Solubilities and diffusion coefficients of carbon dioxide and nitrogen in polypropylene, high-density polyethylene, and polystyrene under high pressures and temperatures

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Abstract

Solubilities of carbon dioxide and nitrogen in molten polypropylene (PP) and high-density polyethylene (HDPE) were measured at temperatures 433.2, 453.2, and 473.2 K and pressures up to 17 MPa. The solubilities increased almost linearly with pressure. While the solubilities of carbon dioxide decreased with increasing temperature, those of nitrogen increased in the temperature range examined. The solubility of nitrogen in glassy polystyrene (PS) was measured at 313.2, 333.2, and 353.2 K and pressures up to 17 MPa. Temperature dependence on the solubility in this system was distinctive, where minimal solubility of 310 $cm^3(STP)/(kg$ MPa) was observed around 350 K, by taking into account of our previous data above 373.2 K. Henry's constants, K_P, and their temperature dependence were determined from the experimental data. A linear relationship between $\ln(1/K_P)$ and $(T_C/T)^2$ was obtained for each system. Diffusion coefficients of gases in molten polymers were determined for the nitrogen + PP, nitrogen + HDPE, and carbon dioxide + HDPE systems at 453.2 K. The diffusion coefficients showed weak concentration dependence and had an order of magnitude of 10^{-9} m^2/s. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymeric foams are widely used as heat insulators, food trays, and support materials. because of their many advantageous characteristics such as low thermal conductivity, light weight, and high

impact strength. CFC-11 and CFC-12 had been used as physical blowing agents for these type of industrial foaming processes. Since the production of these gases has been prohibited, new environmentally benign alternative blowing agents such as carbon dioxide and nitrogen, are being considered. However, solubility and diffusivity of these gases in polymers necessary for optimal design of the foaming process are lacking.

Solubility and diffusivity data of gases in molten or thermally softened polymer systems were investigated by several authors. Newitt and Weale [1] studied the solution and diffusion of hydrogen, nitrogen, carbon dioxide, and ethylene in polystyrene (PS) at temperatures up to 190°C and pressure range of 8–30 MPa. Lundberg et al. [2–5] considered the systems nitrogen + low-density polyethylene (LDPE), methane + LDPE, methane + high-density polyethylene (HDPE), methane + PS, and methane + polyisobutylene at temperatures from 100 to 227°C and pressures up to 67.8 MPa. Durrill and Griskey [6,7] investigated a number of gas + polymer systems at temperature of 188.3°C. Lee and Flumerfelt [8] reported the solubility of nitrogen in LDPE at 394–450 K and 1–12.6 MPa. Wang et al. [9] investigated the solubility of carbon dioxide in poly(vinyl acetate) and poly(butyl methacrylate) at 313–353 K and up to 10 MPa by using a piezoelectric quartz sorption method. For highly soluble and dense gases, the quantity of dissolved gas can be appreciable and usually leads to polymer swelling. The solubility of the gas measured by using a volumetric method should be corrected by using the amount of gas existing in the swelling volume. For a gravimetric method, the gas solubility should be corrected by considering gas buoyancy acting on the polymer's volume. Kamiya et al. [10] carefully measured the polymer swelling and exactly determined the solubility of nitrogen, argon, and carbon dioxide in poly(vinyl benzoate) at 25–65°C and up to 5 MPa. Sato et al. [11] reported on the solubility of nitrogen and carbon dioxide in PS at 373–453 K and 2–20 MPa, and used the Sanchez and Lacombe equation of state (S–L EOS) to correct for polymer swelling.

In many gas + polymer systems, the solubility increases almost linearly with pressure. Therefore, Henry's constant, K_P, is an effective property to estimate gas solubilities even at high pressures. Several correlations have been proposed for the estimation of Henry's constant in molten polymers. For example, Stern et al. [12] proposed a linear relationship between $\log(1/K_P)$ of Henry's constant and $(T_C/T)^2$ for polyethylene (PE). Maloney and Prausnitz [13] proposed an improved correlation of K_P for LDPE based on the Flory–Huggins theory. Stiel and coworkers [14,15] developed generalized correlations for PS, LDPE, and polyisobutylene, respectively, based on the approach of Stern et al. [12]. Zhong and Masuoka [16] proposed improved correlations for polypropylene (PP), poly(dimethyl siloxane), and PE. Although the above methods can predict Henry's constant for organic vapors, those cannot be applied to gases which have low critical temperatures such as nitrogen and hydrogen, because these substances tend to show a so-called ''reverse solubility'' at high temperature, where solubility increases with temperature. Therefore, investigation of the solubility of gases which have low critical temperatures as well as other gases that could be used as suitable blowing agents is needed.

