Investigation of Sorption and Diffusion of Supercritical Carbon Dioxide in Polycarbonate

J. J. Zhao, Y. P. Zhao, B. Yang

Department of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 200240 Shanghai, China

ABSTRACT: Sorption and desorption of carbon dioxide (CO_2) in polycarbonate (PC) with different dimensions were systematically investigated at temperatures of 40, 60, and 80°C; pressures ranged from 7 to 20 MPa; and soaking time ranged from 0.5 to 4 h. The experimental data were analyzed by a mass-loss analysis. With the assumption of Fickian diffusion, the sorption amount and the sorption diffusivities (D_s) under supercritical conditions, and desorption diffusivities (D_d) under ambient temperature and pressure were determined. The crossover of the sorption isotherms was presented, which indicated that the change of mass transfer mechanism had occurred. It was found that D_s increased with temperature, whereas D_d showed a contrary trend. Moreover, the linear relationship between sorption amount and specific surface area was also observed, which suggested that the specific surface area was one of the important factors on the sorption amount for thick samples in swelling process. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1661–1666, 2008

Key words: swelling; diffusion; specific surface area; supercritical carbon dioxide; polycarbonate; adsorption; surfaces

INTRODUCTION

The application of compressed carbon dioxide or supercritical carbon dioxide (SC-CO_2) as a green plasticizing agent for many polymers has become an area of increased attention. The properties like high diffusivity, solubility, plasticizing, nontoxic, and environmentally benign make supercritical carbon dioxide to be convenient for many applications, such as the extraction, polymerization, the impregnation of low-molecular-weight additives and the production of polymer foam. The infusion of additives into polymer substrate offers considerable possibilities for modification of specific polymer properties and preparation of materials. The CO_2-assisted impregnation of monomers,[1] organometallic compounds,[2,3] dyes[4] in polymer substrates has been disclosed. Other new applications include the production of microcellular foams obtained by the saturation of polymers and a rapid depressurization of the swollen polymers.[4,5] This approach has obvious advantages over conventional solvents, which may be time consuming and potentially toxic. For further application of SC-CO_2 in polymer processing, the sorption and diffusion of SC-CO_2 in polymers must be investigated. Although the researches about the swelling process in supercritical carbon dioxide have been reported, and some experimental diffusion data and sorption amounts have been given in the papers,[6–8] the interaction of polymers with absorbed carbon dioxide is not very well understood and further research is still necessary for providing explanation on the molecular interaction in polymer processing.

Various methods and apparatus have been used to measure the diffusion coefficient and sorption amount of carbon dioxide in polymers. Schnitzler and Eggers[4] measured the equilibrium and kinetic data by a magnetic coupled balance. Nikitin[9] studied the dynamics of diffusion front propagation in polystyrene samples during the swelling process by the use of an optical microscope. Royer[10] studied the kinetics of swelling of polymer melts by monitoring the position of the phase boundary. However, the above measurements often require sophisticated equipments. To provide further kinetic data and sorption amounts at various experimental conditions, a simple and reliable method should be applied. Berens et al.[11,12] introduced a gravimetric method to obtain diffusion coefficient and sorption amount by measuring the mass gain in polymers. The basis of this method is the *in situ* measurement of CO_2-desorption kinetics of polymers at ambient conditions, followed by an extrapolation procedure based on Fickian diffusion to evaluate the sorption kinetics. Using this method, sorption and diffusion of supercritical carbon dioxide in poly(vinyl chloride) (PVC),[13] poly(methyl methacrylate) (PMMA),[5] poly(ethylene terephthalate) (PET),[4] polystyrene (PS),[14] polysulfone (PSF),[15] polycarbonate (PC)[16] have been reported. Applying reasonable assumption

of Fickian diffusion, the diffusivities can be evaluated.

