High-pressure phase behavior and FT-IR study of poly(methyl methacrylate) + ethanol systems with addition of supercritical CO₂

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Abstract. The phase equilibria of carbon dioxide (CO₂) + poly(methyl methacrylate) (PMMA; Mw = 15 k) + ethanol ternary systems were measured at temperatures ranging from 293.3 to 359.7 K and pressures up to 14.1 MPa. In order to determine the phase boundary, we observed the cloud points and bubble points by using a variable volume view cell. Furthermore, the dissolution process of PMMA in CO₂-expanded ethanol was studied using FTIR spectroscopy. Although both CO₂ and ethanol are nonsolvents for PMMA at 303 K, PMMA dissolved in CO₂-expanded ethanol. The noticeable band was carbonyl stretching band for PMMA. No peak shifts and/or no contributions were obtained for PMMA in pure ethanol at 303 K, because ethanol is nonsolvent for PMMA. With addition of CO₂ in the mixture of PMMA and ethanol, the carbonyl stretching band of PMMA has a weak contribution at lower wave numbers. It is indicated that a strong interaction between PMMA and ethanol via hydrogen bonding exists.

1. Introduction
CO₂-expanded liquids are a novel class of sustainable solvents because they offer several advantages over both the conventional organic solvents and supercritical CO₂. CO₂-expanded liquids exhibit lower viscosity and higher diffusion coefficients than the conventional organic solvents. As the result of these advantages, CO₂expanded liquids can be applied in several processes such as nanoparticle formation, homogeneous reactions, catalytic reactions, and polymeric materials formation[1]. Furthermore, CO₂-expanded liquids are advantageous for polymer processing because many polymers dissolve in CO₂-expanded liquids as compared to supercritical CO₂ with a small amount of cosolvent. In previous studies, we demonstrated the use of the pressure-induced phase separation (PIPS) of CO₂-expanded ethanol in obtaining polymeric microparticles and polymer composite particles[2]. In these particle formation techniques, CO₂-expanded ethanol is generally selected as the solvent since it is an environmentally benign solvent. In order design and optimize these processes, it is important to understand the phase behavior of CO₂-expanded liquids because the product morphology is strongly affected by the phase behavior. However, polymer solutions containing CO₂ exhibit extremely complex phase equilibrium behaviors because the large differences among the physical properties of the polymer, solvent, and CO₂ induces complicated physicochemical interactions in polymer solutions containing CO₂[3]. Therefore, many researchers have reported the phase behavior of polymer

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solutions containing CO\textsubscript{2}[4]. In order to develop an effective method for the production of polymeric materials by using CO\textsubscript{2}-based technology that employs CO\textsubscript{2}-expanded liquids and/or supercritical CO\textsubscript{2} with cosolvents, it is essential to understand the phase behavior of CO\textsubscript{2} + polymer + cosolvent systems under elevated pressures and temperatures. Furthermore, the dissolution mechanism of polymer in CO\textsubscript{2}-expanded ethanol has not yet been elucidated at the molecular level.

In this study, the phase equilibria of CO\textsubscript{2} + poly(methyl methacrylate) (PMMA; M\textsubscript{w} = 15 k) + ethanol systems are determined. The effects of pressure and temperature on the phase equilibria are discussed. Furthermore, we discussed the dissolution mechanism of PMMA in CO\textsubscript{2}-expanded ethanol by FTIR spectroscopy.

2. Experimental Section

2.1 Materials
Carbon dioxide (CO\textsubscript{2}) with a minimum purity of 99.9 % was purchased from Fukuoka Sanso Co., Ltd. Ethanol with purities greater than 99.5 % was obtained from Wako Pure Chemical Industry Co., Ltd. The poly(methyl methacrylate) (PMMA; M\textsubscript{w} = 15,000) was purchased from Aldrich Co.

2.2 Phase behavior
The details of the variable volume view cell used in the procedures for the measurement of the cloud point of the polymer solution containing CO\textsubscript{2} are described in our previous paper[5,6]. The experimental apparatus included a variable volume view cell, hand pump, and heater jacket. The internal volume of the cell could be varied from 10 to 150 cm\textsuperscript{3} by moving a free piston with a distance of 50 mm along the cell. A Teflon-coated magnetic stirring bar was used to ensure thermal and phase equilibria. The phase transition was observed through a quartz glass window, and the images were captured with an optical unit (CCD camera) and displayed on a monitor.