The purpose of this work is to study the solubility and diffusion properties of gas + polymer systems at elevated pressures and temperatures. The solubilities of carbon dioxide and nitrogen in molten PP and HDPE were measured at temperatures from 433.2 K to 473.2 K and pressures up to 17 MPa. Diffusion coefficients of nitrogen in PP and HDPE and that of carbon dioxide in HDPE were obtained at temperature of 453.2 K. Solubility of nitrogen in glassy PS was measured at temperatures from 313.2 K to 353.2 K and pressures up to 17 MPa.

2. Experimental

PP ($\overline{M}_w = 4.51 \times 10^5$, $\overline{M}_w/\overline{M}_n = 7.05$, $T_m = 431$ K) and HDPE ($\overline{M}_w = 1.11 \times 10^5$, $\overline{M}_w/\overline{M}_n = 13.6$, $T_m = 402$ K) were supplied by Nippon Petrochemicals, (Kawasaki). PP ($\overline{M}_w = 2.20 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.23$) used in the solubility measurements with carbon dioxide at 453.2 K was supplied by Idemitsu Petrochemical, (Ichihara). Polystyrene ($\overline{M}_w = 1.87 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.67$, $T_g = 373.6$ K) was obtained by Mitsui Toatsu Chemicals, (Yokohama). Carbon dioxide ($> 99.5\%$ purity) was obtained from Iwatani Industrial Gases (Hiroshima). Nitrogen ($> 99.8\%$ purity) was purchased from Chugoku Sanso (Hiroshima). All chemicals were used as received.

The solubilities were measured by using a pressure decay method with three sorption cells. The details of the experimental apparatus and procedures have been described elsewhere [11]. The volume of the polymers under high temperatures and high pressures that is required to determine solubility accurately was obtained by *PVT* measurements [17]. Correction to the polymer volume change due to dissolution of gases was predicted using the S–L EOS [18,19] as discussed later. Maximum value of the predicted volume change was 16 vol.% for CO_2 and was 1.3% for nitrogen. Measurement of swollen molten polymer volume turned out to be difficult, and therefore it was predicted using the S–L EOS.

Diffusion coefficients of gases in polymers were determined by measuring pressure vs. time curves during gas dissolution. A polymer disk of about $\phi48$ in diameter and 4 mm in thickness was placed in a stainless steel Petri dish of $\phi48 \times$ depth 8 mm in the sorption cell to satisfy diffusion conditions described below. Assuming that the diffusion in a plane sheet can be expressed by Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} \right) \tag{1}$$

with boundary and initial conditions:

B.C.1: $\quad C = Cs(P(t))$ at $x = 0$, $t > 0$ $\tag{2}$

B.C.2: $\quad \partial C/\partial x = 0$ at $x = L$, $t > 0$ $\tag{3}$

I.C.: $\quad C = C_{\text{Initial}}$ at $x = 0 \sim L$, $t = 0$ $\tag{4}$

where C is concentration of gas in polymer, t is time, L is thickness of polymer, D is the diffusion coefficient of gas. The material balance of gas is as follows:

$$\frac{\partial n_L}{\partial t} + \frac{\partial n_G}{\partial t} = A\int_0^L \frac{\partial C}{\partial t}dx + \frac{V_G}{RT}\frac{\partial(P/Z)}{\partial t} = 0 \tag{5}$$

$$n_L + n_G = n_L^0 + n_G^0 \tag{6}$$

where n_L and n_G are amount of gas at t in the liquid and gas phases, respectively, n_L^0 and n_G^0 are initial amounts of gas in the liquid and gas phases, V_G is volume of gas phase, A is the area of gas–polymer interface, and Z is the gas compressibility factor obtained from Jacobsen [20] and Angus et al. [21] for nitrogen and carbon dioxide, respectively.

Thicknesses of the polymer and diffusion coefficient of gas were assumed to be constant during each stepwise pressure change, which was below 3 MPa in most cases. The thickness at the middle of initial and final pressures was estimated from mass of the polymer, *PVT* data, swelling estimated by using the S–L EOS, and inner diameter of the Petri dish. In each stepwise pressure change, the thickness change was small and was less than 3%.

3. Results and discussion

3.1. Solubility

In Fig. 1, a relationship between pressure decay and elapsed time due to dissolution of N_2 in HDPE at 453.2 K is shown as an example. When the gas is introduced to the sorption cell, the pressure changes rapidly from 0 to about 2.83 MPa and then decreases slowly until final pressure (2.735 MPa) due to the dissolution. The pressure decay is obtained from a difference in pressure between calculated value from the cell and the polymer volumes and measured one. The solubility and the diffusion coefficient are obtained from the pressure decay data.

