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Swelling measurement of polymers in high pressure carbon dioxide using a spectroscopic reflectometer

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ABSTRACT

We developed an in situ thickness monitor using a spectroscopic reflectometer to measure the swelling behaviors of polymer thin films in carbon dioxide up to 30 MPa. Because the change in thickness was measured under high-pressure CO_2, the measurement was performed through a sapphire window with a relatively high refractive index. We found that the window effect on the reflectivity can be successfully eliminated. To confirm the accuracy of the analysis, we measured the swelling behaviors of four polymers (poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(*n*-butyl methacrylate) (PBMA), and poly(dimethylsiloxane) (PDMS)), and compared the swelling measurements with reported data. The swelling ratios of the polymers were in reasonable agreement with literature data. Notably, anomalous swelling was observed for PBMA and PDMS, although anomalous swelling has been observed in films much thinner than those of our samples, probably due to the low glass transition temperatures and high swelling ratios of PBMA and PDMS.

1. Introduction

Supercritical carbon dioxide is being increasingly utilized as an alternative for conventional organic solvents [1,2]. For processes involving polymers, CO_2 has been used as a plasticizer [3–5], a micro- or nano-foaming agent [6–8], a compatibilizer of polymer blends [9], and an additive to tune block copolymer morphologies [10–14]. Most polymers do not dissolve, but rather swell in CO_2 depending on the temperature and pressure. Therefore, the swelling ratios of polymers in CO_2 are critical for the CO_2 processes.

Numerous methods have been proposed to measure polymer swelling ratios in CO_2. Changes in polymer volumes have been observed visually [15–18] or by a cathetometer [19–21]. ATR-IR or near-IR spectroscopy has been used to measure the swelling of polymers such as poly(dimethylsiloxane) (PDMS) [22] and poly(ethylene glycol) [23] in CO_2. Magnetic suspension balance (MSB), a gravimetric method, has been combined with mass-loss analysis (MLA) to obtain swelling data [18]. Optical interferometry was used to measure the swelling of 6-μm-thick polycarbonate films [24], and waveguide spectroscopy was used to measure the swelling of 1.1-μm-thick poly(methyl methacrylate) (PMMA) films [25].

In the last decade, the swelling behavior of polymer thin films has attracted significant attention. Near the critical point of CO_2 (31.1 °C and 7.38 MPa), polymer thin films exhibit unique anomalous swelling [26–30], where the density fluctuation of supercritical fluids is believed to induce significant swelling. Koga and coworkers [27–29] reported that the anomalous swelling of polymers is strongly correlated with the parameter obtained by dividing the sample thickness by the radius of gyration (R_g), and is clearly observed in films of which the thickness is less than several times of R_g. They also recently reported that anomalous swelling can be observed in supercritical methane [29].

Compared to swelling measurements of bulk samples, a limited number of techniques are available to measure the swelling ratio of films thinner than several hundred nanometers. Neutron reflectivity (NR) has been used to measure the swelling of (deuterated) polymer films [10,27–29,31]. Similarly, X-ray reflectivity can also be used for in situ measurements, but measurable conditions are relatively limited compared to NR [32]. In situ spectroscopic ellipsometry has been used to measure the thickness of thin films [11,26,30,33,34]. In ellipsometry, polarized light passes through the birefringent windows of high-pressure vessels, and the complex window effect must be corrected. Even when a non-birefringent material is used for the window, the internal pressure of the vessel

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Table 1
Properties of polymer samples used in this study.

Polymer	M_n [g mol^{-1}]	T_g [°C] [37]	Source
PMMA	3.5×10^5	100	Aldrich
PS	2.8×10^5	100	Aldrich
PBMA	3.36×10^5	20	Aldrich
PDMS	1.25×10^5	−125	Polymer Source, Inc.

induces stress and birefringence. While this problem can be overcome [33], it was recently pointed out that the in situ ellipsometry is subject to the mirage effect caused by temperature gradients in sample cells [34].

In this study, we developed an in situ thickness monitor using a spectroscopic reflectometer. Such reflectometry analysis has been used to measure thickness changes of polymer films under solvent vapor [35,36]. However, to the best of our knowledge, reflectivity measurements for high-pressure systems, in which the window effect of high-pressure vessels could potentially be a problem, has not been reported. Here, we show that the window effect can be easily corrected and swelling ratios can be successfully determined by a spectroscopic reflectometer. Furthermore, we observed anomalous swelling in relatively thick films.

2. Materials and methods

2.1. Materials

Poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(*n*-butyl methacrylate) (PBMA) and poly(dimethylsiloxane) (PDMS) were used as received. The properties of the polymers are listed in Table 1. The glass transition temperatures shown in Table 1 were obtained from literature [37]. Each polymer was dissolved in toluene (Wako Pure Chemical Industries) and the solution was spun-cast on a Si (1 0 0) wafer. The typical thickness of the polymer film was 150–300 nm. Prior to the swelling measurements in CO_2, the sample films were dried under vacuum for 1 d.