2.3 FTIR measurement
The details of the experimental apparatus and procedures for the FTIR spectra of CO\textsubscript{2}-expanded ethanol containing PMMA are described in our previous paper[7]. Measurements were performed using an FTIR spectrometer equipped with a germanium-on-KBr beamsplitter and MCT detector. The authors measured the IR spectra at a wavenumber resolution of 4 cm\textsuperscript{-1} to obtain the desired signal-to-noise ratio. We used a special stainless steel cell with a volume of 25 cm\textsuperscript{3} in our laboratory. The cell was equipped with ZnS windows separated by a zinc spacer, yielding a path length of 0.5 mm.

3. Results and Discussion

3.1 Phase behaviour for CO\textsubscript{2} + PMMA-15k + ethanol system
For the CO\textsubscript{2} + PMMA + ethanol ternary system, the measured phase transition pressure at various concentrations of CO\textsubscript{2} is summarized in Figure 1. In this study, three types of phase behavior were observed. These were exhibited as the L-LV coexistence curves, L-LL coexistence curves, and LL-LLV coexistence curves. The L-LV coexistence curves indicate the liquid $\rightarrow$ liquid + vapor transition points. The L-LL coexistence curves indicate the liquid $\rightarrow$ liquid\textsubscript{1} + liquid\textsubscript{2} transition points. The LL-LLV coexistence curves indicate the liquid\textsubscript{1} + liquid\textsubscript{2} $\rightarrow$ liquid\textsubscript{1} + liquid\textsubscript{2} + vapor transition points. The concentration of PMMA in ethanol (CO\textsubscript{2}-free) was fixed as ca. 5 wt\% in this system. When CO\textsubscript{2} up to 11.4 wt\% was added to the PMMA + ethanol solutions, PMMA was completely dissolved in the CO\textsubscript{2}-expanded liquid (ethanol) phase at temperatures ranging from 293.3 to 359.7 K. As shown in Figure 1(a), only L-LV coexistence points were observed at low concentrations of CO\textsubscript{2}. The L-LV curve denotes the phase-transition points (bubble point) of the polymer solution from a single-liquid phase to L + V phases. On the other hand, the solid PMMA phase was observed at 0 wt % CO\textsubscript{2} under our experimental conditions. Furthermore, when CO\textsubscript{2} up to 41.4 wt\% was added, the upper critical solution temperature (UCST) curve appeared as shown in Figure 1(b). The UCST curve represents the
phase transition points (cloud point) from a single-liquid phase to the $L + L$ phases under reduced pressure. In the present study, it was not possible to accurately measure the upper critical end point (UCEP) and lower critical end point (LCEP) values at which the $LV$, $LLV$, and $LL$ loci converge. However, the existence of a UCEP can be predicted in the region where the $L-LV$ and UCST curves coexist. The UCEP shifted to higher temperature regions from ca. 305 to 312 K, as shown in Figure 1(c). Also, the phase-transition pressure increased significantly with the amount of CO$_2$ added to the system. When the CO$_2$ concentration is increased to 56.9 wt%, we can obtain a $P$-$T$ diagram to show the dramatic disappearance of the UCST curves, as illustrated in Figure 1(d).

![Figure 1](image1.png)

**Figure 1.** Pressure and temperature phase diagrams for the CO$_2$ + PMMA-15 k + ethanol system. (a) 11.4 wt% CO$_2$ + 4.5 wt% PMMA + 84.1 wt% ethanol, (b) 41.4 wt% CO$_2$ + 2.9 wt% PMMA + 55.7 wt% ethanol, (c) 51.2 wt% CO$_2$ + 2.5 wt% PMMA + 46.3 wt% ethanol, (d) 56.9 wt% CO$_2$ + 2.2 wt% PMMA + 40.9 wt% ethanol. Symbols: ○, liquid $\rightarrow$ liquid + vapor (LV) transition point (bubble point); ▲, liquid $\rightarrow$ liquid$_1$ + liquid$_2$ (LL) transition points (cloud point); ■, liquid$_1$ + liquid$_2$ $\rightarrow$ liquid$_1$ + liquid$_2$ + vapor (LLV) transition points.

