Density Measurement of Polymer/CO$_2$ Single-Phase Solution at High Temperature and Pressure Using a Gravimetric Method

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ABSTRACT: The densities of two polymer/CO$_2$ single-phase solutions, poly(ethylene glycol) (PEG)/CO$_2$ and polyethylene (PE)/CO$_2$, were measured at temperatures higher than melting temperature of the polymer under CO$_2$ pressures in the range 0–15 MPa using a newly-proposed gravimetric method. A magnetic suspension balance (MSB) was used for the density measurement under the high pressure CO$_2$: A thin disc-shaped platinum plate was submerged in the considered polymer/CO$_2$ single-phase solution in the MSB high-pressure cell. The weight of the plate was measured while keeping CO$_2$ pressure and temperature in the sorption cell at a specified level. Since the buoyancy force exerted on the plate by the polymer/CO$_2$ solution reduced the apparent weight of the plate, the density of the polymer/CO$_2$ solution could be calculated by subtracting the true weight of the plate from its measured weight. Experimental results showed that the density of the PE/CO$_2$ solution increased with the increase of CO$_2$ pressure and the density of PEG/CO$_2$ solution decreased with the increase of CO$_2$ pressure. To differentiate the effect of CO$_2$ dissolution in polymer from that of mechanical pressure, the density of polymer/CO$_2$ solution was compared with the density of neat polymer under the given mechanical pressure, which was calculated using the Sanchez–Lacombe equation of state and Pressure–Volume–Temperature data of the polymer. The comparison could elucidate that the dissolution of CO$_2$ in polymer reduced density of both PEG/CO$_2$ and PE/CO$_2$ systems but the degree of CO$_2$ induced-density reduction was different between two polymer/CO$_2$ systems. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3060–3068, 2007

Key words: density; swelling; magnetic suspension balance; buoyancy effect; solubility; CO$_2$

INTRODUCTION

Several applications of supercritical carbon dioxide (scCO$_2$) are being explored in polymer processing, chemical separation, and nanoparticle production fields for developing the organic solvent-free material processing techniques and environmental benign processes. In polymeric foaming process, for example, scCO$_2$ is being utilized as an environmental benign foaming agent replacing the conventional chlorofluorocarbons, hydrofluorocarbon, and hydrocarbon foaming agents. When CO$_2$ is dissolved into polymer, several physical properties of polymer such as glass transition temperature, melting temperature, surface tension, and viscosity are changed depending on solubility of CO$_2$ into the polymer. There have been several studies on CO$_2$ solubility and diffusivity in polymer and associated change in polymer property.[1–7] Recently, Tomasko et al. made a comprehensive review on CO$_2$ solubility and diffu-

sivity in polymer, the effects of CO$_2$ dissolution on the polymer property, and their applications.[1]

Sorption and diffusion of CO$_2$ in polymer are fundamental transport phenomena for the CO$_2$-applications to polymer processing. The volumetric and gravimetric methods have been widely used to measure the solubility and diffusivity of CO$_2$ in polymer.[8–17] However, either gravimetric or volumetric method alone cannot measure the sorption phenomena in swelling polymers. In general, the method needs correction of the volume change, swelling, which are obtained either by direct experimental measurement or prediction using the equation of state for polymer. Several techniques of directly measuring polymer swelling have been described in literature. Among them, an *in situ* visual observation is the most popular scheme, where the length change in one or more dimensions is measured in the presence of high pressure CO$_2$.[12–17] Wissinger et al. measured the swelling of poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polystyrene (PS) in contact with CO$_2$ at temperature from ~306 to 338 K and pressure up to 10 MPa.[12] They used a cathetometer for measuring the length of the thin polymer films in a high pressure view cell and identified two distinct type of swelling and sorption

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isotherms. One is characterized by swelling and sorption that begin to level off at elevated pressures. The other is swelling and sorption that continue to increase with CO$_2$ pressure. Zhang et al. measured CO$_2$ sorption and swelling of PMMA, poly(vinyl pyridine), polyisoprene, and three block copolymers in the presence of CO$_2$ at 308 K and at the pressure up to 10 MPa[13]. They also used a cathetometer to directly measure the dimension of polymer samples in a high-pressure view cell. Royer et al.[14] observed CO$_2$ induced swellings of three poly (dimethylsiloxane) (PDMS) samples with different molecular weights in a view cell and found that the molecular weight did not affect the magnitude of swelling at 303, 323, and 343 K under pressures ranging from 0 to 27.6 MPa. Nikitin et al. used a visual observation cell to study the swelling of PS/CO$_2$ solutions at 335 K.[15] They observed the diffusion front of CO$_2$ in PS and calculated a diffusion coefficient. Rajendran et al.[16] and Bonavoglia et al.[17] also employed a direct visual observation method to measure polymer swelling in CO$_2$. Bonavoglia et al.[17] measured the swelling of PMMA, poly(tetrafluoroethylene), poly(vinylidene fluoride), and tetrafluoroethylene–perfluoromethylvinylether in CO$_2$ (5–23 MPa) at temperatures in the range (313–353 K). As can be seen, the visual observation scheme was a most widely used method to measure the polymer swelling. However, in the application of the method, polymer had to be pretreated carefully to release internal stresses and ensure the isotropic behavior. Furthermore, the measurement should be conducted at temperatures below glass transition temperature of polymer to keep an appropriate shape of the sample. Some researchers proposed nondirect measurement schemes, which combining both gravimetric and volumetric methods. Using so-called combined gravimetric-dynamic method, Keller et al.[18] studied the swelling of PC at temperature, 293 K, under pressures ranging from 0 to 6 MPa. They combined the gravimetric method with a dynamic method where the inertia of the polymer sample was determined by slow oscillations of a rotational pendulum or by the relaxation motion of a floating rotator. The dynamic method showed the same order of magnitude of polymer swelling as Wissinger and Paulatitis showed for the PC/CO$_2$ system.[12] Using a pressure-decay apparatus with a vibrating-wire force sensor, Hilic et al.[19] conducted simultaneous measurement of the solubility of nitrogen (N$_2$) at pressures up to 70 MPa and CO$_2$ at pressure up to 45 MPa in PS and the associated polymer swelling. The vibrating-wire sensor acted as a balance to weigh the polymer sample. They measured the swelling of PS with a precision of 0.5% at three isotherms from 313 to 353 K, which were below the glass transition temperature of PS and observed a significant change in