2.2. Swelling measurement in CO_2

Fig. 1 shows a schematic diagram of the high-pressure cell. The cell was connected to a high pressure liquid chromatography pump (JASCO PU-2086) equipped with a cooling head and a backpressure regulator (JASCO BP-2080) to control the CO_2 pressure. The temperature of the cell was controlled by a ribbon heater (AS ONE JK-1) rolled around the cell, and a PID temperature controller (AS ONE TXN700B). The pressure and temperature in the cell were controlled to within 0.3 MPa and 0.5 °C, respectively.

To measure the swelling of the polymers in CO_2, a sample film was placed in the cell. Visible light from an iodine lamp (Otsuka Electronics MC-2530) was incident vertically on the sample film through a sapphire window, and the reflected light was sent to a detector (Otsuka Electronics MCPD-3700).

To eliminate the window effect, the reflectivity spectrum of the sample (R) was approximated by Eq. (1):

$$R = \frac{I_S - I_W}{I_R - I_W} R_{Si}, \tag{1}$$

where I_S and I_R are the raw reflective intensities of a sample film and reference (a bare Si wafer), respectively, measured through a sapphire window. I_W is the reflective intensity from the sapphire window, measured independently from I_S and I_R (see the Supplementary Information for the setup for I_W measurements).

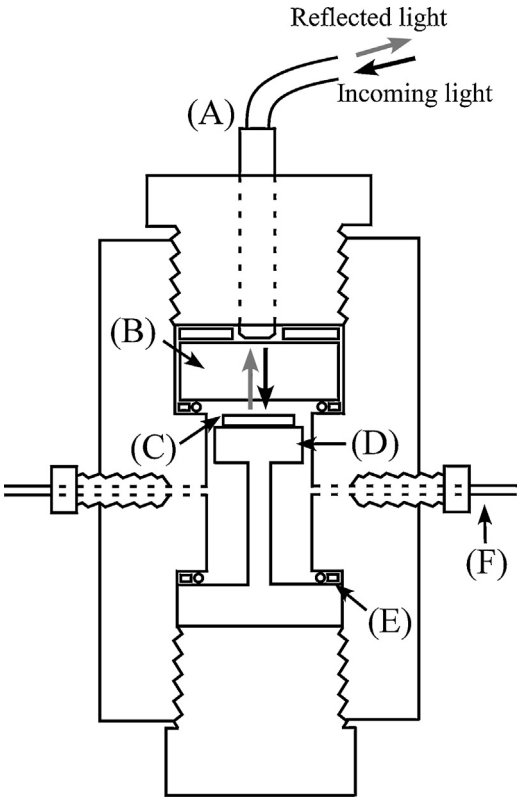

Fig. 1. A schematic illustration of the high-pressure cell. Incident light comes from the light source through the optical fiber (A) and the sapphire window (B). The incoming light is vertically reflected at the sample film on a Si wafer (C) placed onto the sample stage (D). The reflected light then passes through the same window and optical fiber to reach to the detector. The cell is sealed by Teflon O-rings supported by backup rings (E). The cell is connected with the HPLC pump and backpressure regulator by stainless tubes (F).

R_{Si} is the calculated reflectivity spectrum of a bare Si wafer as in Eq. (2) [38]:

$$R_{Si} = \frac{(n_{Si} - n_{CO_2})^2 + k_{Si}^2}{(n_{Si} + n_{CO_2})^2 + k_{Si}^2}, \tag{2}$$

where n_i and k_i are the refractive index and attenuation coefficient of component i, respectively; n_{CO_2} was calculated as a function of CO_2 density ρ [25,39]:

$$\left(\frac{n_{CO_2}^2 - 1}{n_{CO_2}^2 + 2}\right)\frac{1}{\rho} = A_R + B_R\rho + B_R^2\rho, \tag{3}$$

where A_R, B_R, and C_R are virial coefficients. $A_R = 6.649\,\mathrm{cm^3\,mol^{-1}}$, $B_R = 1.9\,\mathrm{cm^6\,mol^{-2}}$, and $C_R = -287\,\mathrm{cm^9\,mol^{-3}}$ were employed, based on reports by Obriot et al. [25,39]. The CO_2 density was obtained from literature [40]. The validity of this approximation will be discussed in Section 3.1.

2.3. Calculation of the swelling ratios from sample thicknesses

The reflectivity spectrum of the sample was then fitted by a three-layer model (CO_2/polymer/Si wafer) in the range 360–800 nm to calculate the thickness and refractive index of the sample. In the model [38], reflectivity R is given by Eq. (4):

$$R = \left|\frac{r_{12} + r_{23}\exp(-i2\beta)}{1 + r_{12}r_{23}\exp(-i2\beta)}\right|^2, \tag{4}$$

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