Polycarbonate is an important polymer in industrial processes for optical, electronic, and medical properties. Therefore, the investigations of PC modification by supercritical fluid (SCF) technologies (e.g., by impregnation, foaming) seem to be very promising and of great importance. Some studies have been conducted about the sorption and swelling of SC-CO_2 in PC. Chang et al.[17] investigated the swelling process of polycarbonate in the presence of sub- and supercritical carbon dioxide at pressure up to 30 MPa at 35.2 and 50.2°C, and the experimental data showed the monotonic increase/level-off sorption behavior with pressures. The swelling values were about 80 cm^3 (STP) CO_2 per cm^3 of polymer, which are in good agreement with those of Wissinger and Paulaitis.[18] Tang et al.[16] studied the interaction of SC-CO_2 with PC at temperature up to 60°C and pressure up to 40MPa. The equilibrium CO_2 sorption amount in PC specimen varies from 7.6 wt % (60°C, 10 MPa) to 14.7 wt % (40°C, 40 MPa). The differences between the measurements are owed to the different methods and apparatus. However, the crossover phenomenon of the sorption isotherms observed in this paper is not observed in the above-mentioned works, which indicated a change of mass transfer mechanism has occurred. Moreover, the previous works only focused on the influence of temperature, pressure and time on the sorption amount and diffusivities of SC-CO_2 in filmy polymer specimens (0.5 and 0.19 mm) with fixed dimension. In our research, we studied the relationship of dimensions of samples with sorption amount. It is found that the linear relationship of sorption amount with specific surface area of samples, which was not reported in other papers. The sorption isotherm, sorption and desorption diffusivities were also presented.

EXPERIMENTAL

Materials

PC sheets with 1.5 mm thickness were purchased from Shanghai Quanfu (Shanghai, China). The sheet was cut into the experimental specimens with dimensions of 5 × 10 × 1.5 mm^3, 15 × 10 × 1.5 mm^3, 30 × 10 × 1.5 mm^3, 60 × 10 × 1.5 mm^3, respectively. The specimens were cleaned with ethanol to remove surface impurities. A high-purity CO_2 (>99.5%) purchased from Taicang Xintai Alcohol (Taicang, China) was used.

Experimental equipment and procedures

The general scheme of experimental setup is described in Figure 1. The pump is used to compress
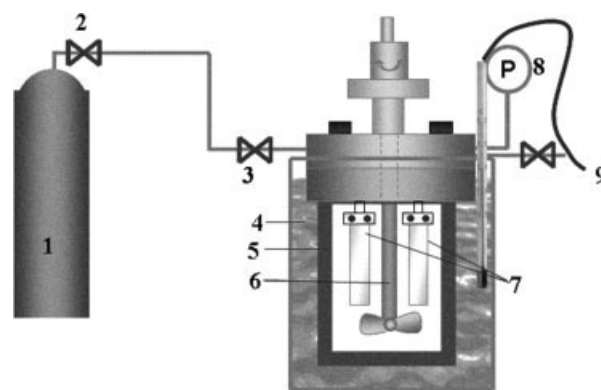

Figure 1 Schematic illustration of the experimental apparatus. (1) CO_2 tank; (2) pump; (3) valve; (4) oil/water bath; (5) reactor; (6) stirrer; (7) sample; (8) pressure sensor; (9) temperature control device.

CO_2 to the operating pressure. The high pressure vessel with an inner volume of ~ 25 mL is made of stainless steel, which will be placed in a constant temperature bath. The vessel is also supplied with electronic sensors of pressure and temperature. In a typical experiment, the PC samples with dimensions 30 × 10 × 1.5 mm^3 were weighed by an analytical scale (Mettler AB104N, sensitivity 0.1 mg) to record the initial weight, then one or two pieces of PC sheets were placed inside the high-pressure vessel, which after expulsion of air by CO_2, was closed. After heating the vessel up to the desired temperature, a certain amount of CO_2 was purged into the vessel. The sorption processes were conducted by variation of pressure (7–20 MPa), temperature (40–80°C) and sorption time (0.5–4 h). The sorption period ended with a quick depressurization procedure followed by quick transport of sample to the analytical scales to record the mass loss during the desorption process. Inside the vessel, the CO_2 of concentration in the high-pressure vessel remains unchanged because very tiny amount of CO_2 compared to the whole amount is absorbed into the specimens. For this reason, the diffusivity of sorption is only related with the experimental conditions, such as temperature, pressure, time, and so on.