both solubility and swelling at temperature between 363 and 383 K. The most proposed methods of measuring polymer swelling required a specific shape or state of the polymeric material. There is few paper of swelling measurements of molten polymers or polymeric solution at temperatures higher than the glass transition temperature.

In this study, a new gravimetric method of directly measuring density of polymer/CO$_2$ solution at high temperature under pressurized CO$_2$ was developed using a magnetic suspension balance (MSB). The densities of polyethylene (PE) and poly (ethylene glycol) (PEG) were measured at temperatures higher than their melting temperatures in contact with different CO$_2$ pressures ranging from 0 to 15 MPa. By comparing experimental data with the density calculated by the equation of state and Pressure–Volume–Temperature data, the pure effect of CO$_2$ dissolution on the polymer density was evaluated.

EXPERIMENTAL

Materials

CO$_2$ 99.9% (Kyoto Teisan, Japan) in purity was used. PE (M_w = 4000) and PEG (M_w = 2000) were purchased from Aldrich Chem and Wako Pure Chem, Japan, respectively. The melting temperature of each polymer was measured by a differential scanning calorimeter (Pyris 1, Perkin–Elmer) at the scan rate of 10 K/min in N$_2$ atmosphere. The weight average molecular weight and the melting temperature of each polymer sample are shown in Table I.

Apparatus

Figure 1 shows a schematic diagram of the MSB (Rubotherm, German and BEL Japan, Osaka, Japan), which is often used for measuring solubility of CO$_2$ in molten polymer.[9,11,16] The measurement system consists of CO$_2$ cylinder (Kyoto Teisan, Japan), a syringe pump (Model 260D, ISCO), a microbalance (AT261, Mettler Toledo, Switzerland), and a sorption cell. As shown in Figure 2(a), in the sorption cell, a measuring load hook connects a sample to a so-called coupling unit. The coupling unit is composed of a permanent magnet, a position sensor, a load coupling and decoupling device, a titanium sinker,

TABLE I
Properties of polymers

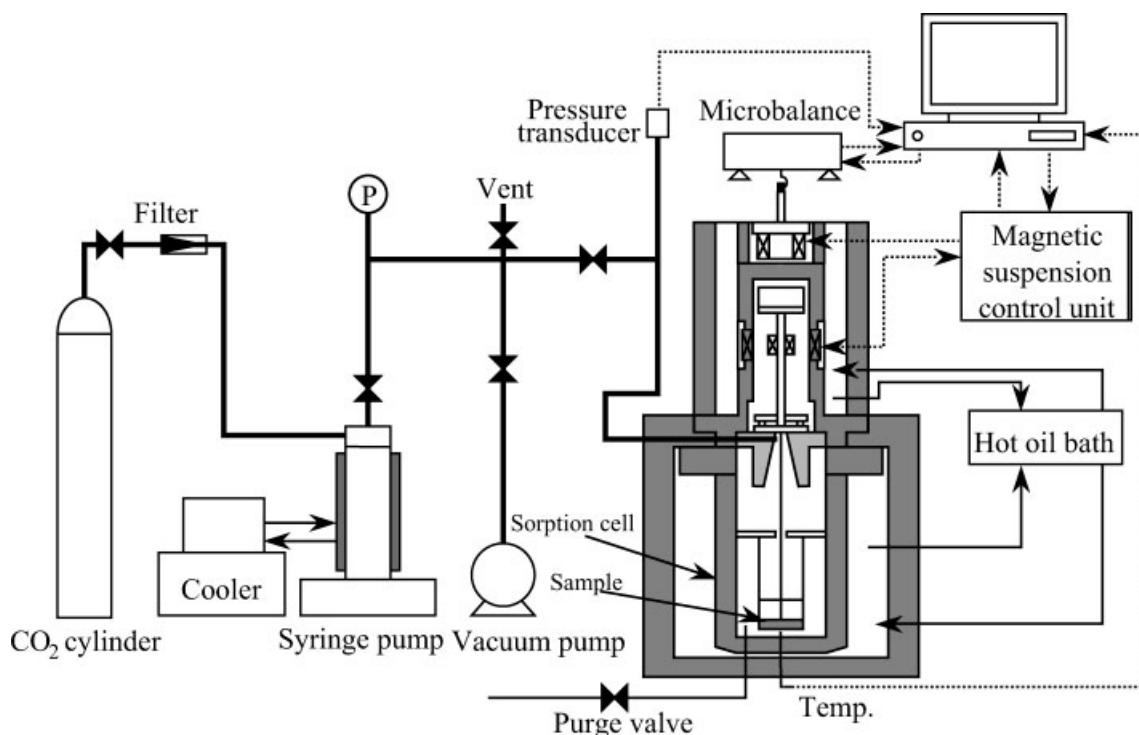|	$\overline{M_w}$ (g/mol)	T_m (K)
Polyethylene	4000	372.35
Polyethylene glycol	2000	324.35

