specific volume vs. temperature plot for PVCH.

TABLE I
Henry's Law Parameters for CO_2 in PVCH

T (°C)	k_D $\left(\dfrac{cm^3 \text{ (STP)}}{cm^3 \text{ (polymer)} \cdot atm} \right)$
45	1.02
55	0.866
65	0.752
75	0.653
85	0.560

TABLE II
Dual Sorption Parameters for CO_2 in PVCH

T (°C)	k_D $\left(\dfrac{cm^3 \text{ (STP)}}{cm^3 \text{ (polymer)} \cdot atm} \right)$	C_H' $\left(\dfrac{cm^3 \text{ (STP)}}{cm^3 \text{ (polymer)}} \right)$	b (atm^{-1})
5	2.19	1.15	1.87
10	1.97	0.830	2.11
15	1.77	0.684	1.85
20	1.60	0.559	1.57
25	1.46	0.373	1.69
30	1.32	0.230	1.57
35	1.22	0.227	1.04

Table II. These dual-mode parameters are plotted in the form of the apparent Henry's law parameter, $k_D + C_H'b$, as a function of temperature in Figure 4. Similar van't Hoff plots have been obtained by measuring the sorption isotherms above and below T_g.[7,11] The values of C_H' are also plotted as a function of temperature in Figure 5 and the tendency to decrease with increasing temperature is revealed.
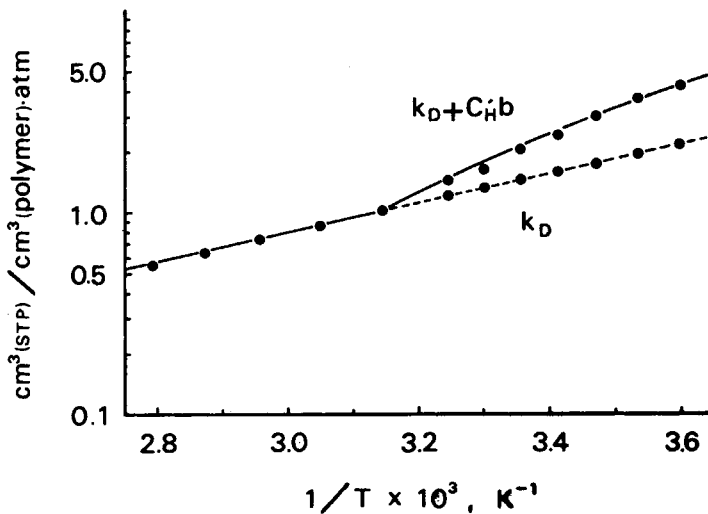

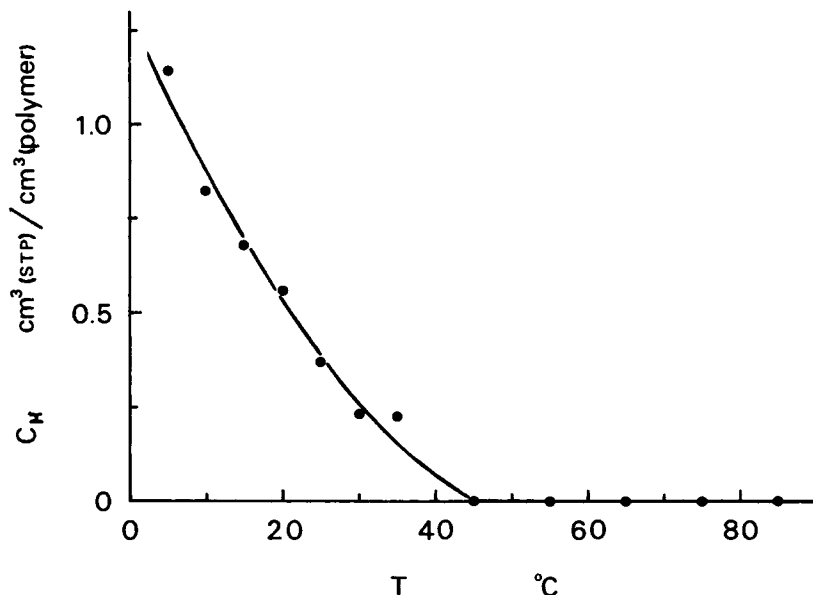Fig. 4. Van't Hoff plot of true and low-pressure apparent Henry's dissolution law parameters.

Fig. 5.   Langmuir capacity constant vs. temperature plot.

The sample was exposed to 50 atm of CO_2 before the measurement. It is known that exposure of glassy polymers to high-pressure CO_2 causes the increase of the sorption capacity, especially the increase of C'_H, of the polymers.[8,9,11] In spite of the high-pressure CO_2 conditioning, C'_H obtained on PVCH are rather small compared to the data of other glassy polymers.[2-9,14] The exposure effect of high-pressure CO_2 seems to be diminished quickly by the relaxation of the polymer even at ambient temperature. This phenomenon has not been reported for other CO_2-polymer systems yet, but the polymers which have been studied hitherto have high T_g's. The low T_g of this polymer should be the reason why the exposure effect disappeared so soon without annealing.

