Effect of Crosslinking Structure on Sorption of CO_2 in Photocrosslinked PVCA Film

MASANOBU MATSUGUCHI, JUNICHI MIURA, YOSHIRO SAKAI

Department of Applied Chemistry, Faculty of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

ABSTRACT: The sorption behavior of CO_2 gas in photocrosslinked poly(vinyl cinnamate) film was examined under atmospheric pressure. The sorption isotherm was well described by the Langmuir equation, suggesting that sorption of CO_2 is mainly governed by adsorption in the microvoids. The amount of sorbed CO_2 was significantly affected by the degree of crosslinking. The CO_2 sorption was enhanced at a lower degree of crosslinking but was decreased at a higher degree of crosslinking. The unexpected increase in the amount of adsorbed CO_2 correlated with the increase in the number of microvoids that occurred as a result of the crosslinking reaction. However, further crosslinking led to a decrease in the mean size of the microvoids. The smaller microvoids, in comparison to CO_2 molecules, did not act as adsorption sites, so that the amount of sorbed CO_2 decreased. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1744–1750, 2000

Key words: CO_2 sorption; microvoid; photocrosslinked PVCA; crosslinking structure

INTRODUCTION

The sorption behavior of CO_2 in various polymer films is currently being investigated because of the theoretical and practical significance of these films.[1–4] Consequently, it is valuable to reveal the factors that affect CO_2 sorption of the polymer. One of the most important factors affecting the gas sorption ability of a polymer is the primary structure, that is, the chemical structure. It is well known that the sorption of water is enhanced by introducing hydrophilic groups into the polymer. Acid gases such as CO_2 and NO_2 are sorbed in amine-functionalized polymers.[1,5,6] In addition to the primary structure, other factors related to molecular packing must be considered. In the case of a glassy polymer that has no strong ad-

sorption site, the sorption site of a gas seems to be in the free volume of the polymer.[7,8] Gas transport in polymers is a complex process that is controlled by the total free volume, the distribution of the free volume, the dynamics of the free volume, and the solubility of the gas molecules in the polymer. Attempts have been made to correlate the gas permeability in polymers with various measures of the free volume. The contributions of various functional groups to van der Waals volumes is quite different, and packing density seems to be dependent on the chemical structure of the polymer. To obtain the volume occupied by the polymer chains, a Bondi's group contribution method and its modified method have been used.[9–11] The treatment of volumetric change, that is, changes in the free volume distribution, in glassy polymers has also been studied.[12–14]

With respect to molecular packing, it is expected that crosslinking structures also affect the gas sorption behavior of the polymers. In the crosslinked state, where the segmental mobility is low or even absent, gas permeability is also governed by the
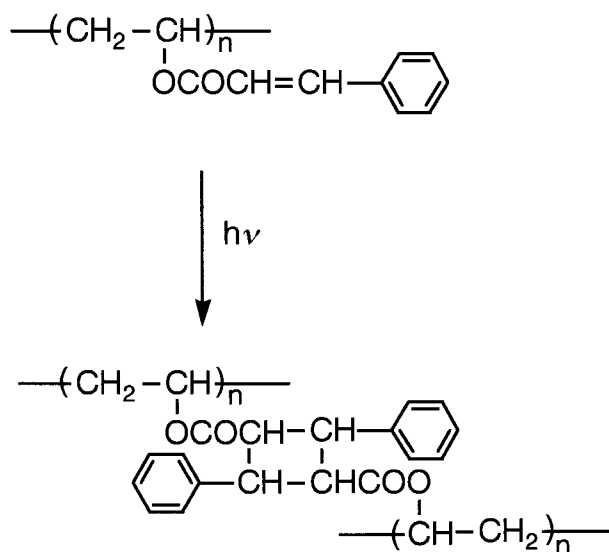
Figure 1 Chemical structure of the crosslinked form of PVCA.

microvoid (frozen free volume). The degree of crosslinking influences the distribution of the microvoids. However, there have been few reports on this subject, and only a few reports on water sorption behavior have been presented.[15–19] We have found recently that the sorption of polar molecules such as water, some alcohols, and CO_2 depends on the degree of crosslinking in the photocrosslinked PVCA film.[20–22]

This article reports on a examination of the effect of the degree of crosslinking in photocrosslinked poly(vinyl cinnamate) (PVCA) film on CO_2 sorption using a gravimetric method with a quartz crystal microbalance (QCM).