3.2 FT-IR spectra of MMA monomer and PMMA-15k in CO$_2$-expanded ethanol

Figure 2 shows the IR spectra of the carbonyl stretching band of the MMA monomer in CO$_2$-expanded ethanol. A weak band attributed to ethanol was obtained at 1758 cm$^{-1}$. With increasing ethanol concentration, the carbonyl stretching band of MMA at 1730 cm$^{-1}$ shifts to a lower wavenumber, and the new peak is observed at 1712 cm$^{-1}$. This new peak is attributed to the interaction of the carbonyl stretching band with ethanol, and the peak increases with increasing ethanol concentration. This indicates that the hydrogen bonding between the carbonyl group of MMA and the hydroxyl group of ethanol becomes stronger with increasing ethanol concentration.

The IR spectra of PMMA in CO$_2$-expanded ethanol were measured at 303 K and 6 MPa. Under our experimental conditions, PMMA completely dissolved in CO$_2$-expanded ethanol (feed compositions: CO$_2$, 13 wt%; ethanol, 85 wt%; PMMA, 2 wt%). A typical carbonyl stretching band of pure PMMA was observed at 1730 cm$^{-1}$. No peak shift was obtained for the PMMA film immersed in pure ethanol.
at 303 K as shown in Figure 3(a), because ethanol is a nonsolvent for PMMA at 303 K and PMMA is not directly in contact with ethanol. On the other hands, the carbonyl stretching band of PMMA dissolved in CO₂-expanded ethanol has a weak contribution at a lower wavenumber of 1715 cm⁻¹, as shown in Figure 3(b). The carbonyl stretching band at 1715 cm⁻¹ is attributed to the occurrence of hydrogen bonding between the carbonyl group of PMMA and the hydroxyl group of ethanol. It is possible that PMMA in CO₂-expanded ethanol is directly in contact with ethanol. All of these observations suggest that the dissolution process of PMMA in CO₂-expanded ethanol consisted initially of swelling of the PMMA by the CO₂ allowing the ethanol to penetrate into the PMMA and specifically interact by means of hydroxyl-carbonyl hydrogen bonds with the polymer to separate the polymer chain.

Therefore, to confirm the advantages of CO₂-expanded ethanol over a conventional liquid solvent (ethanol), we measured the IR spectra of PMMA in pure ethanol at 353 K, shown in Figure 3(c). At lower wavenumbers, the carbonyl stretching bands of both PMMA immersed in ethanol at 353 K (Figure 3(c)) and PMMA immersed in CO₂-expanded ethanol at 303 K (Figure 3(b)) have weak contributions. Under this condition, the dissolution process of PMMA in ethanol consisted initially of swelling of the PMMA by the increasing of temperature allowing the ethanol to penetrate into the PMMA and specifically interact by means of hydroxyl-carbonyl hydrogen bonds with the polymer to separate the polymer chain. Compared to ethanol, CO₂-expanded ethanol is a better solvent for PMMA because PMMA can dissolve in CO₂-expanded ethanol at relatively low temperature.

**Figure 2.** IR spectra of MMA monomer in CO₂-expanded ethanol at 10 MPa and 303 K. MMA monomer concentration: 2 wt%; ethanol concentration (MMA-free): (a) 0 wt%, (b) 22.5 wt%, (c) 54.8 wt%, and (d) 85.2 wt%.

**Figure 3.** IR spectra of carbonyl stretching band of (a) PMMA immersed in ethanol at 303 K and 0.1 MPa, (b) PMMA dissolved in CO₂-expanded ethanol at 303 K and 6 MPa, and (c) PMMA dissolved in ethanol at 353 K and 0.1 MPa.

### 4. Conclusion
In order to obtain the fundamental knowledge of a polymer material formation technique that uses CO₂-expanded ethanol solution, the phase behaviors of mixtures containing CO₂, PMMA and ethanol were examined. Furthermore, the IR spectra of carbonyl stretching band of PMMA in CO₂-expanded ethanol were measured. The use of CO₂ as a plasticizing and swelling agent for PMMA in order to dissolve PMMA in CO₂-expanded ethanol is the key novel feature of this study.

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