



## Phase behavior of Carbon dioxide/Tetramethyl orthosilicate/polymer ternary systems



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### ABSTRACT

The phase behaviors of carbon dioxide (CO<sub>2</sub>)/tetramethyl orthosilicate (TMOS)/poly(methyl methacrylate) (PMMA) and CO<sub>2</sub>/TMOS/poly(styrene) (PS) ternary systems were measured. The measurements were performed using a synthetic method involving observations of the bubble point and cloud point. The phase boundaries were measured at temperatures ranging from 313.2 K to 393.2 K and CO<sub>2</sub> weight fractions ranging from 0.01 to 0.40. At a constant TMOS:polymer weight ratio of 9:1, both systems showed similar CO<sub>2</sub> mass fraction dependence of their phase behaviors. When the vapor-liquid (VL) and vapor-liquid-liquid (VLL) phase boundaries of the ternary systems were compared with those of the binary CO<sub>2</sub>/TMOS system using polymer-free bases, they were found to be nearly identical. On the other hand, the two systems showed completely opposite polymer mass fraction dependence of their phase behaviors at a constant CO<sub>2</sub> ratio.

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## 1. Introduction

In recent years, the issues of energy consumption and environmental conservation have attracted increasing attention. In Japan, around one-third of the total energy consumption is attributed to commercial and residential buildings, i.e., for air conditioning, heating, and hot water supply [1]. Thus, there is a critical requirement for high-performance insulation materials to ensure that the buildings are energy-efficient. The development of high-performance insulation materials based on polymer foams is considered as a promising approach for energy conservation. Polymer foams consist of gas bubbles dispersed inside a polymer

matrix. Hence, they are lightweight. Moreover, they offer several advantages, such as resource saving, cushioning, and electric insulation. Thus, they have a wide range of applications.

Chemically stable fluorocarbons, chlorofluorocarbons, alternative fluorocarbons (hydrofluorocarbons), and hydrocarbons are used for mass production of macromolecule cellular porous media [2,3]. However, to reduce ozone layer depletion and global warming, it is important to establish a foaming process that does not produce greenhouse gases. Therefore, there is an urgent need to develop new foaming reagents.

Supercritical carbon dioxide (scCO<sub>2</sub>) is regarded as a promising new foaming agent [4] owing to its relatively small environmental impact. Polymeric foam formed with scCO<sub>2</sub> as the blowing agent is called microcellular foam and is known to contain finer bubbles with a much higher number density compared to conventional foam [5–7]. Therefore, practical applications of a foam molding process using scCO<sub>2</sub> as a physical foaming agent have not only been

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studied but also realized in some cases. Such foam materials can be used in buildings only if their heat insulation performance is at least as good as that of Freon-based rigid urethane foams. However, scCO<sub>2</sub>-based insulation materials cannot attain the insulation level of Freon-based insulators.

Silica aerogel [8,9], which is a porous lightweight material having a porosity of more than 99%, has excellent insulating properties. The thermal conductivity of silica aerogel is reported to be in the range of 0.014–0.02 W/(m K) at room temperature [10], which is much higher than that of existing polymeric foams. In addition, because of its high optical transparency, silica aerogel can be used as an optically transparent thermal insulating material in windows. However, its low mechanical strength and high manufacturing cost limit its applications.

Recently, polymeric foams inside foam filled with silica aerogel have been developed. The thermal conductivity of this composite material has been reported to be as high as 0.026 W/(K m), i.e., similar to that of air. Mass production of this composite material can be achieved by CO<sub>2</sub>-assisted extrusion of a polymer and tetraalkoxysilane, which is a raw material used in the production of silica aerogel [10]. At the exit of the extruder, nucleation and growth of CO<sub>2</sub> bubbles occur from the thermodynamically stable ternary mixture of CO<sub>2</sub>/tetraalkoxysilane/polymer as the pressure decreases. The bubbles thus formed are gradually filled with tetraalkoxysilane-rich liquid that bleeds from the bubble walls, which is gelled by subsequent hydrolysis in humid conditions and/or by a catalyst in air. The structure of the composite material is mainly determined by the initial separation of CO<sub>2</sub> from the mixture, which depends on the phase behavior of the systems. Therefore, the phase behaviors of the CO<sub>2</sub>/tetraalkoxysilane binary system and the CO<sub>2</sub>/tetraalkoxysilane/polymer ternary system are important factors that affect the design of the new process. Data for CO<sub>2</sub>/tetraethoxysilane (TEOS) binary systems [11–13] have already been reported. Previously, the phase behaviors of the CO<sub>2</sub>/tetramethoxysilane (TMOS) system [13], CO<sub>2</sub>/trimethoxy(methyl)silane (MTMS) system, and CO<sub>2</sub>/methyl silicate 51 (MS-51) system [14] have also been reported. In this study, the phase behaviors of the carbon dioxide (CO<sub>2</sub>)/tetramethyl orthosilicate (TMOS)/polymethyl methacrylate (PMMA) ternary system and CO<sub>2</sub>/TMOS/polystyrene (PS) ternary system are measured over wide ranges of temperature, pressure, and polymer mass fraction. In addition, the effects of polymer molecular weight, polymer species, and polymer ratio on TMOS are examined.