EXPERIMENTAL

Poly(vinyl cinnamte) (PVCA) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI), and used without further purification. It is well known that PVCA undergoes an intermolecular photodimerization of the cinnamate moiety in the solid state, resulting in a highly crosslinked structure,[23] which is why PVCA was chosen for this study. The chemical structure of PVCA and its crosslinked form are shown in Figure 1.

A QCM-type device was prepared as follows. PVCA was dissolved in toluene. A sensitizer was not used in order to avoid negative effects on the sorption behavior resulting from impurities. The solution was spin-coated on an AT-cut quartz

crystal oscillating element (4 MHz) with a silver electrode on both sides. After drying by heating at 150°C in N_2, the film was photoirradiated in N_2 at 320 nm using a 500-W high-pressure mercury lamp (USHIO, USH-500D). The degree of crosslinking was controlled by changing the photoirradiation time. The sample was then postheated at 150°C for 1 h in a N_2 atmosphere. A sandwich-type device was also prepared for the dielectric loss measurement. The PVCA solution was coated on an alumina substrate with a platinum lower electrode. The film was photocrosslinked, followed by evaporating a gold upper electrode. The area of the electrode was 2×4 cm. Illustrations of these devices are shown in Figure 2.

The amount of sorbed CO_2 was measured gravimetrically with a QCM. The QCM has been widely used for measuring mass change and is useful for observing the sorption change *in situ* in a thin film state. The principles of this technique have been described elsewhere.[20] The technique is particularly reliable for a crosslinked polymer.[24] The quartz crystal oscillator was placed in
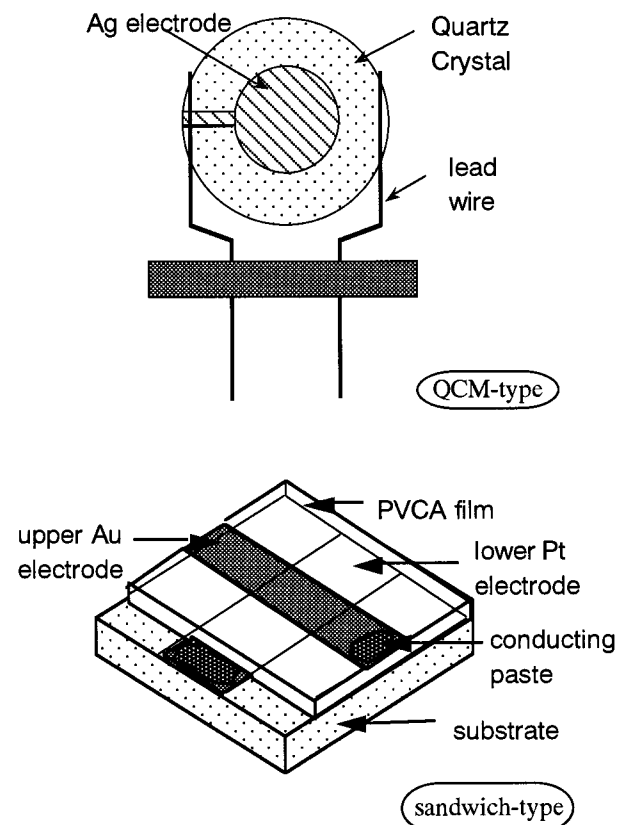

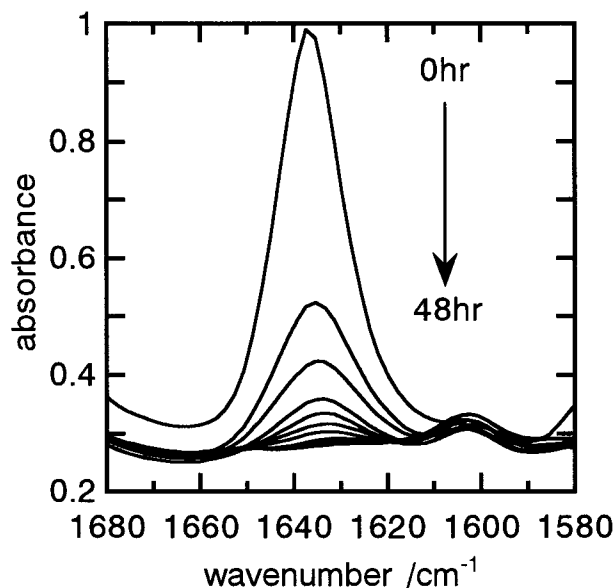**Figure 2** Illustrations of QCM-type and sandwich-type devices.