For the study of gas transport, D is an important parameter because the product by the solubility coefficient means the permeability. It is related to the half-time ($t_{1/2}$) of the sorption experiment, and for the present gravimetric method it is relatively easy to follow the process. $t_{1/2}$ was determined from the recorded charts and D was calculated by Eq. (2). Below T_g, D estimated by the equation are the apparent diffusion coefficients and they showed concentration dependence. That is to say, the apparent diffusion coefficient of sorption process was larger than that of desorption process and they increased with the increase of pressure. The concentration dependence was rather clear at low temperatures but not near T_g. In this paper, therefore, the average values of D of some measurements in both sorption and desorption processes are shown in the form of Arrhenius plot both above and below T_g in Figure 6. The plot reveals the change from the glassy to the rubbery state of polymer again, that is, the intersection of the plot is observed at about 45°C, which is in good agreement with the change of character of sorption isotherms.

It is shown that the CO_2 sorption isotherms in PVCH can be determined below 1 atm by the gravimetric method using an electromicrobalance. The isotherms are analyzed by the dual-mode sorption model. From the small hole
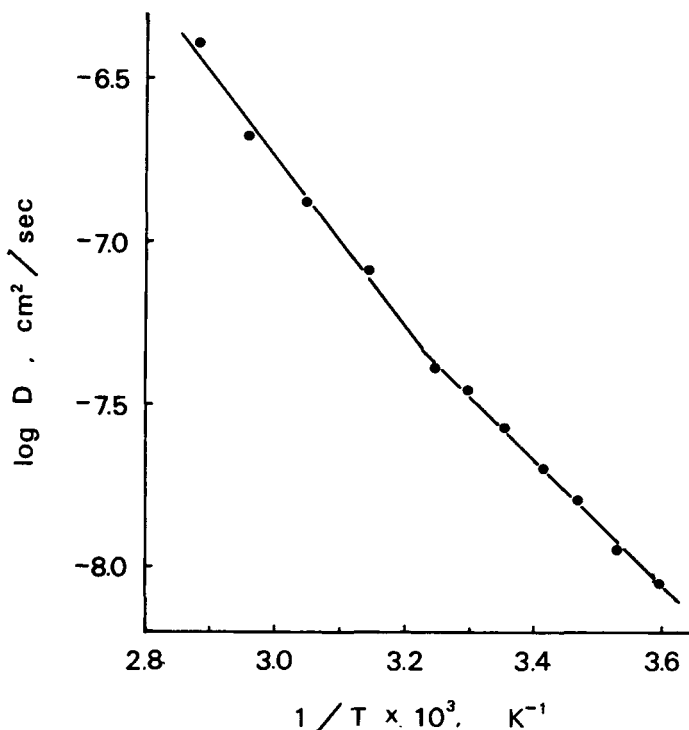
Fig. 6. Temperature dependence of the diffusion coefficients for CO_2 in PVCH.

saturation constants, C'_H, it is shown that the polymer has a few microvoids even after exposure to 50 atm of CO_2. Because of the relatively low T_g, the relaxation of this polymer seems to be easy and it is the cause of small values of C'_H. At the same time, D is also determined from the half-time of the sorption and desorption processes. These data will be referred in our next report on the permeation of some gases in this polymer.[21] On the other hand, as the plasticizing effect of sorbed CO_2 at pressures as high as 50 atm is known to be large, it is expected that this polymer will also change from the glassy to the rubbery state below its T_g as PVB.[11] It is very interesting to know how the sorption isotherms of CO_2 change at high pressures.

References

1. R. M. Barrer, J. A. Barrie, and J. Slater, *J. Polym. Sci.*, **27**, 177 (1958).
2. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
3. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
4. W. R. Vieth and J. A. Eilenberg, *J. Appl. Polym. Sci.*, **16**, 945 (1972).
5. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci.: Polym. Phys. Ed.*, **14**, 687 (1976).
6. S. A. Stern and A. H. DeMeringo, *J. Polym. Sci.: Polym. Phys. Ed.*, **16**, 735 (1978).
7. W. J. Koros and D. R. Paul, *J. Polym. Sci.: Polym. Phys. Ed.*, **16**, 1947 (1978).
8. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).
9. S. A. Stern and S. S. Kulkarni, *J. Membr. Sci.*, **10**, 235 (1982).
10. K. Toi, *Polym. Eng. Sci.*, **20**, 30 (1980).
11. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, *J. Polym. Sci.: Part B: Polym. Phys.*, **24**, 535 (1986).

12. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci.: Part B: Polym. Phys.*, **24**, 1525 (1986).

13. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).

14. W. R. Vieth, H. H. Alcalay, and J. Frabetti, *J. Appl. Polym. Sci.*, **8**, 2125 (1964).

15. K. Toi, *J. Polym. Sci.: Polym. Phys. Ed.*, **11**, 1829 (1973).

16. J. A. Barrie and D. Machin, *J. Macromol. Sci.-Phys.*, **B3**, 645 (1969).

17. J. A. Barrie, M. J. L. Williams, and K. Munday, *Polym. Eng. Sci.*, **20**, 20 (1980).

18. A. R. Berens, *Angew. Makromol. Chem.*, **47**, 97 (1975).

19. A. R. Berens, *Polymer*, **18**, 697 (1977).

20. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic Press, Oxford, 1968, Chapter I.

21. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, in press.

22. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **30**, 401 (1985).