The measured solubilities of carbon dioxide and nitrogen in PP and HDPE at 433.2, 453.2 and 473.2 K are listed in Tables 1 and 2 and plotted in Figs. 2 and 3.

The solubilities of both the gases increased almost linearly with pressure, and those of carbon dioxide decreased with an increase in temperature. The solubility of nitrogen, however, increased with temperature. The solubilities of carbon dioxide in lower molecular wight PP ($\overline{M}_w = 2.20 \times 10^5$) were in excellent agreement with those of higher molecular weight PP ($\overline{M}_w = 4.51 \times 10^5$). Molecular weight dependence on solubility was found to be negligible for the ranges studied in this work.

The solubility of nitrogen in PS at 313.2, 333.2, and 353.2 K is also listed in Table 1 and plotted in Fig. 4. In our experiments, the solubility decreased with an increase in temperature. By contrast, the
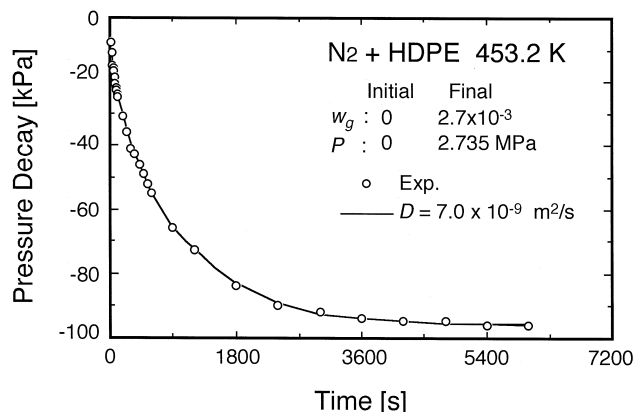

Fig. 1. Relationship between pressure decay and time due to dissolution of gas.

Table 1
Solubility of nitrogen in polypropylene, high-density polyethylene, and polystyrene

Polypropylene		High-density polyethylene		Polystyrene	
Pressure (MPa)	Solubility $\times 10^3$ (g-gas/g-polym.)	Pressure (MPa)	Solubility $\times 10^3$ (g-gas/g-polym.)	Pressure (MPa)	Solubility $\times 10^3$ (g-gas/g-polym.)
453.2 K		*433.2 K*		*313.2 K*	
4.233	4.39	2.541	2.58	4.934	2.20
7.115	7.58	4.278	4.32	8.378	4.40
9.031	9.74	5.463	5.52	10.771	5.95
10.898	11.87	7.935	7.79	12.450	6.31
12.699	13.70	10.089	9.54	16.136	8.25
14.938	17.04	11.555	11.57		
17.999	19.28	14.629	14.65		
473.2 K		*453.2 K*		*333.2 K*	
4.013	4.52	3.743	3.72	5.037	1.82
6.726	8.55	6.330	6.56	6.149	2.15
8.545	10.59	8.192	8.49	7.882	3.06
9.878	12.21	9.401	9.66	9.868	3.56
11.998	15.14	11.809	12.61	11.034	4.28
14.819	19.99			11.674	4.30
17.838	22.49			13.457	4.86
				16.542	6.34
		473.2 K		*353.2 K*	
		2.818	2.88	2.989	1.06
		4.704	5.19	3.645	1.31
		5.958	6.70	5.053	1.88
		6.792	7.60	5.295	1.80
		8.386	9.85	6.476	2.33
		10.695	11.84	7.945	2.96
		12.682	14.94	9.042	3.09
		15.214	17.24	9.535	3.40
				11.660	3.97
				11.770	4.19
				14.071	4.99
				17.521	6.31

temperature dependence of nitrogen in PS in the rubbery state at 373–453 K showed the positive dependence which had been reported by our group [11].

In this work, the experimental solubility data were correlated by using the S–L EOS [18,19]:

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}\left[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}\right] \tag{7}$$

$$\tilde{P} = P/P^*, \quad \tilde{\rho} = \rho/\rho^*, \quad \tilde{T} = T/T^*, \quad \text{and} \quad r = MP^*/RT^*\rho^* \tag{8}$$

The values of the characteristic parameters, P^*, ρ^*, and T^* of the S–L EOS are listed in Table 3.