Figure 3 FTIR spectra showing the characteristic peak change during the crosslinking of PVCA.

a thermostated small vessel, and the oscillation frequency was monitored with a frequency counter (ADVANTEST, TR5822). The sandwich-type device was set in a measuring cell, and the dielectric loss was measured at 10 kHz at temperatures ranging from room temperature to 300°C using an LCR meter (Yokogawa Hewlett Packard, 4277A). These measurements were performed in flows of CO_2 and N_2 under atmospheric pressure. The partial pressure of CO_2 in the measuring atmosphere was achieved by mixing high-purity CO_2 and N_2, which were supplied from each gas cylinder. The degree of crosslinking was determined with FTIR analysis (JASCO, FT-IR300).

RESULTS AND DISCUSSION

FTIR Analysis

The degree of crosslinking (d.c.) of the prepared film was determined using FTIR analysis based on the variation in the absorbance at 1630 cm^{-1}, which is assigned to the C=C stretching vibration.[21] Irradiation of the film for a short period caused a rapid decrease in this peak, as shown in Figure 3. Judging from the reaction in Figure 1, it is clear that photodimerization proceeded because of photoirradiation. Further, photoirradiation resulted in a slight decrease in the magnitude of the peak, and the peak disappeared after 48 h. The

ratio of the absorbance at 1630 cm^{-1} and of that at 1500 cm^{-1} (which is assigned to a phenyl group, a group that does not participate in this reaction) was defined as the degree of crosslinking. The obtained degree of crosslinking is plotted against the photoirradiation time, as shown in Figure 4. A steep rise in the degree of crosslinking was observed below 10 h of photoirradiation, and the crosslinking reaction was completed in 48 h. The thinner the film is, the higher the degree of crosslinking at the same photoirradiation time. It is presently estimated that a nearly 100% degree of crosslinking was obtained after 48 h of photoirradiation. It is true that there was some uncertainty in the estimation of the degree of crosslinking. However, the values in this study were reproducible. Consequently, we believe that the use of the obtained values is reasonable for the present qualitative or for a comparative study. Furthermore, any peaks from the decomposition of the PVCA were scarcely visible throughout the entire spectrum, even after a long period of photoirradiation.

Dielectric Loss Measurement

Figure 5 shows the temperature dependence of the loss tangents (tan δ) measured for the unphotoirradiated PVCA and the photocrosslinked PVCA film in a N_2 atmosphere. One distinct peak
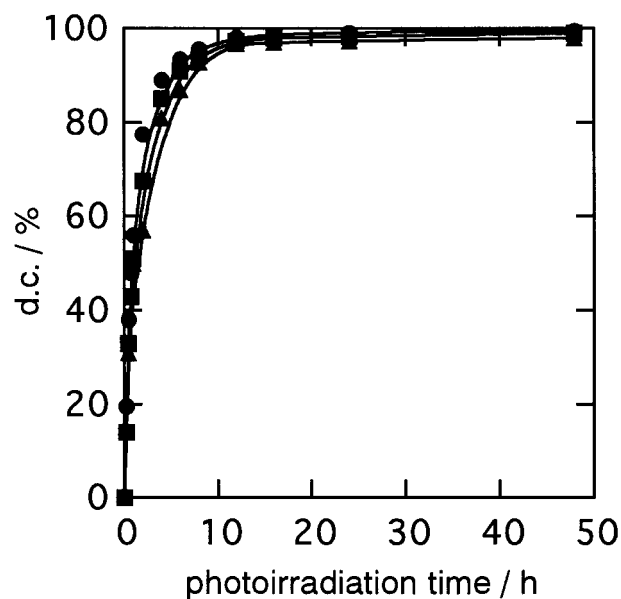