Data analysis

A schematic illustration of the sorption process and mass-loss analysis to evaluate the experimental values is demonstrated in Figure 2. For a Fickian diffusion, M_d is a linear function of the square root of desorption time t_d, and the linear fit gives M_s at $t_d = 0$. Moreover, M_s is obtained by extrapolating the desorption amount M_d to the zero desorption time.

The methods in analyzing the sorption and desorption data can be described according to Crank and Park[19] by eq. (1)
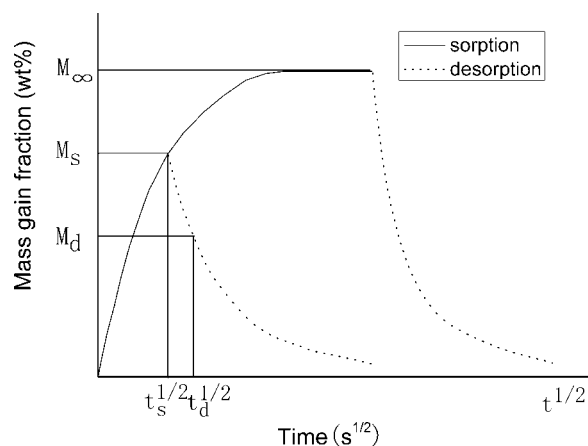
Figure 2 Schematic illustration of the sorption and diffusion process according to the method by Berens et al. M_s = absorbed amount of CO_2 at time t_s, M_d = the measured weight at t_d during the desorption process, M_∞ = the saturation amount.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{\iota^2}\right) \quad (1)$$

where M_t is the CO_2 sorption amount into the polymer sample at time t, M_∞ is the saturation amount, D is the diffusion coefficient and ι is the sample thickness. Simplification of eq. (1) by truncating at the first term on the right-hand side yields eq. (2) for the longer time sorption process.

$$\frac{M_s}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D_s \pi^2 t_s}{\iota^2}\right) \quad (2)$$

where M_s is the sorption amount after a certain period sorption time, t_s.

Equation (2) was also used to determine the sorption diffusivity D_s by plotting $\ln(1-M_s/M_\infty)$ against (t_s/ι^2). The short-time approximation of eq. (1) can be directly introduced to analyze the desorption process, eq. (3)

$$\frac{M_d}{M_s} = -\frac{4}{\iota}\sqrt{\frac{D_d t_d}{\pi}} \quad (3)$$

where M_d is the sorption amount after desorption time, t_d.

The desorption diffusivity D_d was thus determined by plotting (M_d/M_s) against $(t_d^{1/2}/\iota)$.

RESULTS AND DISCUSSION

Sorption isotherms

The sorption amount of CO_2 in PC samples, M_s, can be determined by eq. (3). A plot of M_d versus the
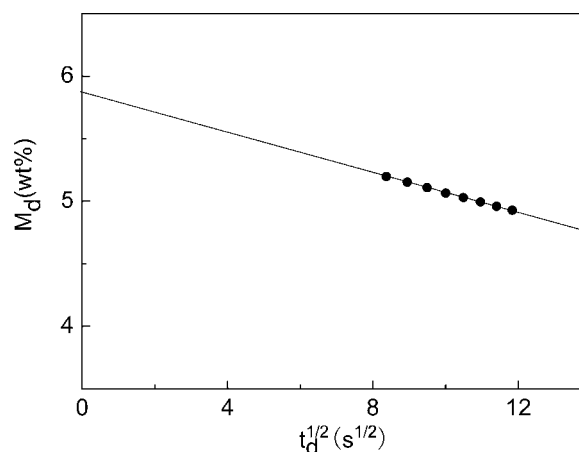