Table 2
Solubility of carbon dioxide in polypropylene and high-density polyethylene

Polypropylene		High-density polyethylene	
Pressure (MPa)	Solubility $\times 10^2$ (g-gas/g-polym.)	Pressure (MPa)	Solubility $\times 10^2$ (g-gas/g-polym.)
433.2 K			
7.400	5.03	6.936	4.07
11.803	9.48	11.066	7.47
14.558	12.53	13.644	9.75
16.355	14.51	15.286	11.42
17.529	15.87	16.347	12.30
		17.453	13.20
453.2 K			
5.419	3.23	7.055	3.50
7.160	4.41	11.326	6.71
8.797	5.94	14.013	8.90
10.953	7.87	15.762	10.05
11.558	8.46	16.896	10.94
12.352	9.17	18.123	11.98
14.342	11.19		
14.889	11.58		
16.170	13.06		
17.376	14.18		
7.083[a]	4.17		
11.443[a]	7.98		
14.212[a]	11.10		
16.037[a]	13.24		
17.242[a]	14.27		
473.2 K			
6.204	3.02	6.608	3.19
10.113	6.01	10.731	5.51
12.637	8.30	13.344	7.46
14.296	9.68	15.034	8.73
15.397	10.86	17.019	10.33

[a] $\overline{M}w = 2.20 \times 10^5$, other data are for $\overline{M}w = 4.51 \times 10^5$.

The mixing rules of the S–L EOS are shown by Eqs. (9)–(14):

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \qquad (9)$$

$$P_{ij}^* = \left(1 - k_{ij}\right)\left(P_i^* P_j^*\right)^{0.5} \qquad (10)$$

$$T^* = P^* \sum_i \left(\phi_i^0 T_i^* / P_i^*\right) \qquad (11)$$

$$1/r = \sum_i \left(\phi_i^0 / r_i^0\right) \qquad (12)$$

$$\phi_i^0 = (\phi_i P_i^* / T_i^*) / \sum_j (\phi_j P_j^* / T_j^*) \tag{13}$$

$$\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*) \tag{14}$$

where T_i^*, P_i^*, ρ_i^*, and r_i^0 are characteristic parameters of component i in the pure state. In the calculation of solubilities, it was assumed that the polymer was monodisperse and that it did not dissolve in the gas phase.

The binary interaction parameter, k_{ij}, in Eq. (10) was determined so as to minimize the relative deviations between experimental and calculated solubilities at each temperature and the results are shown in Figs. 2–4. The solid lines in these figures show the correlation results. For carbon dioxide systems, concentration dependent k_{ij} defined in Eq. (15) was introduced, because correlated solubilities with fixed k_{ij} showed large deviations.

$$k_{ij} = a_{ij} + b_{ij} w_g \tag{15}$$

The correlation between the experimental solubilities and the S–L EOS with the above mixing rules and Eq. (15) was satisfactory. Our studies indicate that k_{12} can also be treated as temperature-dependent in these systems.

The solubilities of carbon dioxide and nitrogen in three polymers at 453.2 K are compared in Figs. 5 and 6, along with S–L EOS calculations. Experimental data of PS from previous work [11] are also shown. The slope of the calculated isotherms for carbon dioxide increased slightly with pressure, whereas those for nitrogen decreased slightly with pressure. Both gases exhibited their highest solubility in PP and their lowest solubility in PS. The solubilities of carbon dioxide in PP and HDPE were about 2 and 1.7 times greater than those in PS, respectively. For nitrogen, amounts of sorbed gas in these polymers were about 1.7 and 1.6 times greater than those in PS. The solubilities of nitrogen in PP and HDPE were similar.