Figure 4 Variations in the degree of crosslinking with photoirradiation time; (●) film thickness = 2 μm, (■) 3 μm, and (▲) 4 μm.
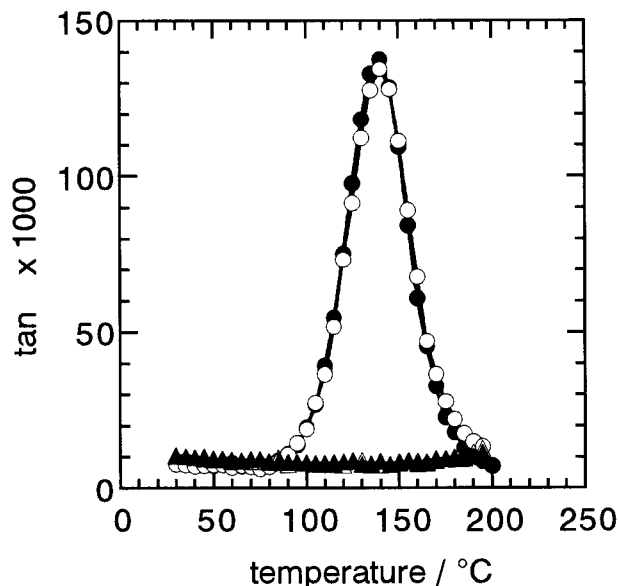
Figure 5 Dielectric relaxation spectra for the unphotoirradiated (●) and photoirradiated for 48 h (▲) film measured at 10 kHz. Closed symbols measured in N_2 atmosphere; open symbols, in CO_2.

in tan δ at ≃140°C can be observed for the unphotoirradiated PVCA film. It is known that the dielectric relaxation of a polymer arises from the segment motion of the main chain and the side chain. Since the peak disappeared after photoirradiating the film, it was confirmed that the formation of the crosslinking structure depressed the segment motion of the main chain. No relaxation peaks resulting from the decomposition of polymer were observed in this measurement. Figure 5 also shows the spectra obtained in a CO_2 atmosphere. CO_2 has been reported to be an effective plasticizer for PMMA.[25,26] However, no difference between the spectra obtained in N_2 and CO_2 was observed. This result suggests that CO_2 does not act as a plasticizer for either unphotoirradiated PVCA or photocrosslinked PVCA under the present experimental conditions. This can probably be attributed to the present measurement condition, that is, the measurement was performed under atmospheric pressure.

CO_2 Sorption in Photocrosslinked PVCA Film

The amount of sorbed CO_2 (W) was determined as a function of the partial pressure of CO_2 (p_C/atm) at 30°C. W is the weight of the sorbed CO_2 per 1 g of film. The sorption isotherms obtained for the photocrosslinked PVCA having different degrees of crosslinking are shown in Figure 6. The thick-

ness of the film was kept constant at around 3.0 μm for comparison. As shown in this figure, W increases monotonously with an increase in p_C for all films. It is well known that the sorption of CO_2 in a glassy polymer is successfully described by the dual-mode sorption model.[2,3] All isotherms shown in Figure 6 are similar in form to the model obtained in the region of low pressure. This result suggests that the sorption behavior of photocrosslinked PVCA is also governed not only by the Henry-type sorption but also the Langmuir-type adsorption. In other words, the free volume in the crosslinked polymer acts as an important adsorption site. In addition, it is shown that W is clearly influenced by the degree of crosslinking.

Figure 7 shows W versus the degree of crosslinking curves measured for the photocrosslinked PVCA at p_C = 1.0 atm and 30°C. Free volume can be expected to decrease on crosslinking and, based on this, a reduction in CO_2 solubility can also be expected. However, W is enhanced up to 95% of the degree of crosslinking. When the degree of crosslinking attained was more than 95%, the sorption of CO_2 was reduced. Here, it should be noted again that the value of 95% is not particularly important, since the estimation includes some uncertainty, as mentioned
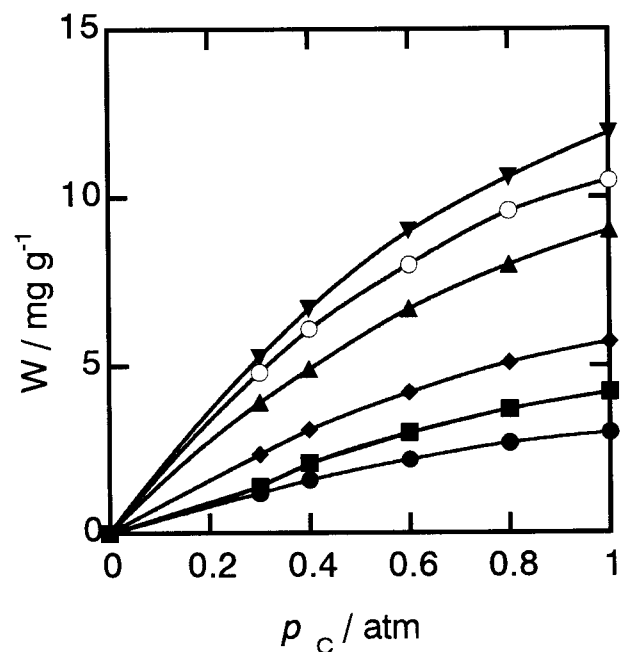