Figure 1 Schematic diagram of the MSB.

an electromagnet, and an electronic control unit. The electromagnet is attached to an under-floor weighing hook of the balance and situated outside the sorption cell. The electronic control unit (magnetic suspension control unit) makes the suspension magnet in a freely suspended state. Using this magnetic suspension, the weight of the sample in the cell can be transmitted to the balance without any physical con-

tacts. In the sorption cell, CO_2-pressure can be built up to 35 MPa and temperature can be increased up to 523.2 K. The resolution and accuracy of microbalance are 0.01 mg and 0.002%, respectively.

Density measurement for polymer/CO_2 solutions was conducted in the following way: The polymer powders were loaded at an aluminum basket. The basket, 20 mm in diameter and 9 mm in depth, was
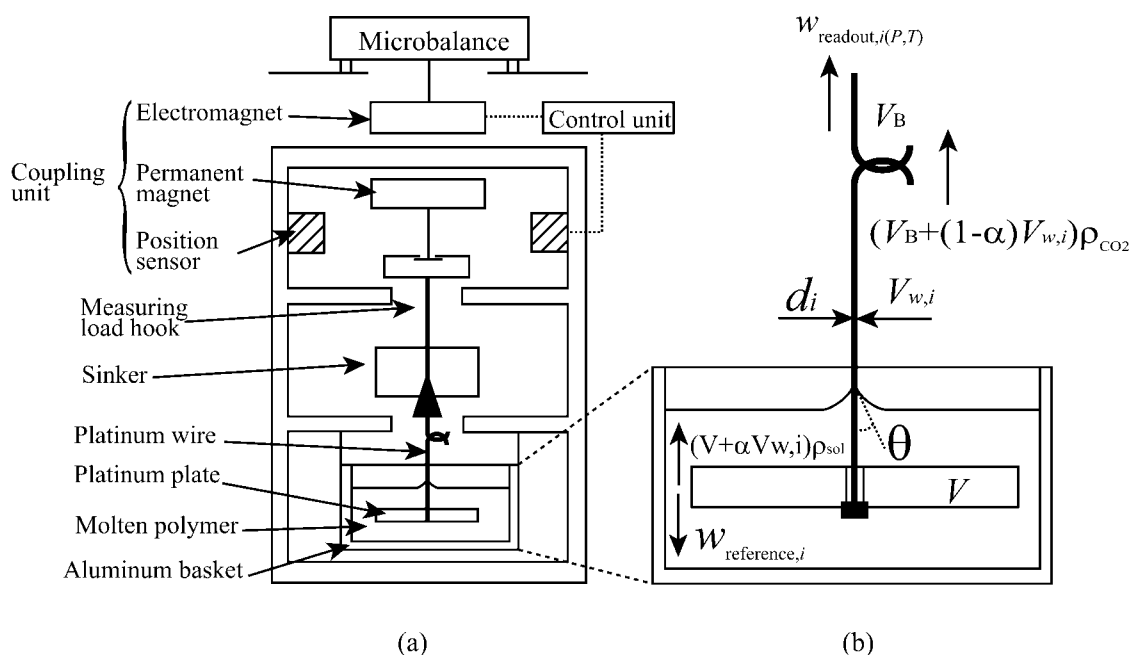

(a)   (b)

Figure 2 Details of MSB for density measurement.

fixed to the sorption cell wall to prevent chattering. A platinum plate was connected to the measuring load hook with a platinum wire and submerged into the sample polymer in the basket as illustrated in Figure 2(b). The sorption cell was heated up to a desired temperature, which was above the melting temperature of the polymer, to make the polymer sample be in molten state. After heating the sorption cell up to the desired temperature, the high pressure CO$_2$ was charged into the sorption cell to dissolve CO$_2$ into the molten polymer in the basket. Then, the weight of the platinum plate submerged in the polymer/CO$_2$ solution was measured.

The balance was operated in three positions: In position ''0,'' the coupling and decoupling device decouples the titanium sinker, the measuring load hook and the plate from the coupling unit. Only coupling unit is lifted while the titanium sinker, the measuring load hook and the plate are at rest. Then zero point is adjusted. In position ''1,'' the device connects the coupling unit to the measuring load hook and plate. The load hook and plate are lifted and weighed while the titanium sinker is at rest. In position ''2,'' the load hook, the plate, and the titanium sinker are lifted and weighed. From the measurements in position ''0,'' ''1,'' and ''2,'' the apparent weights of the plate and the sinker can be calculated.