As mentioned in the Section 1, it is of interest to industry to replace fluorocarbons being used as physical blowing agents in foaming processes. Consequently, we compared solubilities of fluorocarbons (HCFC-22, CFC-12, and CFC-11) in PS, HDPE, and PP reported by Gorski et al. [26] with those
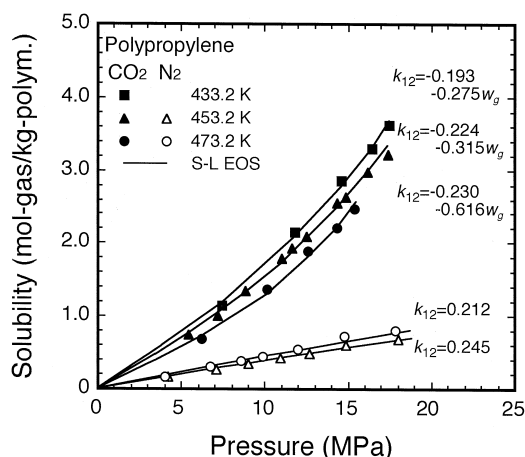
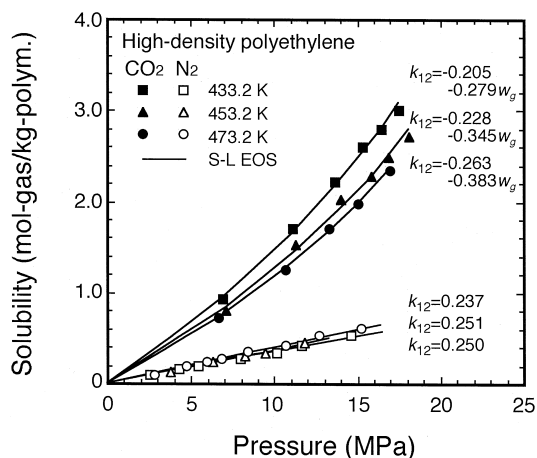Fig. 2. Solubility of carbon dioxide and nitrogen in polypropylene.

Fig. 3. Solubility of carbon dioxide and nitrogen in high-density polyethylene.

of carbon dioxide. The comparison was carried out at temperature of 453.2 K and pressure of 1 MPa and the results are listed in Table 4. Solubilities of CO_2 corresponded to about half those of HCFC-22, and were from one-half to one-third of those of CFC-12. CO_2 solubilities were lower than those of CFC-11 by factors of 10, 26, and 11 for PS, HDPE, and PP, respectively.

3.2. Henry's constant

Henry's constants, K_P [kg MPa cm^{-3}(STP)], were evaluated using the S–L EOS. A linear expression between $\ln(1/K_P)$ and $(T_C/T)^2$ proposed by Stern et al. [12] was used to correlate the data. The critical temperatures, T_C, were obtained from Reid et al. [27].
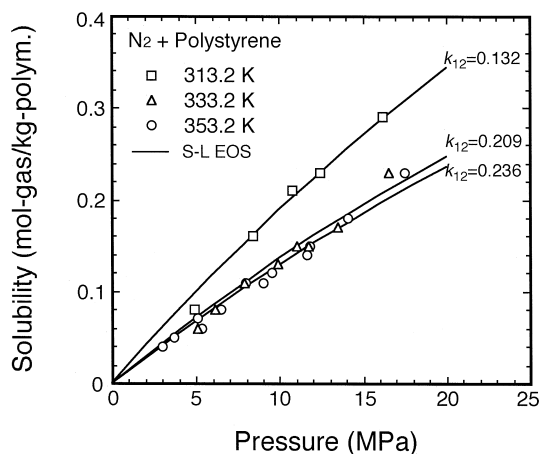

Fig. 4. Solubility of nitrogen in polystyrene.

Table 3
Characteristic parameters for Sanchez–Lacombe EOS

Substance	P^* (MPa)	ρ^* (kg/m^3)	T^* (K)	Ref.
Nitrogen	103.6	803.4	159.0	[22]
Carbon dioxide	720.3	1580	$208.9 + 0.459T - 7.56 \times 10^{-4}T^2$	[23]
Polypropylene	297.5	882.8	692.0	[24]
High-density polyethylene	288.7	867.0	736.0	[25]
Polystyrene	387.0	1108	739.9	[11]

Henry's constants for carbon dioxide in PP, PE, and PS are compared with literature values in Fig. 7. In Fig. 7, PE was not distinguished by its density, because solubility will not depend on density of PE. Stiel et al. [15] also mentioned that Henry's constant correlation equation for LDPE was applicable for HDPE. Henry's constant in HDPE obtained in this work extrapolated to low temperature was in good agreement with that of LDPE obtained by a chromatographic method, but the Henry's constant at higher temperatures showed deviation with the literature [28]. Polymer difference (LDPE and HDPE) or less reliable at higher temperature for the chromatographic method was seemed as the deviation. Contrary to this work, $1/K_P$ of PE reported by Durrill and Griskey [6] was higher than that of PP.

Henry's constants for nitrogen in PP, PE, and PS are compared with literature values in Fig. 8. Henry's constants obtained in this work were in good agreement with those of Durrill and Griskey [6] for PP and PE, of Lundberg et al. [5] for LDPE, and of Atkinson [29] for LDPE. Although $1/K_P$ for LDPE reported by Lee and Flumerfelt [8] showed a similar slope to other data, the values were much larger than those of other researchers.

