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Containerless melting and crystallization of diamagnetic organic materials under magnetic levitation condition

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Abstract. Containerless crystallization of benzophenone and containerless melting of a cycloolefin polymer were performed under magnetic levitation conditions. It was found that the growth mechanism changes from dendritic growth to facet growth with decreasing the supercooling degree in the crystallization of benzophenone. In the case of containerless melting and solidification of a cycloolefin polymer, spherical samples were obtained by a homogeneous heating in an electric furnace with a heatproof bore scope.

1. Introduction
Magnetic levitation of diamagnetic materials has received much attention as a new method for materials processing in high magnetic fields [1-5]. In the magnetic levitation state, the magnetic force acting on materials balances with the gravitational force. Since such a balance holds for each molecule or atom constituting the materials, the magnetic levitation is considered to be almost equivalent to microgravity condition. Its application to materials synthesis enables many novel techniques such as containerless crystal growth. A containerless technique provides clean environment that is free from contamination from a container. Suppressing uncontrollable heterogeneous nucleation, the liquid easily undergoes a supercooled or supersaturated state. The first application of magnetic levitation to crystal growth was the solidification of a water droplet [6]. In this case, supercooled liquid state survived down to −10°C. Next, we have performed crystal growth of ammonium chloride in a levitating aqueous solution [7]. The result showed that the number of growing crystals in the solution is reduced and the droplet surface affects the growth direction of the crystal. The dendritic growth appeared two-dimensionally along the surface of the droplet. In this paper, we show the in-situ observation for crystallization of a melt droplet of benzophenone under the magnetic levitation condition.

The containerless technique has been applied to melt-solidification of levitating materials. A levitating cubic glass was melted without a crucible in the CO$_2$ laser furnace and became a complete sphere after cooling [8]. In the case of the containerless melting of paraffin by homogeneous heating with the YAG laser furnace, the magnetic orientation of paraffin molecules was observed after solidification [9]. Recently, we have developed a new levitation furnace with an electric heater and a heatproof bore scope. This furnace enables homogeneous heating of organic polymers and its in-situ observation. The melt of organic polymers is difficult in the laser furnaces, because clear plastics, for example, have no absorption of the YAG laser light and thermal decomposition occurs before melting in the CO$_2$ laser furnace.
2. Experiments

2.1. Containerless crystallization of benzophenone

Benzophenone crystal (molecular formula: C_{13}H_{10}O) belongs to the orthorhombic symmetry with space group \textit{P2}_1\textit{2}_1\textit{2}_1, and the unit cell dimensions are \(a = 10.26\), \(b = 12.09\), \(c = 7.88\) Å [10]. The magnetic susceptibilities of the crystal have been reported to be \(\chi_a = -88.0 \times 10^{-6}\), \(\chi_b = -88.6 \times 10^{-6}\) and \(\chi_c = -149.3 \times 10^{-6}\) cm$^3$/mol [11]. Since the anisotropy of the susceptibility is very large, a magnetic orientation effect is expected when the crystal grows in magnetic fields. In the case of crystal growth from the solution in magnetic fields, it has been reported that the crystals grew as the \(c\)-axis is perpendicular to the magnetic field [12].

Benzophenone (Wako Pure Chemical Industries, Ltd., 98.0 %) with melting point of 48-50°C was used for containerless crystallization experiments. The CO$_2$ laser furnace with a thermostatic bath was used to melt a crystal and to control the temperature during crystallization. Figure 1 shows the schematic illustration of the experimental setup in a hybrid magnet (28T-HM). A benzophenone crystal stuck on a Pt wire (0.5 mm in diameter) was melted by irradiation of CO$_2$ laser light at the central field of 22.1 T, and a droplet of the melt levitated on the tip of the Pt wire at 92 mm above the center of the magnet. In this case, a crystal was not melted entirely in order to leave a nucleus. The crystal growth in a supercooled melt was observed at each constant temperature of 10, 30, 40 and 45°C.

![Figure 1](image_url)

**Figure 1.** Schematic illustration of a CO$_2$ laser furnace combined with a thermostatic bath in a hybrid magnet.

Figures 2 and 3 show the crystallization process of benzophenone at 30 and 45°C, respectively. The dendritic growth was observed at 30°C, while the facet growth appeared in the melt at 45°C. The final shape of crystals is not sphere-like, but more as a flattened object with the larger axis perpendicular to the magnetic field. Results suggest that the growth mechanism changed with decreasing the growth rate due to decrease of the supercooling degree. Furthermore, in the case of 45°C, it was observed a large square grain appears in left side of the crystal. This grain was considered to be a single crystal,
but we could not check the growth direction of the grain because it was broken in handing the sample unfortunately.

Figure 2. Crystallization process of benzophenone at 30°C under the magnetic levitation condition. Times in figures show the elapsed time from the crystallization starts.

Figure 3. Crystallization process of benzophenone at 45°C under the magnetic levitation condition.

2.2. Containerless melting of a polymer
A sample was a cycloolefin polymer; ZEONEX (ZEON Corp.), which is a clear plastic used for optical lenses. The magnetic susceptibility per unit mass was \( \chi = -10.63 \times 10^{-9} \) m/kg measured by a SQUID magnetometer. The melting point is not clear but the glass transition temperature is 138°C. In order to achieve the magnetic levitation state, a cryocooled hybrid magnet (27.5T-CHM) with a 52 mm room temperature bore [13] was used.

Containerless melting experiments were performed by using an electric furnace, which can produce high temperature up to 1200°C in high magnetic fields [14]. In order to observe a levitating sample in heating process, a heatproof bore scope (Schölly Fiberoptic GmbH) was used. The bore scope with optical relay lenses cooled by a water jacket can be used up to 800°C. A piece of ZEONEX sample almost levitated, when the central field became 17.0 T. The temperature was raised to 226°C at a rate of 15°C/min in a N\(_2\) gas atmosphere. After the sample began to melt around 150°C, the magnetic field was adjusted to 18.0 T from 17.0 T. The sample melted and solidified in the situation of slightly contacting with a sample holder.

Figure 4. Cycloolefin polymer, ZEONEX, melted and solidified (a) under the magnetic levitation condition and (b) in zero field. Arrows show directions of diameters measured.
The sample solidified in a spherical shape as shown in figure 4(a). For the comparison, the sample solidified in zero field is shown in figure 4(b). Sphericity was determined by measuring the diameter of the sample in two directions as shown in figure 4(a). The diameter, $d_1$, in the horizontal plane and $d_2$ in the tilted direction were $d_1=3.212\pm0.007$ and $d_2=3.237\pm0.017$ mm, respectively. The coincidence of diameter between two directions means that the melt of the sample was under the microgravity condition. Small bubbles were observed in the solidified samples. In order to prepare sample for optical applications, heating and cooling processes must be optimized.

3. Summary
We have performed containerless crystallization experiments of benzophenone and containerless melting experiments of a cycloolefin polymer under the magnetic levitation conditions. The former experiment demonstrated the in-situ observation of dendritic and single crystal growth from the levitating melt. The later shows that a homogeneous heating enables containerless melting of polymers. Magnetic levitation surely has a potential enough to provide a novel technique for materials synthesis.

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