Principle of measurement

When the platinum plate is submerged in polymer/CO$_2$ solution, the measured weight of the plate becomes smaller than the true weight of the plate due to a buoyancy force exerted on the plate by the polymer/CO$_2$ solution. The buoyancy force is equal to the weight of polymer/CO$_2$ solution displaced by the plate and it is calculated by multiplying the plate volume by the density of polymer/CO$_2$ solution. Therefore, knowing the volume and mass of the plate *a priori*, the density of polymer/CO$_2$ solution can be calculated from the buoyancy force or the apparent weight of the platinum plate.

The force balance equation around the plate and the wire is expressed by

$$w_{\mathrm{readout}}(P, T) = w_{\mathrm{ref}} - (V + \alpha V_w)\rho_{\mathrm{sol.}}$$
$$- ((1 - \alpha)V_w + V_B)\rho_{\mathrm{CO_2}} + \frac{\pi d\gamma \cos\theta}{g} \quad (1)$$

where ρ_{sol} and $\rho_{\mathrm{CO_2}}$ are the density of polymer/CO$_2$ solution and CO$_2$, respectively. $w_{\mathrm{readout}}(P, T)$ is the readout value of the apparent total weight of the plate, wire and measuring load hook at the experimental temperature, T, and CO$_2$ pressure, P, condition. w_{ref} is the apparent total weight of the plate, wire and measuring load hook at a reference tem-

perature and pressure condition. V and V_w are the volume of the platinum plate and that of the wire, respectively. V_B is the volume of measuring load hook. α is the volume fraction of the wire submerged in the solution. d is diameter of the wire connecting the platinum plate to the measuring load hook. γ is surface tension of polymer/CO$_2$. θ is contact angle between the wire and the polymer/CO$_2$ solution as shown in Figure 2(b). g is the gravitational constant. The subscript i, for example d_i and $V_{w,i}$ in Figure 2(b), indicates that it is the value in the case of using the i-th wire.

Because the sample basket is fixed to the sorption cell wall and the weight of coupling unit is tarred to be zero by position operations, the weights of the basket and coupling unit do not affect the weight measurements and do not appear in Eq. (1). The buoyancy force is exerted not only on the plate but also on the wire and the measuring load hook as shown in Figure 2(b). The buoyancy force exerted on the plate and the submerged part of the wire is the weight of the displaced volume of polymer/CO$_2$ solutions, which is expressed by the second term of right hand side of Eq.(1), $(V + \alpha V_w)\rho_{\mathrm{sol}}$. The buoyancy force exerted on the rest of the wire and the load hook is weight of the displaced volume of CO$_2$, which is expressed by the third term of right hand side of Eq.(1), $((1 - \alpha)V_w + V_B)\rho_{\mathrm{CO_2}}$. The fourth term in Eq. (1) indicates the surface tension between polymer/CO$_2$ and wire. These buoyancy forces are calculated and used to correct the apparent total weight of the plate, wire and loading hook, $w_{\mathrm{readout}}(P, T)$.

The volume of measuring load hook, V_B, was determined in a preliminary experiment: Without loading any samples, the weight of measuring load hook was measured in contact with various CO$_2$ pressures and temperatures and it was also measured *in vacuo* at the same temperatures. The volume, V_B, was calculated from the weight difference between two measurements. Because the buoyancy force exerted on the loading hook is the weight of the displaced volume of CO$_2$, the volume of the hook was calculated by dividing the weight difference by the density of CO$_2$ at measuring temperature and pressure. $V_B = 0.373$ cm^3 was determined by averaging all volumes calculated from the weights of the loading hook measured at 200°C at pressure in the range of 0.1–15 MPa. The volume is apparently a function of temperature and mechanical pressure. However, the change in volume of the hook against temperature and pressure was negligible in this study. The volume change in the temperature and pressure range where the experiments were conducted was estimated to be 0.15% and error caused by the volume change of V_B for density measurement was estimated to be 0.16%.

In this experiment, a disk shape platinum 12 mm in diameter and 1.6 mm in thickness was used. Although the effect of change in V_B with temperature and pressure on the density measurement was negligible owing to the material property and location of the loading hook, the temperature and pressure dependencies of the volume of platinum plate and the wire was not negligible and had to be taken into account in Eq. (1). Considering that the plate and wire were both made of platinum, the temperature and pressure corrections of the volumes, V and V_w, were made using Eq. (2).

$$V/V_{\text{ref}} = V_w/V_{w,\text{ref}} = \left(1 - 3\frac{1-2v}{E}(P - P_{\text{ref}})\right) \times \exp(\varsigma(T - T_{\text{ref}})) \quad (2)$$

where V_{ref} and $V_{w,\text{ref}}$ are reference volumes of platinum plate and wire. v and E are Poisson's ratio and Young's modulus of the platinum, respectively. They are given by 0.38 and 1.68 MPa, respectively.[20] ς is the coefficient of thermal expansion, which is 9.1×10^{-6} K^{-1}.[20]

As for ρ_{CO_2}, one can use the literature value. In this experiments, the density ρ_{CO_2} was calculated from in-site measurements. Because the temperature and pressure dependencies of the volume of sinker was also given in the similar form to Eq. (2) ρ_{CO_2} could be calculated from the given volume of sinker and the weight

difference at position 1 and 2, which is equivalent to the buoyancy force exerted on the sinker by CO_2.

The surface tension of polymer/CO_2, γ, and contact angle, θ, were unknown and no literature value was available. To eliminate γ and θ from the balance equation, Eq. (1), two wires in different diameter, d_1 and d_2, were used. The density measurements were conducted using each wire individually at the same temperature and pressure.