Our data for PP and HDPE are very similar, which may be due to the similar structure of the two polymers. Zhong and Masuoka [16] reported a similar result in the correlation of K_P for organic vapors in PP and PE.
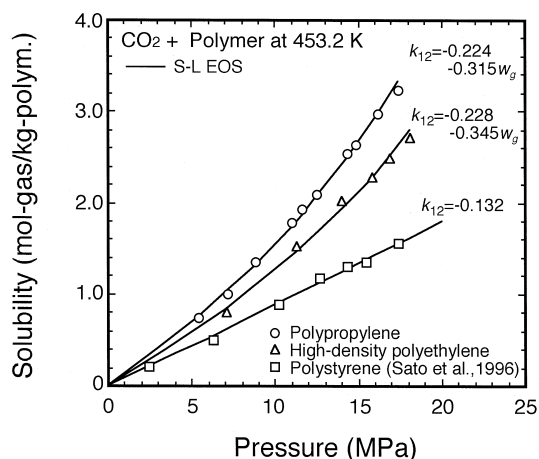

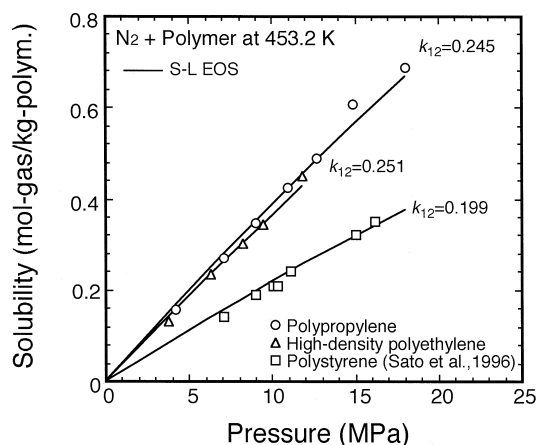Fig. 5. Solubility of carbon dioxide in polymers at 453.2 K.

Fig. 6. Solubility of nitrogen in polymers at 453.2 K.

Sato et al. [11] formulated correlation equations for nitrogen and carbon dioxide by using a least-squares method to determine a linear relationship between $\ln(1/K_P)$ and $(T_C/T)^2$ for PS as follows:

For CO_2 + PS,

$$\ln(1/K_P) = 6.498 + 2.380(T_C/T)^2 \tag{16}$$

For N_2 + PS,

$$\ln(1/K_P) = 6.970 - 9.587(T_C/T)^2 \tag{17}$$

In the present work, similar equations for nitrogen were fitted to our data for HDPE and PP:

For CO_2 + HDPE,

$$\ln(1/K_P) = 6.571 + 2.764(T_C/T)^2 \tag{18}$$

For CO_2 + PP,

$$\ln(1/K_P) = 6.255 + 3.706(T_C/T)^2 \tag{19}$$

For N_2 + HDPE,

$$\ln(1/K_P) = 7.395 - 7.905(T_C/T)^2 \tag{20}$$

For N_2 + PP,

$$\ln(1/K_P) = 8.407 - 20.39(T_C/T)^2 \tag{21}$$

Table 4
Comparison of solubility of gases in PS, HDPE, and PP at temperature of 453.2 K and pressure of 1 MPa

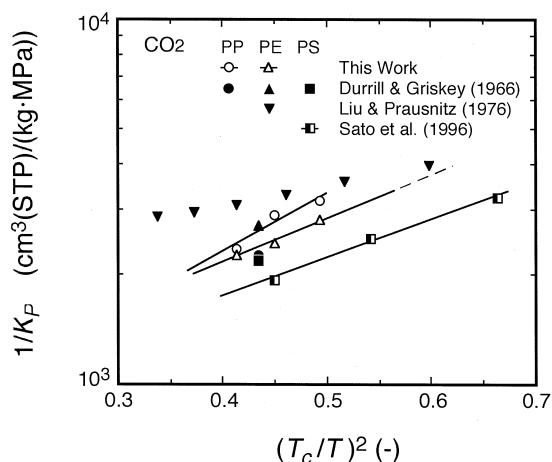| | Solubility (mol-gas/kg-polym.) | | | |
	CFC-11[a]	CFC-12[a]	HCFC-22[a]	CO_2
PS	0.87	0.20	0.17	0.09
HDPE	3.13	0.35	0.25	0.12
PP	1.53	0.44	0.30	0.14

[a]Gorski et al. [26].

Fig. 7. Correlation of Henry's constants for carbon dioxide in polypropylene, polyethylene, and polystyrene.