Figure 6 Sorption isotherms for crosslinked PVCA having different degrees of crosslinking measured at 30°C; (●) d.c. = 0%, (■) 33, (◆) 51, (▲) 85, (▼) 94, and (○) 99.
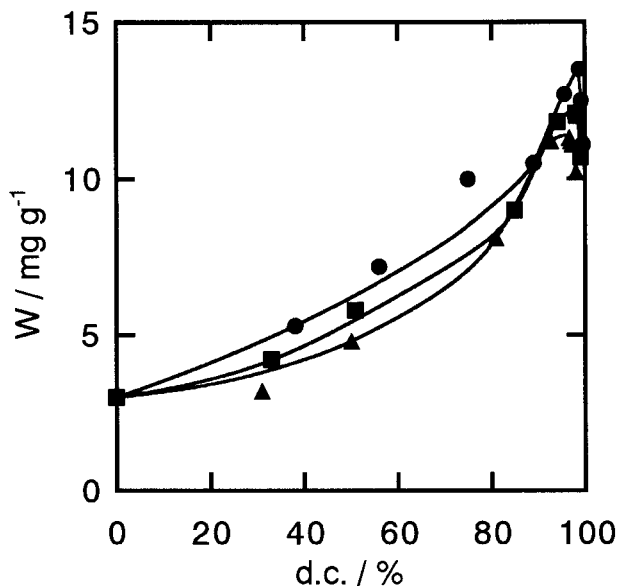
Figure 7 Dependence of the amount of sorbed CO_2 on the degree of crosslinking for the crosslinked PVCA film measured at $p = 1.0$ atm 30°C; symbols are the same as in Figure 4.

above. It is significant, however, that the curve reaches a maximum at a high degree of crosslinking. This phenomenon was more significant for the sorption of relatively large molecules such as acetone in photocrosslinked PVCA.[22] The sorp-
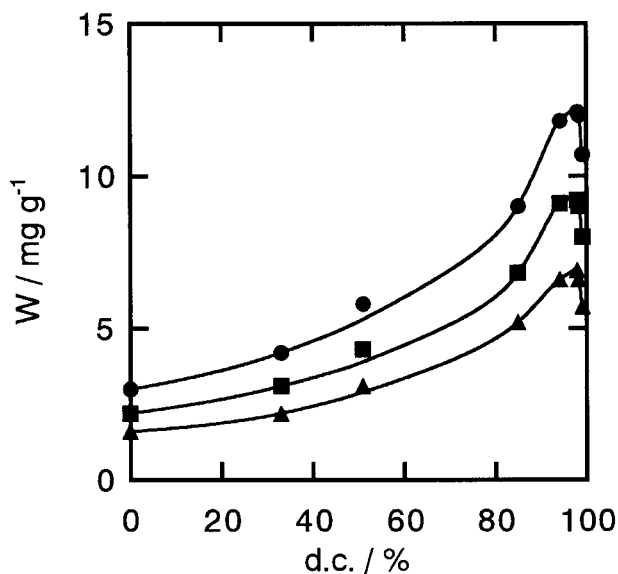

Figure 8 Dependence of the amount of sorbed CO_2 on the degree of crosslinking for crosslinked PVCA film measured at different temperatures; (●) 30°C, (■) 40°C, and (▲) 50°C. The film thickness is 3.0 μm.