## 2. Experimental

### 2.1. Materials

Carbon dioxide (CO<sub>2</sub>, CAS number [124-38-9], purity > 99.99%) was purchased from Showa Yozai Co. Tetramethyl orthosilicate (TMOS, CAS number [681-84-5], purity > 98.0%) was purchased from Tokyo Kasei Co. Poly(methylmethacrylate)s (PMMA, CAS number [9003-56-9]) with different molecular weights were purchased from Sigma Aldrich Co. (Mw = 15,000, Mw/Mn = 1.603, Mw = 120,000, Mw/Mn = 2.347) and Kanto Kagaku Co. (Mw = 35,000, Mw/Mn = 1.936). Poly(styrene)s (PS, CAS number [9003-53-6]) with different molecular weights were purchased from Sigma Aldrich Co. (Mw = 35,000, Mw/Mn = 2.020) and Kanto Kagaku Co. (Mw = 250,000, Mw/Mn = 2.348). All the materials used were tabulated in Tables 1 and 2, and used as received.

### 2.2. Experimental apparatus and procedure

Before the experiments, the polymers were dissolved in TMOS in a sealed bottle by vigorous stirring for 24 h. It should be noted

that TMOS is a good solvent for both PMMA and PS; PS dissolves in TMOS more readily than PMMA. The solubility parameter is defined as the square root of the cohesive energy density. Substances with similar solubility parameters are easily mixed. The solubility parameters of PMMA and PS are 9.1 (298 K) and 8.5–9.1, respectively [15]; thus, TMOS should have a similar solubility parameter. Thus, the solution behavior could be expected to be similar with each other.

In this work, the ternary system phase diagram was deduced using a synthetic method. The details of the experimental apparatus and procedures have been described previously [13]. In summary, appropriate amounts of CO<sub>2</sub>, TMOS, and the polymers were sealed in the front side of a viewing cell containing a moving piston. The temperature was raised to the desired value and the cell was pressurized until a single phase was achieved by pushing the moving piston from the back side. Then, the pressure was slowly decreased until the phase separation occurred. The cloud-point (CP) pressure is defined as the pressure at which the solution becomes so opaque that it is no longer possible to see the magnetic stirring tip in the cell. The bubble-point (BP) pressure is defined as the pressure at which small bubbles appear in the cell. The CP and BP were observed visually by the eye through the view window. After the cloud point and bubble point were obtained, the mixture was recompressed into a single phase and the process was repeated at least five times.

For all the measurements, the total uncertainties were  $\pm 0.1$  K,  $\pm 0.01$  MPa, and  $\pm 1.31 \times 10^{-3}$  (CO<sub>2</sub>/TMOS/polymer system) in terms of temperature, pressure, and composition, respectively (see Supporting Information).

## 3. Results and discussion

Schematic views of the phase behaviors of the ternary systems are shown in Fig. 1. When the CO<sub>2</sub> mass fraction was low, the BP (Fig. 1(b)), at which the vapor-liquid (VL) phase separation occurs, was observed in the initially uniform mixture (Fig. 1(a)). Further decrease in pressure led to clear VL phase separation (Fig. 1(c)). On the other hand, when the CO<sub>2</sub> mass fraction was high, the CP (Fig. 1(d)), at which the liquid-liquid (LL) phase separation occurs, was observed. After the mixture was allowed to stand still for several hours, clear LL equilibrium could be observed (Fig. 1(e)). Further decrease in pressure led to the formation of the vapor phase (Fig. 1(g)) at the vapor-liquid-liquid (VLL) boundary (also defined as BP (Fig. 1(f))).

### 3.1. CO<sub>2</sub>/TMOS/polymer system

The experimental results are shown in Figs. 2–4 and 6–7 and summarized in Tables 3–15 for the CO<sub>2</sub>/TMOS/PMMA ternary system and CO<sub>2</sub>/TMOS/PS ternary system, respectively. Fig. 2 shows the typical phase diagram of CO<sub>2</sub>/TMOS/polymer systems for samples with similar molecular weights (Mw = 35,000). The horizontal axis represents the CO<sub>2</sub> mass fraction and the vertical axis represents the pressure. The CO<sub>2</sub>/TMOS/polymer systems exhibited two different types of phase behaviors with changes in the CO<sub>2</sub> mass fraction as described above. It can be seen from the figure that the VLL lines extend along the VL lines. Further, the VLL and VL lines for both polymers are identical. These facts are discussed in detail in Section 3.4.

Unlike the VL and VLL lines, the LL lines differ from each other significantly. The LL line of PS separates from the VL line at a lower CO<sub>2</sub> mass fraction compared to PMMA, and it shows greater CO<sub>2</sub> mass fraction dependence. The LL phase separation may be attributed to CO<sub>2</sub> being a poor solvent for the polymer solution. Although PS and PMMA are insoluble in CO<sub>2</sub> [16], CO<sub>2</sub> dissolves into

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