Figure 3 Plot of the measured desorption weight fraction (M_d) against the square root of desorption time (t_d). The sorption process lasts 4 h at 40°C and 10 MPa, sample dimensions: $30 \times 10 \times 1.5$ mm³

square root of desorption time, t_d, should be initially linear according to the assumption of Fickian diffusion. Figure 3 demonstrates this behavior. Extrapolating to $t_d = 0$ gives M_s, the absorbed amount of CO_2 at the beginning of desorption process and simultaneously the end of the sorption period. The linear relationship between M_d and $t_d^{1/2}$ at small desorption time period indicates that assumption of Fickian diffusion is acceptable. A series of experiments under different temperatures from 40 to 80°C and pressures from 7 to 20 MPa were carried out, from which the corresponding sorption amount of CO_2 in PC is determined. The sorption isotherms are shown in Figure 4.

As shown in Figure 4, the resulting sorption isotherms of PC at pressures between 7 and 20 MPa and temperatures between 40 and 80°C were mea-
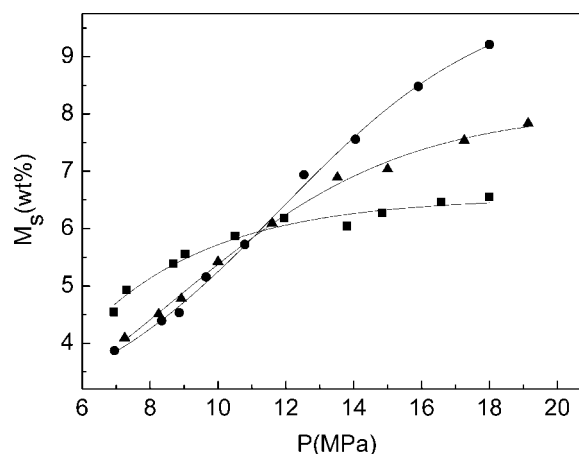

Figure 4 Plot of the CO_2 sorption amount (M_s) against the pressure at various temperatures: ■ 40°C; ▲ 60°C; ● 80°C; sample dimensions: $30 \times 10 \times 1.5$ mm³; sorption time = 4 h.

sured. The M_s values increase with increasing pressure for each isotherm, which has been observed in the investigation of the sorption and diffusion of SC-CO_2 in poly(vinyl chloride)[13] and poly(methyl methacrylate).[5] However, the increasing rates of three sorption isotherms are different, which lead to the crossover. This phenomenon was not observed in the previous researches about polycarbonate.[16] It is evident that there is a crossover for the sorption isotherms at approximate 11.2 MPa, which indicates a change in the tendency of the temperatures influence has occurred. At pressure below 11.2 MPa, the sorption amount decreases with increasing temperature, and at pressure above 11.2 MPa the sorption amount increases with increasing temperature. The profile of a single isotherm shows a characteristically "S-blend." The same relation is also found for the mass transfer in poly(ethylene terephthalate).[4] It has been suggested that a change in the mass transfer mechanism occurred, as discussed by Berens[20]: dual mode sorption at lower pressures and Fickian diffusion at higher pressures. At lower pressures, dual mode sorption dominated where SC-CO_2 was absorbed up to the second layer of a polymer site. With increasing temperature, the kinetic motion of SC-CO_2 increases, and hence results in a decrease in sorption amount. At higher pressure, the sorption amount increases with temperature owing to the enhancement in polymer chain mobility to accommodate more CO_2 molecules. Although glass transition temperature (T_g) of PC is commonly over 100°C, higher than experimental temperature in this study, numerous studies have discussed that there is an influence of the pressure on T_g due to the plasticizing effect of absorbed CO_2: Polymer's T_g can decrease with increasing pressure, sometimes even lower than ambient temperature.[17,21] In our experiment, the crossover phenomenon observed in Figure 4 suggests a significant physical change in the polymer phase. The mobility of the polymer chain was enhanced during this transition, and the polymer may change from its glassy state to rubbery state as temperature increasing from 40 to 60 or 80°C. Therefore, the slope of sorption isotherms at 80°C increases greatly. As a result, the polymer chain can have mobility under its intrinsic T_g in this study.