Let $w_{\text{readout,1}}$ and $w_{\text{readout,2}}$ be the measured apparent total weight of the plate, measuring load hook with the wire d_1 in diameter and that with the wire d_2 in diameter, respectively. Assuming that the two wires have the same surface tension, γ, and contact angle, θ, against the polymer, eq. (1) can be transformed into

$$\frac{\pi\gamma\cos\theta}{g} = \frac{1}{d_1}\left(w_{\text{readout,1}} - w_{\text{ref,1}} \right. \\ \left. + (V + \alpha_1 V_{w,1})\rho_{\text{sol.}} + ((1-\alpha_1)V_{w,1} + V_B)\rho_{CO_2}\right) \\ = \frac{1}{d_2}\left(w_{\text{readout,2}} - w_{\text{ref,2}} + (V + \alpha_2 V_{w,2})\rho_{\text{sol.}} \right. \\ \left. + ((1-\alpha_2)V_{w,2} + V_B)\rho_{CO_2}\right) \quad (3)$$

where $V_{w,i}$ is the volume of wire in diameter d_i. $W_{\text{ref},i}$ is the reference weight of the plate, measuring load hook and the wire in diameter d_i.

Thus, the density of polymer/CO_2, ρ_{sol} is given by

$$\rho_{\text{sol}} = \frac{d_2\{w_{\text{readout,1}} - w_{\text{ref,1}} + ((1-\alpha_1)V_{w,1} + V_B)\rho_{CO_2}\} - d_1\{W_{\text{readout,2}} - W_{\text{ref,2}} + ((1-\alpha_2)V_{w,2} + V_B)\rho_{CO_2}\}}{d_1(V + \alpha_2 V_{w,2}) - d_2(V + \alpha_1 V_{w,1})} \quad (4)$$

RESULTS AND DISCUSSION

The reference weight, $w_{\text{ref},i}$, the reference volume of plate, V_{ref}, and that of the wire, $V_{w.\text{ref},i}$, were determined before conducting the density measurement of polymer/CO_2 solution. The reference weight, $w_{\text{ref},i}$, was measured at the room temperature, i.e., T_{ref} = 298.2 K under the atmospheric pressure, P_{ref} = 0.1013 MPa with the assumption that the buoyancy exerted on plate, wire and measuring load hook by air was small and it was negligible compared to the buoyancy exerted by polymer/CO_2 solution or high pressure CO_2. The resulting reference weight, w_{ref}, excluding the weight of the measuring load hook, was 3.73957 g for the set of the platinum plate and the wire d_1 in diameter and 3.86199 g for the other set of plate and wire d_2 in diameter. The measurements of the reference volumes, V_{ref}, and $V_{w.\text{ref},i}$, were measured in the following way: The platinum plate and the wire was submerged into

distilled water and the weight was measured by MSB at T_{ref} = 298.2 K in atmospheric pressure, P_{ref} = 0.1013 MPa. Using the density of the pure water at the specified temperature and pressure, the volume of the plate, V_{ref}, and those of two wires in different diameter, V_{wi}, were calculated from the weight difference between readout and w_{ref}. The obtained volumes are listed in Table II.

The value of α_i, i.e., the ratio of the submerged part to the nonsubmerged part of wire, was determined before measuring the polymer/CO_2 solution under the pressurized CO_2. It was conducted in the following way: The density of polymer alone was firstly measured at 453.1, 473.5, and 491.8 K *in vacuo* at the initial stage of every experiment and it was then substituted to density term, ρ_{sol} in Eq.(4). Then, assuming that α_1 and α_2 of Eq. (4) took the same value in the high-pressure condition, the α value was determined by solving Eq. (4) with ρ_{CO_2} = 0.

TABLE II
Size of platinum plate and other parts at 298.2 K and 0.1013 MPa

Diameter of Pt wire d_i (mm)	Volume of plate, V (cm³)	Volume of wire, $V_{w,i}$ (cm³)	V_B (cm³)
0.20	0.1768	0.0012	0.373
0.50		0.0070	

Note that we confirmed the validity of the aforementioned assumption by independently conducting the solubility measurements and estimated the change in level of the solution in basket with gas dissolution as well as error in density measurements caused by the change in α value: The maximum change in level was expected to occur when the pressure was changed from 0 to 15 MPa, the highest experimental pressure in the experiment, and at 220°C, highest temperature in the experiments. The level change, h/h_o, against the gas dissolution or the density change of the polymer/CO$_2$ solution was estimated by the following equation.