The fitted results are shown in Figs. 7 and 8 by solid lines. For nitrogen + PP system, the amount of experimental data were not sufficient to determine the temperature dependence of the Henry's constant.

Henry's constants for nitrogen in PS are shown in Fig. 8 by a smoothed line. The $1/K_P$ for PS exhibited a distinct minimum at a temperature of about 350 K. Burgess et al. [30] reported a similar tendency for a series of noble gases in poly(methylacrylate) at its glass transition temperature. The temperature of minimal solubility in this work is lower than its glass transition temperature of PS (372.6 K). Burgess et al. [30] explained that the minimum solubility was caused by a hole filling contribution to gas sorption. However, the hole filling contribution probably varies depending on the gas, due to differences in gas–polymer interactions and molecular sizes of the gas and the holes. Kumar and Suh [31] determined the Henry's constant for nitrogen in polystyrene at temperature
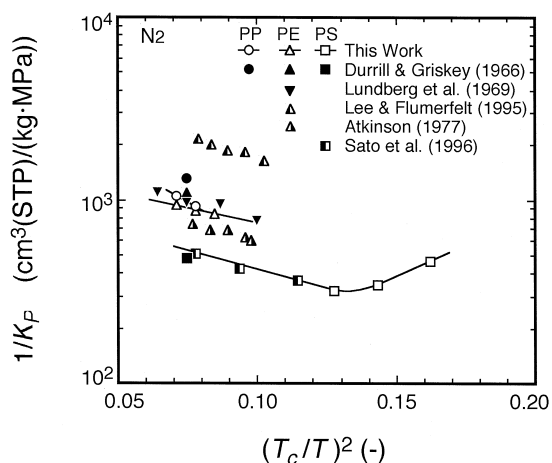

Fig. 8. Correlation of Henry's constants for nitrogen in polypropylene, polyethylene, and polystyrene.

between 20 and 115°C and only mentioned that $1/K_P$ decreased with rising temperature. Their data are scattered, but their data seem to exhibit a minimum in solubility between 80 and 100°C.

Temperature dependence of Henry's constant, K_P, is given by [32,33]:

$$\left(\frac{\partial \ln K_P^{-1}}{\partial T}\right)_P = \frac{\Delta \bar{h}_g}{RT^2} \tag{22}$$

where

$$\Delta \bar{h}_g \equiv \bar{h}_g^L - h_g^G = \left(h_g^L - h_g^G\right) + \left(\bar{h}_g^L - h_g^L\right). \tag{23}$$

The first term on the right-hand side of Eq. (23) is the enthalpy of condensation of the pure gas and, since the enthalpy of a liquid is generally lower than that of a gas at the same temperature, this quantity can be expected to be negative. The second term is the partial enthalpy of mixing for the liquid solute and its quantity tends to be positive. Therefore, condensation of gas probably dominates at lower temperatures whereas mixing of the solute–solvent probably dominates at the higher temperatures for this system. For the case of carbon dioxide systems, the temperature dependence of the Henry's constant is most likely dominated by condensation of gas. If the experimental temperature is extended to lower and higher ranges, the minimum in solubility can also be seen at lower temperatures for other nitrogen systems and at higher temperatures for carbon dioxide systems.

3.3. Diffusion coefficient

The solid line shown in Fig. 1 denotes the fitting result of diffusion equation with $D = 7.0 \times 10^{-9}$. Diffusion coefficients of $N_2 + PP$, $N_2 + HDPE$, and $CO_2 + HDPE$ at 453.2 K are shown in Fig. 9. Since thermodynamic and transport properties including the diffusion coefficient in liquid phase are
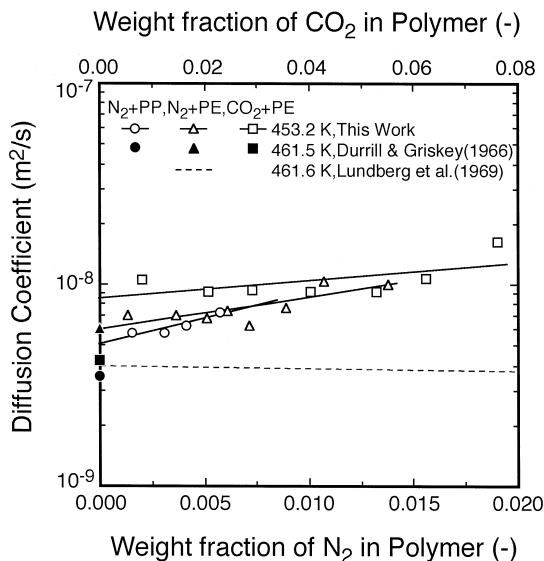