Desorption kinetics

According to eq. (3), the desorption diffusivity of CO_2 from PC specimens at ambient temperature and pressure could be estimated from the negative slope of M_d/M_s versus the square root of desorption time. A typical example is presented in Figure 3. Similar method is employed to determine the D_d values based on other sorption conditions. A plot of the D_d values as a function of the absorbed amount, M_s, is
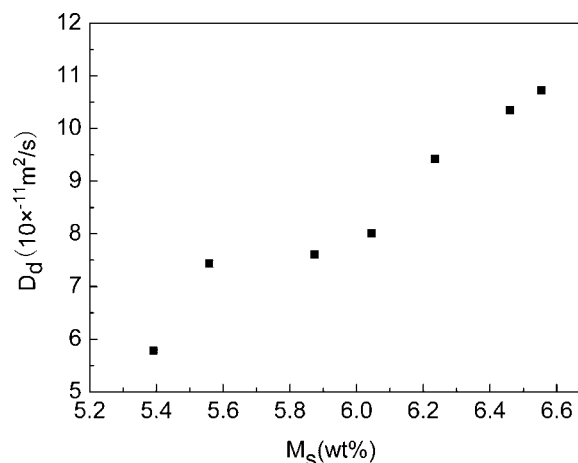
Figure 5 Desorption diffusivity (D_d) at ambient temperature and pressure, as a function of the sorption amount, M_s; sample dimensions: $30 \times 10 \times 1.5$ mm^3.

shown in Figure 5. It is indicated that D_d increases with the CO_2 concentration inside the PC specimen and reaches the maximum value, $D_d = 8.095 \times 10^{-11}$ m^2/s, with highest M_s. It is suggested that plasticizing effect of CO_2 on PC is the dominating factor in this study. The mobility of the polymer chain was gradually enhanced with CO_2 concentration increasing, therefore, more CO_2 molecules could escape from polymer at ambient temperature and pressure, which resulted in the significant increase in desorption diffusivities as shown in Figure 5. Similar effect has also been observed in literature for other polymers.[13,15]

Sorption kinetics

The sorption diffusivities, D_s, were determined from a stepwise variation of the sorption time, t_s. The diffusion model eq. (2) is capable of describing the sorption process well. The slope of the sorption data $\ln(1-M_s/M_\infty)$ plotted against (t_s/ι^2) could yield D_s. Table I and Table II summarized the calculated sorption diffusivities under various experimental conditions and M_∞, and the calculated desorption diffusivity D_d under ambient temperature and pressure. It was found that D_d and D_s values show an opposite

TABLE I
Effects of Pressures on the Sorption Amount, Desorption, and Sorption Diffusivities

T (°C)	P (MPa)	M_s (wt %)	D_s (10^{-11} m^2/s)	D_d (10^{-11} m^2/s)
40	10	5.8745	4.2746	7.6078
40	15	6.01496	5.9212	7.5118
40	18	6.45268	9.3047	8.0954

M_s, the sorption amount; D_s, sorption diffusivity; D_d, desorption diffusivity at ambient conditions.

TABLE II
Effects of Temperatures on the Sorption Amount, Desorption, and Sorption Diffusivities

T (°C)	P (MPa)	M_s (wt %)	D_s (10^{-11} m²/s)	D_d (10^{-11} m²/s)
40	10	5.8745	4.2746	7.6078
60	10	5.74187	3.6903	2.261
80	10	5.36152	4.5164	1.3232

M_s, the sorption amount; D_s, sorption diffusivity; D_d, desorption diffusivity at ambient conditions.

trend of changing with temperature. The D_d values decrease with increasing temperature and the D_s values increase at constant pressure. It is believed that the driving force of mass transfer increases and the resistance decreases due to higher polymer chain mobility at higher temperature. For this reason, the diffusivities of sorption are greatly enhanced with temperature rise at a fixed experimental pressure. On the contrary, diffusivities of desorption are based on gravimetric data at ambient temperatures and pressures, which depends strongly on the CO_2 sorption amount in the polymer. When the temperature increases, the sorption of CO_2 will decrease and the plasticization will be accordingly suppressed, which reduces the mobility of polymer chains, therefore, D_d decreases with temperature rise. Moreover, D_s and D_d are found to be proportional to the experimental pressure. The calculated data of this work fit well with the literatures.[4,7,12,16]