$$\frac{h}{h_o} = \frac{\frac{m_p + m_p S}{\rho_{sol}}}{\frac{m_p}{\rho_{pol}}} = \frac{(1+S)\rho_{pol}}{\rho_{sol}} \qquad (5)$$

where h and h_o are the level of polymer/CO$_2$ solution in the MSB basket and that of polymer alone, respectively. m_p is weight of the polymer loaded in the basket. S is the solubility of CO$_2$ to polymer. The density of polymer alone, ρ_{poly}, and polymer/CO$_2$ solution, ρ_{sol}, were calculated by the SL-EoS. The maximum value of h/h_o was estimated to be 11%. In the experiments, the initial level of the polymer solu-
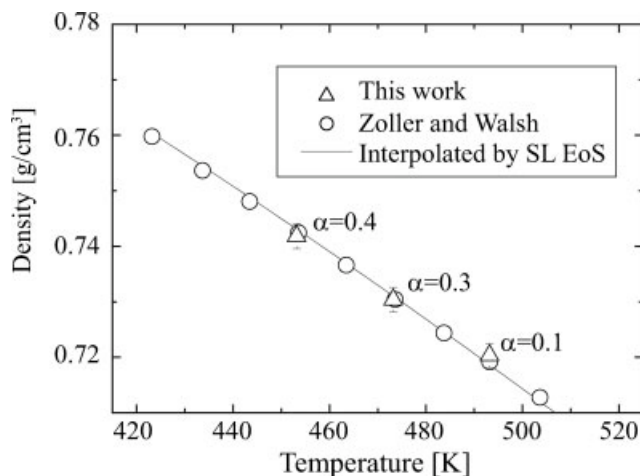
tion was about 6 mm. Thus, the change in level was about 0.66 mm. Because the total length of the wire was 34 mm, the change in α value with the level change became 2%. Then, the density measurement error caused by the 2% change in α value was estimated to be <0.03%. Therefore, for the sake of calculation simplicity, we assumed that $\alpha_1 = \alpha_2 = \alpha$ (constant) when using Eq.(4).

The resulting α value and PE density were shown in Figure 3. The open triangle symbol, △, represents the measured PE density and the open circle symbol, ○, represents the literature values of Zoller and Walsh.[21] In Figure 3, the solid line represents estimates of the Sanchez–Lacombe equation-of-state (SL-EoS), i.e., Eq.(5)[22] for PE alone.

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] = 0. \qquad (6)$$

where $\tilde{P}$, $\tilde{\rho}$, and $\tilde{T}$ are the reduced pressure, density and temperature, respectively, and they are defined by $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{\rho} = \rho/\rho^*$, $\rho^* \cong \overline{M}_w/v^*$, and $r = P^*v^*/RT$. r is the size parameter representing the number of lattice sites occupied by a polymer molecule. R is the gas constant and $\overline{M}_w$ is the weight average molecular weight. P^*, T^*, v^*, and ρ^* are characteristic parameters. The characteristic parameters of the SL-EoS for polymer alone were determined by correlating the literature data of Pressure–Volume–Temperature obtained in the temperature range from 394.4 to 522.9 K and the pressure range from 0 to 40 MPa. The resulting parameters are listed in Table III. As shown in Figure 3, the measured density and the estimate of the SL-EoS showed a good agreement with the literature values. This means that the proposed schemes and apparatus are useful and can provide the density of solution with an acceptable accuracy.

The density of polymer/CO$_2$ solution was measured by introducing pressurized CO$_2$ to the sorption cell after obtaining the α value and the density of polymer alone. The measured densities of PE/CO$_2$ are plotted against CO$_2$ pressures as shown in Figure 4 and Table IV. The open square symbol, □, represents the density of PE/CO$_2$ solution measured

Figure 3 Density of PE/CO$_2$, △: This work, ○: the literature values (Zoller and Walsh[21]) and solid line: estimate of the SL-EoS.

TABLE III
Characteristic parameters for Sanchez–Lacombe equation of sate

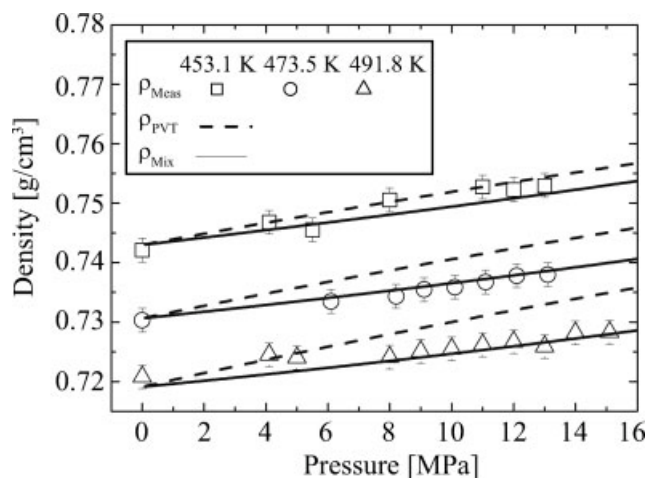|	P^* (MPa)	ρ^* (kg/m³)	T^* (K)	Ref. of PVT data
Polyethylene (PE)	379.6	864.2	678.8	[21], $\overline{M}_w = 1000$
Polyethylene glycol (PEG)	553.2	1178.3	640.2	[21], $\overline{M}_w = 1590$
Carbon dioxide (CO$_2$)	369.1	1253.0	341.2	

Figure 4 Density of PE/CO_2 versus CO_2 pressure. □: 451.3 K, ○: 473.5 K, △: 491.8 K. The solid line: density, ρ_{mix}, calculated by SL-EoS with consideration of CO_2 dissolution, dashed line: density, ρ_{PVT}, calculated by SL-EoS without considering CO_2 dissolution.

at 451.3 K, ○ represents at 473.5 K and △ at 491.8 K. As shown in Figure 4, the density of PE/CO_2 solution decreased as temperature increased. The density increased with the increase of CO_2 pressure. The solid lines represent the density of PE/CO_2 solution calculated by the SL-EoS. When the SL-EoS was used for the polymer/CO_2 solution, a mixing rule was employed with an interaction parameter, k_{12}. The values of the interaction parameter at each temperature were determined from the solubility experiments conducted using MSB independently. They are listed in Table V. The increase in density was proportional to the CO_2 pressure but the slope of

density versus CO_2 pressure lines became slightly smaller as the temperature increased.