Table I   Estimated Differential Heat of Sorption

d.c. (/%)	q^a (/kJ mol^{-1})
0	12.8
33.0	12.4
51.0	13.7
85.0	13.1
94.2	13.4
98.0	14.1
99.0	15.6

[a] The value is obtained for films of 3 μm thickness.

tion ability of the unphotocrosslinked PVCA film was hardly affected by the film thickness; that of the photocrosslinked film, however, was slightly affected. The thinner the film is, the larger the CO_2 sorption ability. That W is affected by the film thickness indicates the inhomogeneous CO_2 sorption in the film. Because the amount of sorbed CO_2 near the surface is larger than that in the bulk, W becomes larger for thinner film. The degree of crosslinking where the maximum appears, however, is scarcely affected by the film thickness.

The CO_2 sorption ability is also affected by the measuring temperature, as shown in Figure 8. An elevation in temperature results in a reduction in W for all films having different degrees of crosslinking and film thickness. However, the position of the maximum was almost independent of the measuring temperature. The different heat of sorption (q/kJ mol^{-1}) can be obtained by employing the Clausius–Clapeyron formula for the isotherms. The estimated q values given in Table I are an increasing function of the degree of crosslinking. This is attributed to the increment of a specific interaction between CO_2 and the segments of photocrosslinked PVCA after the crosslinking reaction.

Isotherm Analysis

For a glassy polymer, the curve representing the amount of sorbed gas is concave downward in relation to the pressure. Isotherms of this kind are usually described in terms of the dual-mode sorption model, especially at a high CO_2 pressure.[2,3,27] In practice, however, those isotherms shown in Figure 6, especially those obtained for films with more than 50% crosslinking, were well described only by the Langmuir equation. Dissolution in the Henry's law mode must include a process to make the inter-

Table II Summary of Langmuir Adsorption Parameters

d.c. (/%)	$W_H'^a$ (/mg g^{-1})	b^a (/atm^{-1})
51.0	15.0	0.63
85.0	21.1	0.75
94.2	32.0	0.66
98.0	26.7	0.89
99.0	23.3	0.87

[a] These values are obtained for films of 3 μm thickness at 30°C.

chain space large enough to accommodate CO_2. However, rigid crosslinked film, in which the segmental mobility is low or even absent, makes the process difficult. In addition, the measurement was carried out under atmospheric pressure. Consequently, it seems that the contribution of Henry's law to the total sorption was small. This result suggests that the progress of the crosslinking reaction has a greater effect on the formation of microvoids, that is, Langmuir-type adsorption sites. The calculated Langmuir's law parameters are summarized in Table II. It is noteworthy that the maximum W_H' (Langmuir capacity constant) occurred at around 95% of the degree of crosslinking, irrespective of the film thickness. This result is in accord with the result shown in Figure 7. As the origin of this unexpected behavior, the decomposition of the polymer and the formation of a novel sorption site by exposure to UV light was then ruled out from the IR analysis and the dielectric measurement. Furthermore, as confirmed from the dielectric loss measurement, the effect of CO_2 plasticization does not seem to be large. Consequently, the morphology change of the polymer after the crosslinking reaction should be taken into consideration. As mentioned above, the adsorption site is the free volume in the polymer, and the free volume is referred to as microvoids because the free volume is frozen by the crosslinked structure. The crosslinking reaction is involved in the change in morphology of the film. Although at the moment we don't have a useful tool in morphological investigation of polymers, the following circular reasoning would be possible from the data accumulated in this study. It is expected that the distribution of microvoids in the crosslinked polymer changes as the crosslinking reaction proceeds. The mean size of the microvoids becomes smaller with the degree of crosslinking because the microvoids are divided into small mi-

crovoids, resulting in an actual increase in the number of microvoids. Consequently, the increment of the sorption ability at the lower degree of crosslinking is explained by the increment of the effective microvoids for CO_2 adsorption. On the other hand, if the ratio of microvoids smaller than the size of the CO_2 molecule to the total number of microvoids increases at the high degree of crosslinking (ca. 95%), the sorption ability decreases, as observed in this study. An effect of the relative size of the adsorbed gas molecule and microvoids on the sorption behavior (molecular sieve effect) has been observed previously.[22] The value of the Langmuir affinity constant (b/atm^{-1}) is nearly equal to that of the reported polyimide films.[3] The value is an increasing function of the crosslinking degree, similar to q shown in Table I. From this result it can be inferred that specific interactions between CO_2 and the segments of the photocrosslinked PVCA increase as the size of the microvoids becomes smaller.