Effects of different dimensions on sorption amount

In the previous literatures, many investigators studied systematically the effects of temperature, pressure and time on sorption and swelling process of polymers in supercritical media, especially in supercritical carbon dioxide, such as PMMA,[5] PET,[4] PC,[16] etc. However, the influence of the dimensions of specimens on the sorption process has never been reported, which is also usually available in actual process.[9] Therefore, the relation of the sorption amount with dimensions of samples will be studied in this works. The gravimetric method in analyzing the sorption and desorption processes was described by previous investigations. For thin, flat and filmy polymer samples, when the ratio of thickness to length or width was less than 0.16, the kinetics of Fickian sorption and desorption could be given by eqs. (2) and (3), respectively.[22] As to filmy polymer (0.5 mm and 0.19 mm used by other investigators), one-dimensional diffusion along the thickness ι of the polymer, edge effect is negligible and the surface area or the specific surface area) is constant, which is not related with variation of dimensions (length and width) of samples. However, for thick polymer
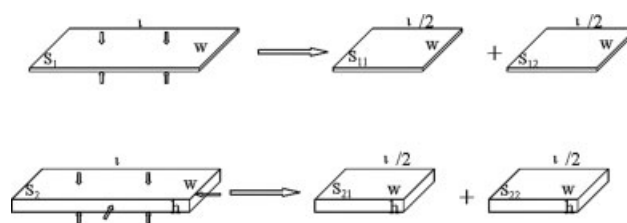

Figure 6 Schematic illustration of variation of surface area and specific surface area; S = the surface area; V = volume; ε = the specific surface area; ι = length; w = width; h = high; to filmy polymer: $S_1 = 2 \times (\iota \times w)$, $S_{11} = 2 \times (\iota/2 \times w)$, $S_{12} = 2 \times (\iota/2 \times w)$, $S_{11} + S_{12} = 2 \times (\iota \times w)$, $S_1 = S_{11} + S_{12}$, S_1, and V_2 are constant, $\varepsilon_1 = S_1/V_1$ is constant; to thick polymer: $S_2 = 2 \times (\iota \times w + \iota \times h + w \times h)$, $S_{21} = 2 \times (\iota/2 \times w + \iota/2 \times h + w \times h)$, $S_{22} = 2 \times (\iota/2 \times w + \iota/2 \times h + w \times h)$, $S_{21} + S_{22} = 2 \times (\iota \times w + \iota \times h + w \times h) + 2 \times (w \times h)$, $S_2 < S_{21} + S_{22}$, $\varepsilon_2 = S_{21} + S_{22}/V_2$, S_2 increase, V_2 is constant, ε_2 increase.

(1.5 mm used in our study), although the ratio was less than 0.16 and Fickian diffusion could be used to analysis the sorption and desorption data, the surface area or the specific surface area increases with the reducing dimensions (length and width). Schematic illustration is shown in Figure 6. Four specimens with the length being 5, 15, 30, and 60 mm are used to investigate respectively. After plotting sorption amounts against the specific surface area of different dimensions samples, the linear tendency was observed in Figure 7. This observation suggests a significant difference between filmy and thick planar polymer samples in the swelling process. For filmy specimens (usually 0.5 mm, even less), it is believed that one-dimensional diffusion along the thickness ι of the polymer samples exists and the variation of surface area, or specific surface area, owing to changing dimensions (length and width) could be negligible. However, as to thick samples (1.5 mm in this study), with reducing the dimensions, the sur-
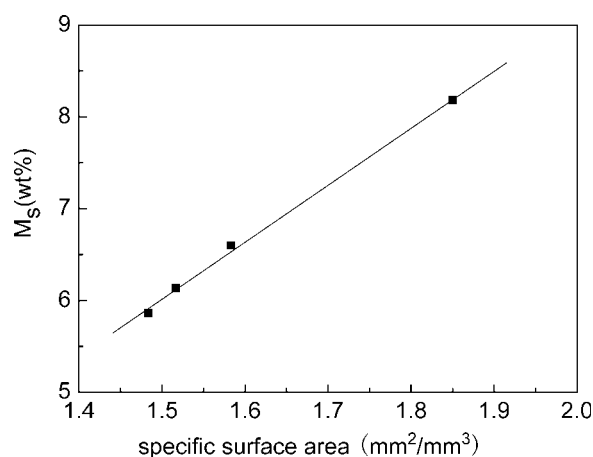