The density of the PE/CO_2 solution is a function of temperature, pressure and dissolved CO_2 concentrations. When the mechanical pressure is exerted on the polymer, the density of the polymer alone increases as can be seen in any PVT data. On the other hand, when CO_2 dissolves in polymer, generally the polymer swelling occurs, i.e., the density of the polymer decreases. To clearly differentiate the pure effect of dissolved CO_2 concentration from those of pressure, the change in density of PE against the mechanical pressure was calculated. The density of PE under the mechanical pressure was calculated by the SL-EoS, of which characteristic parameters were determined from PVT data of the polymer. The dashed line in Figure 4 represents the density of PE under the mechanical pressure. As expected, the density increased as the mechanical pressure increased. Hereafter, the density of polymer/CO_2 solution calculated by the SL-EoS with mixing rule is denoted by ρ_{mix} and the density of polymer under the mechanical pressure is denoted by ρ_{PVT}. The difference between measured density and ρ_{PVT} at the same pressure level can be regarded as the pure effect of gas dissolution on density and the difference became larger as CO_2-pressure increased. The solubility of CO_2 increases with the increase of CO_2 pressure. The concentration of dissolved CO_2 in the solution increases as CO_2 pressure increases. Thus, it can be concluded that the dissolution of CO_2 in polymer reduced the density of PE/CO_2 but the degree of density increase with the increase of mechanical pressure was larger than that of density decrease with the increase in CO_2

TABLE IV
Density of PE/CO_2 solution

Temperature (K)	Pressure (MPa)	Density (g/cm^3)	Temperature (K)	Pressure (MPa)	Density (g/cm^3)
491.8	0.0	0.7208	473.5	0.0	0.7304
	4.1	0.7245		6.1	0.7328
	5.0	0.7240		8.2	0.7334
	8.0	0.7241		9.1	0.7343
	9.0	0.7251		10.1	0.7346
	10.0	0.7255		11.1	0.7353
	11.0	0.7262		12.1	0.7363
	12.0	0.7267		13.1	0.7363
	13.0	0.7259	453.1	0.0	0.7418
	14.0	0.7282		4.1	0.7460
	15.1	0.7283		5.5	0.7444
				8.0	0.7493
				11.0	0.7511
				12.0	0.7505
				13.0	0.7510
				14.0	0.7694
				15.0	0.7717

pressure. Competitive effects of both pressure and gas dissolution on the density determined overall density increase for PE/CO₂ solution.

Similarly, the density of PEG/CO₂ mixture was measured at 374.3 K under the pressure ranging from 0 to 13 MPa to confirm the effect of CO₂ dissolution on density reduction. Figure 5 shows the measured density of PEG/CO₂ solution with the calculated density of PEG alone, ρ_{PVT}. The ρ_{PVT} of PEG was calculated by the SL-EoS at the temperature under the mechanical pressure equivalent to CO₂ pressure in density measurements. The characteristic parameters for PEG alone were determined by fitting the SL-EoS to PVT literature data ranging 344.8–474 K and 0–40 MPa[21] and the resulting parameters are listed in Table III.

For the case of PEG/CO₂ mixture, the experimental condition was limited to one temperature condition, 374.3 K, because PEG evaporated at temperature far above the 374.3 K and the viscosity of PEG/CO₂ becomes too high to lift up the platinum plate at temperature far below the 374.3 K. As shown in Figure 5, the density of PEG/CO₂ solution decreases as the CO₂-pressure increases at 374.3 K. The difference between measured density and ρ_{PVT} increases with the increase of CO₂-presssure. That is, the effect of CO₂ dissolution on the density reduction for PEG is more significant than that for PE.

CONCLUSIONS

A new method of measuring the density of polymer/CO₂ mixture was proposed. It used MSB, which was normally used for solubility and diffusivity measurements. The proposed method could suc-
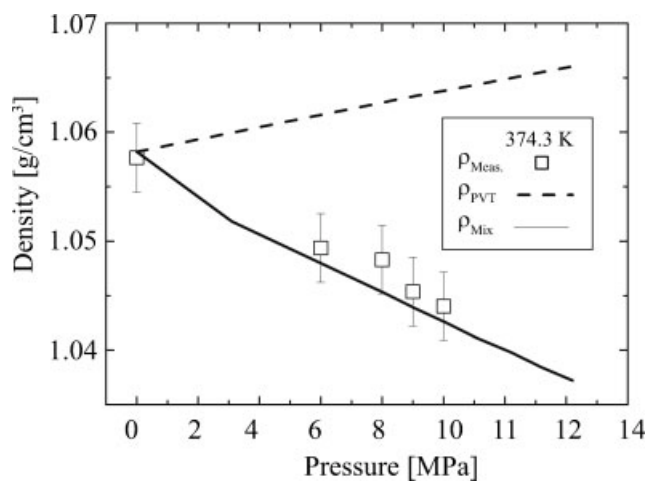

Figure 5 Density of PEG/CO₂ versus CO₂-pressure. □: Experiments and solid line: density, ρ_{mix}, calculated by SL-EoS with consideration of CO₂ dissolution, dashed line: density, ρ_{PVT}, calculated by SL-EoS under mechanical pressure without considering CO₂ dissolution.