CONCLUSION

CO_2 sorption behavior in photocrosslinked PVCA film was examined under atmospheric pressure. The amount of sorbed CO_2 increased monotonously with increases in the partial pressure of CO_2. The sorption isotherm, which was concave downward in relation to the pressure, was well described by the simple Langmuir adsorption theory, suggesting the adsorption of the CO_2 molecule in the microvoids. The CO_2 sorption behavior was affected significantly by the degree of crosslinking. The CO_2 sorption was enhanced with increases in the degree of crosslinking, while the amount decreased at a high degree of crosslinking. This unexpected behavior can be attributed to the change in the distribution of the size of the microvoids that was accompanied by the crosslinking reaction. The mean size of the microvoids becomes smaller as the crosslinking reaction proceeds, while the number of microvoids increases. The increment of the sorption ability at a lower degree of crosslinking is explained by the increase of the effective microvoids for CO_2 adsorption. On the other hand, the increment of the microvoids smaller than the CO_2 molecule caused the reduction in the sorption ability at a high degree of crosslinking. This can be confirmed by the reduction in the Langmuir capacity constant at a high degree of crosslinking.

REFERENCES

1. Diaf, A.; Beckman, E. J. Reactive & Functional Polymers 1995, 27, 45.
2. Toi, K.; Ito, T.; Ikemoto, I.; Kasai, T. J Polym Sci, Part B, Polym Phys, 30 1992, 497.
3. Tanaka, K.; Kita, H.; Okamoto, K. J Polym Sci, Part B, Polym Phys 1993, 31, 1127.
4. Kamiya, Y.; Naito, Y.; Bourbon, D. J Polym Sci, Part B, Polym Phys 1994, 32, 281.
5. Diaf, A.; Beckman, E. J. React Polym 1995, 25, 89.
6. Yamaguchi, T.; Boetje, L. M.; Koval, C. A.; Noble, R. D.; Bowman, C. N. Ind Eng Chem Res 1995, 34, 4071.
7. Kirchheim, R. Macromolecules 1992, 25, 6952.
8. Kirchheim, R. J Polym Sci, Part B, Polym Phys 1993, 31, 1373.
9. Bondi, A. J Phys Chem 1964, 68(3), 441.
10. Alentiev, A. Y.; Yampolskii, Y. P.; Shantarovich, V. P.; Nemser, S. M.; Plate, N. A. J Membr Sci 1997, 126, 123.
11. Park, J. Y.; Paul, D. R. J Membr Sci 1997, 125, 23.
12. Rigby, D.; Roe, R. J. Macromolecules 1990, 23, 5312.
13. Jordan, S. S.; Koros, W. J. Macromolecules 1995, 28, 2228.
14. Niemelä, S.; Leppänen, J.; Sundholm, F. Polymer 1996, 37(18), 4155.
15. Atsuta, M.; Hirasawa, T.; Masahara, E. J Jpn Soc Dental Apparatus Materials 1969, 10, 52.
16. Barton, J. M. Polymer 1979, 20(8), 1018.
17. Turner, D. T.; Abell, A. K. Polymer 1987, 28, 297.
18. Best, M. E.; Moylan, C. R. J Appl Polym Sci 1992, 45, 17.
19. Kalachandra, S.; Kusy, R. P. Polymer 1991, 32(13), 2428.
20. Matsuguchi, M.; Sadaoka, Y.; Shinmoto, M.; Sakai, Y. Bull Chem Soc Jpn 1994, 67, 46.
21. Matsuguchi, M.; Shinmoto, M.; Sadaoka, Y.; Kuroiwa, T.; Sakai, Y. Sensors and Actuators 1996, B34, 349.
22. Matsuguchi, M.; Miura, J.; Sakai, Y. Chem Let 1998, 1998, 229.
23. Skloss, T. W.; Haw, J. F. Macromolecules 1994, 27, 6998.
24. Charlesworth, J. M.; Riddell, S. Z.; Mathews, R. J. J Appl Polym Sci 1993, 47, 653.
25. Sanders, E. S.; Jordan, S. M.; Subramanian, R. J Memb Sci 1992, 74, 29.
26. Handa, Y. P.; Kruus, P.; O'Neill, M. J Polym Sci, Part B: Polym Phys 1996, 34, 2635.
27. Barrer, R. M.; Barrie, J. A.; Slater, J. J Polym Sci 1958, 27(115), 177.