Figure 7 Plot of the specific surface area against M_s of different dimensions of samples.

face area and the specific surface area will increase, which leads to the sorption amount rise.

CONCLUSIONS

In this work, we studied the sorption and swelling process of CO_2 in PC specimens at temperatures ranged from 40 to 80°C and pressures ranged from 7 to 20 MPa. The interesting crossover phenomenon in the sorption isotherm was observed and the change of mass transfer mechanism is suggested. The diffusivities both sorption and desorption processes were determined according to the gravimetric method. It was found that the sorption diffusivities increased with the rise of temperature but desorption diffusivities showed an opposite trend. Moreover, the linear relationship of sorption amount with specific surface area of the thick polymer samples has also been discussed in this study, which is verified by experimental data.

References

1. Watkins, J. J.; McCarthy, T. J. Macromolecules 1994, 27, 4845.
2. Boggess, R. K. J Appl Polym Sci 1997, 64, 1309.
3. Nazem, N.; Taylor, L. T.; Rubira, A. F. J Supercrit Fluids 2003, 23, 43.
4. Schnitzler, J. V.; Eggers, R. J Supercrit Fluids 1998, 16, 81.
5. Tang, Q. Q.; Yang, B.; Zhao, Y. P. J Macromol Sci: Part B 2007, 46, 275.
6. Aubert, J. H. J Supercrit Fluids 1998, 11, 163.
7. Zhang, Y.; Gangwani, K. K.; Lemert, R. M. J Supercrit Fluids 1997, 11, 115.
8. Sato, Y.; Takikawa, T.; Takishima, S.; Masuoka, H. J Supercrit Fluids 2001, 19, 187.
9. Nikitin, L. N. J Supercrit Fluids 2003, 26, 263.
10. Royer, J. R. J Supercrit Fluids 1999, 32, 8965.
11. Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kuning, F. W. J Appl Polym Sci 1992, 46, 231.
12. Berens, A. R.; Huvard, G. S. In ACS Symposium Series, Washington, DC, 1989, Vol. 106, Chapter 14.
13. Muth, O.; Hirth, T.; Vogel, H. J Supercrit Fluids 2001, 19, 299.
14. Arora, K. A.; Lesser, A. J.; McCarthy, T. J. Macromolecules 1998, 31, 4614.
15. Tang, M.; Huang, Y. C.; Chen, Y. P. J Appl Polym Sci 2004, 94, 474.
16. Tang, M.; Du, T. B.; Chen, Y. P. J Supercrit Fluids 2004, 28, 207.
17. Chang, S. H.; Park, S. C.; Shim, J. J. J Supercritical Supercrit Fluids 1998, 13, 113.
18. Wissinger, R. G.; Paulaitis, M. E. J Poym Sci B: Polym Phys 1987, 26, 2497.
19. Crank, J.; Park, G. S. In Diffusion in Polymers; Academic Press, London, 1968.
20. Berens, A. R. In ACS Symposium Series; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990; Vol. 423, p 92.
21. Lockemann, C. A.; Riede, Th.; Magin, P. In Proceeding of the 3rd International Symposium on High Pressure Chemical Engineering; von Rohr, Ph. R.; Trepp, Ch., Eds.; 1996; p 547.
22. Wong, B.; Zhang, Z. Y.; Handa, Y. P. J Polym Sci B: Polym Phys 2025 1998, 12.