TABLE V
Interaction parameter of Sanchez–Lacombe EoS

	Temperature (K)	k_{12} [-]
CO₂/polyethylene	493.2	0.1103
	473.2	0.1099
	453.2	0.1120
CO₂/polyethylene glycol	373.2	0.0411

cessfully measure the density of polymer in contact with high-pressure CO₂. The density of PE/CO₂ solution was measured at 453.1, 473.5, and 491.8 K under the pressures ranging from vacuum to 13 MPa. The density of PEG/CO₂ was measured at 373 K and pressure up to 10 MPa. The density of the polymer/CO₂ solution decreased with the increase of dissolved CO₂-concentration in polymer. It also decreased with the increase of temperature. However, it increased with the increase of pressure. The overall change in density of polymer/CO₂ solution under the pressurized CO₂ was determined in the balance among the effects of mechanical pressure, temperature and dissolved CO₂ concentration. The dissolution of CO₂ in polymer reduced density of both PEG/CO₂ and PE/CO₂ systems but the degree of CO₂ induced density reduction was different between PE/CO₂ and PEG/CO₂ systems. For PE/CO₂ systems, the degree of increase in density against the increase of mechanical pressure was larger than that of decrease in density against the increase in CO₂ dissolution. Thus, the total density of PE/CO₂ solution increased as CO₂ pressure increased.

The proposed density measuring method has some limitations on applicable polymers. When the plate is moving up and down in the polymer melt during the position changeover operation, a dragging force is generated. The position changeover operation could not be performed correctly and the accuracy of the readout could not be guaranteed when viscosity is high. Despite of this limitation, the method provides a new scheme of measuring the density of polymer/gas solution and can be applied to variety of low molecule and CO₂ systems.

References

1. Tomasko, D. L.; Li, H. B.; Liu, D. H.; Han, X. M.; Wingert, M. J.; Lee, L. J.; Koelling, K. W. Ind Eng Chem Res 2003, 42, 6431.
2. Handa, Y. P.; Kruus, P.; O 'Neill, M. J Polym Sci Part B: Polym Phys 1996, 34, 2635.
3. Condo, P. D.; Paul, D. R.; Johnston, K. P. Macromolecules 1994, 27, 365.
4. Gehardt, L. J.; Manke, C. W.; Gulari, E. J Polym Sci Part B: Polym Phys 1997, 35, 523.
5. Kwang, C.; Manke, C. W.; Gulari, E. J Polym Sci Part B: Polym Phys 1999, 37, 2771.

6. Lee, M.; Park, C. B.; Tzoganakis, C. Polym Eng Sci 1999, 39, 99.

7. Areerat, S.; Nagata, T.; Ohshima, M. Polym Eng Sci 2002, 42, 2234.

8. Durrill, P.; Griskey, R. G. AIChE J 1969, 12, 1147.

9. Sato, Y.; Fujiwara, K.; Takikawa, T.; Takishima, S. Masuoka, H. Fluid Phase Equilib 1999, 162, 261.

10. Wong, B.; Zhang, Z.; Handa, Y. P. J Polym Sci Part B: Polym Phys 1998, 36, 2025.

11. Areerat, S.; Funami, E.; Hayata, Y.; Nakagawa, D.; Ohshima, M. Polym Eng Sci 2004, 44, 1915.

12. Wissinger, R. G.; Paulaitis, M. E. J Polym Sci Part B: Polym Phys 1987, 25, 2497.

13. Zhang, Y.; Gangwani, K. K.; Lemert, R. M. J Supercritical Fluids 1997, 11, 115.

14. Royer, J. R.; DeSimone, J. M.; Khan, S. A. Macromolecules 1999, 32, 8965.

15. Nikitin, L. N.; Gallyamov, M. O.; Vinokur, R. A.; Nikolaec, A. Y.; Said-Galiyev, E. E.; Khokhlov, A. R.; Jespersen, H. T.; Schaumburg, K. J Supercritical Fluids 2003, 26, 263.

16. Rajendran, A.; Bonavoglia, B.; Forrer, N.; Storti, G.; Mazzotti, M.; Morbidelli, M. Ind Eng Chem Res 2005, 44, 2549.

17. Bonavoglia, B.; Storti, G.; Morbidelli, M.; Rajendran, A.; Mazzotti, M. J Polym Sci Part B: Polymer Phys 2006, 44, 1531.

18. Keller, J. U.; Rave, H.; Staudt, R. Macromol Chem Phys 1999, 200, 2269.

19. Hilic, S.; Boyer, S. A. E.; Padua, A. A. H.; Grolier, J. P. E. J Polym Sci Part B: Polym Phys 2001, 39, 2063.

20. National Astronomical Observatory, Rika Nen-pyo (Chronological Science Tables), Maruzen Co., Ltd., 1994.

21. Zoller, P.; Walsh, D. J. Standard Pressure–Volume–Temperature Data for Polymers; Technomic Publishing Company, Inc.: Pennsylvania, 1995.

22. Sanchez, I. C.; Lacombe, R. H. J Phys Chem 1976, 80, 2352.