Fig. 9. Diffusion coefficients of $N_2 + PP$, $N_2 + HDPE$, and $CO_2 + HDPE$.

not usually sensitive to pressure, pressure dependence of the diffusion coefficient is neglected. The diffusion coefficients are listed as functions of initial and final pressures and average weight fraction of gas in polymer at each pressure in Table 5. These diffusion coefficients showed weak concentration dependence. In this work, the concentration dependence was fitted as follows:

For N_2 + HDPE:

$$\log D = -8.224 + 15.54 w_g \tag{24}$$

For N_2 + PP:

$$\log D = -8.298 + 25.56 w_g \tag{25}$$

For CO_2 + HDPE:

$$\log D = -8.076 + 2.26 w_g \tag{26}$$

where D is the diffusion coefficient $[m^2/s]$ and w_g is the weight fraction of gases. The diffusion coefficient extrapolated to zero weight fraction for nitrogen + HDPE system was in excellent agreement with Durrill and Griskey [6]. Although literature data were measured at slightly higher temperatures, all data had the same order of magnitude of 10^{-9} m^2/s. Contrary to Durrill and Griskey's data, our data for nitrogen in HDPE was lower than that of carbon dioxide.

Table 5
Experimental data of diffusion coefficient at temperature of 453.2 K

Average weight fraction of gas in polymer $\times 10^3$ (−)	Pressure (MPa)		Diffusion Coefficient $\times 10^9$ (m^2/s)
	Initial	Final	
N_2 + HDPE			
1.4	0	2.735	7.0
3.6	2.735	4.553	7.0
5.1	4.553	5.754	6.8
6.1	5.754	6.544	7.4
7.1	6.544	8.038	6.3
8.9	8.038	10.44	7.7
11	10.44	12.02	10.3
14	12.02	15.03	10.1
N_2 + PP			
1.5	0	3.264	5.7
3.1	3.264	3.283	5.7
4.1	3.283	5.346	6.2
5.7	5.346	6.614	7.3
CO_2 + HDPE			
8.2	0	3.005	10.6
21	3.005	4.925	9.2
29	4.925	6.164	9.2
40	6.164	8.515	9.1
53	8.515	10.97	9.1
62	10.97	12.53	10.7
76	12.53	15.43	16.3

4. Conclusion

Solubilities of carbon dioxide and nitrogen in molten PP and HDPE were measured at temperatures from 433 K to 473 K and pressures up to 17 MPa. The solubility of carbon dioxide decreased with increasing temperature, whereas that of nitrogen increased with temperature. The solubilities of both the gases in PS, HDPE, and PP increased in that order. Solubilities of carbon dioxide in PS, HDPE, and PP were not significantly lower than currently used fluorocarbon blowing agents.

Diffusion coefficients of nitrogen in PP and HDPE and those of carbon dioxide in HDPE at 453.2 K showed weak concentration dependence and the values had the same order of magnitude of 10^{-9} m^2/s.

Solubility of nitrogen in glassy PS was measured at temperatures from 313 K to 353 K and pressures up to 17 MPa. The solubility of nitrogen in PS exhibited a distinct minimum at about 350 K, when considering previous data [11] above 373.2 K.

5. List of symbols

Parameters

A	area of gas–polymer interface	m^2
a_{ij}	interaction parameter defined in Eq. (15)	–
b_{ij}	interaction parameter defined in Eq. (15)	–
C	concentration of gas	mol/m^3
D	diffusion coefficient of gas	m^2/s
h	enthalpy of gas	J/mol
$\bar{h}$	partial molar enthalpy of gas	J/mol
K_P	Henry's constant	kg MPa/cm^3(STP)
k_{ij}	interaction parameter defined in Eq. (10)	–
L	thickness of polymer	m
M	molar mass	kg/kmol
n	amount of gas	mol
n^0	amount of gas at initial state	mol
P	pressure	MPa
R	gas constant ($= 8.314$)	J/(mol K)
r	number of sites occupied by a molecule	–
T	temperature	K
T_g	glass transition temperature	K
T_m	melting point temperature	K
t	time	s
V_G	volume of gas phase	m^3
w	weight fraction	–
x	length from surface exposed to gas in polymer sheet	m
Z	compressibility factor	–

Greek letters

ϕ	segment fraction	–
ρ	density	kg/m^3

Subscripts

c	critical value
G	gas phase
g	gas
Initial	initial state
i, j	component
L	liquid phase

Superscripts

0	pure state
*	characteristic parameter
~	reduced value

Acknowledgements

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