

Surface melting of crystallized poly(vinylidene fluoride) under carbon dioxide

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ABSTRACT

We investigated the melting behavior of the crystallized poly(vinylidene fluoride) (PVDF) under pressurized CO₂ by *in-situ* Hv light scattering measurement. In the heating process, the Hv light scattering intensity started to decrease at low temperature far below the melting temperature while the ordering of the crystallites, estimated by the broadening of the light scattering profile, did not change up to the vicinity of the melting temperature. The decrease of the scattering intensity was steeper with increasing CO₂ pressure and was thermally reversible. These results suggest that surface melting occurs in the crystallized PVDF under pressurized CO₂. The surface melting under CO₂ might be attributed to the dragging of the crystalline chains by the amorphous chains in which the molecular motion is enhanced by the plasticization effect of CO₂. Owing to the decrease of the lamellar thickness by the surface melting, the melting temperature depression occurred under pressurized CO₂.

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1. Introduction

Polymer molecules crystallize via cooling from the melt state. The polymer crystals thus obtained melt in the heating process by first order phase transition. This melting behavior is thermally irreversible; i.e., the melting temperature in the heating process is higher than the crystallization temperature in the cooling process. On the other hand, thermally reversible melting occurs in several crystalline polymers; i.e., melting occurs at almost same temperature in which the crystallization occurs [1–6]. Two possible origins are considered for thermally reversible melting. One is melting of thermally unstable thin lamellae and the other is surface melting.

The surface melting is an unusual phenomenon limited in linear polyethylene and poly(ethylene oxide) [1–5]. The mechanism of the surface melting has been studied experimentally by the results of small-angle X-ray scattering [2,3] and temperature modulated DSC [4,5]. The thickness of the crystalline phase decreases continuously with increasing temperature by the shift of the crystalline–amorphous interface. The excess reversing heat capacity was observed due to an additional contribution of reversible melting on the fold surface. The molecular dynamics simulation suggests that the surface melting is not a process of simple release of the crystalline ordering at the fold surface, but a high longitudinal diffusion within the crystalline phase is an essential prerequisite [7]. Since the crystalline stems are connected to amorphous chains such as tie, loop, folds and cilia, the chain motion of the crystalline stems are correlated to that of the amorphous chains, as suggested by the

NMR measurement [8–10]. Hence, the surface melting is expected to be enhanced by increasing the molecular motion of the amorphous chains. However, so far, influence of the molecular motion on the melting has not been experimentally clarified.

The molecular motion of amorphous chains can be accelerated by dissolving carbon dioxide (CO₂); i.e., the molecular motion increases with increasing CO₂ pressure [11–15]. The dissolved CO₂ causes a plasticization effect such as dilation [16], depression of glass transition temperature [11,17,18], and decrease of viscosity [19]. In several crystalline polymers, melting temperature depression under CO₂ was reported by the results of high pressure DSC measurement [17,18], dilation measurement [20,21] and cloud point method [22]. Because the packing of the crystalline chain is tight, CO₂ is insoluble in the crystalline region and the insolubility was verified by *in-situ* dielectric relaxation measurement under CO₂ [23]. Due to the insolubility of CO₂ in crystalline region, the sorption and solubility of CO₂ into crystalline polymers are much smaller than those of amorphous polymers [24–26]. Since CO₂ is insoluble in the crystalline region whereas it dissolves in the amorphous region and the motion of the amorphous chain is enhanced under CO₂, the influence of the molecular motion of the amorphous chains on the melting can be discussed by the melting behavior and the structure change in the heating process under CO₂ at various CO₂ pressures.

In this paper, we investigated the melting behavior and the structure change of crystallized poly(vinylidene fluoride) (PVDF) in the heating process under CO₂ at various CO₂ pressures by using light scattering apparatus equipped with a high-pressure visualized cell. Here, we used crystallized PVDF as a specimen because insolubility of CO₂ in crystalline region was verified [23], melting

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temperature depression under CO₂ was suggested [20,22], and four-leaf clover type light scattering pattern is observed [27]. *In-situ* observation of the structure change was also carried out by using a high fidelity digital microscope for comparison with the light scattering measurement. The characteristic melting behavior under CO₂ was discussed in terms of the molecular motion of the amorphous chains enhanced by increasing CO₂ pressure.

2. Experimental

The PVDF powder used in this study was supplied by Kureha Chemical Industry Co., Ltd. (KF1000, $M_w = 250,000$, $M_w/M_n = 2.27$). The PVDF powder was dissolved in *N,N*-dimethyl acetamide with a weight concentration of 8 wt%. The solution was cast onto cover glasses, and the solvent was evaporated under a reduced pressure of 10^{-2} mmHg at room temperature. The cast films were further dried under vacuum (10^{-4} mmHg) at room temperature for 3 days and then at 120 °C for 24 h to completely remove any residual solvent. The thin film specimen (ca. 20 μm thick) thus prepared was used for the microscope observation. For light scattering measurements, thick film specimen (ca. 0.1 mm thick) was prepared by compression molding the PVDF powder between two cover glasses at 220 °C for 5 min. In order to obtain the crystallized film specimen, the film specimen thus prepared was annealed for 60 min at the crystallization temperature T_c of 120 °C in hot stage after melting at 220 °C for 5 min by rapid transfer from another hot stage. The specimen crystallized at $T_c = 155$ °C was also prepared for comparison.

In-situ microscope observation and *in-situ* light scattering measurement under high-pressure CO₂ were carried out by using a specially designed custom-made high-pressure cell constructed of stainless steel with an inner volume of 20 mL equipped with two sapphire windows for both through view and transmittance of light, as schematically shown in Fig. 1. The detail of the instrument is described in our previous papers [28,29]. The crystallized film specimen was placed on the glass plate on the lower sapphire window and high-pressure CO₂ was injected into the cell by a syringe pump (NP-KX-500, Nihon Seimitsu Kagaku Co., Ltd.) at room temperature. The specimen was kept in position for 1 h to dissolve CO₂ into the specimen and the temperature was then raised with an

autotune temperature controller unit in conjunction with a thermocouple. The pressure of CO₂ was kept constant in the heating process by using a back pressure regulator.

Microscope observation under CO₂ was performed with a digital high-fidelity microscope (MX-5030SZII, Hirox Co., Ltd.) equipped above the high-pressure visualized cell. For a clear image of the structure, halogen light was irradiated onto the specimen from the lower part of the cell. Light scattering measurement under CO₂ was performed by applying vertically a He–Ne laser with a wavelength of 632.8 nm to the film specimen in the high-pressure cell. The scattered light was passed through an analyzer and then onto a highly sensitive charge-coupled device (CCD) camera with a sensor of 576×382 pixels (Princeton Instruments, Inc., TE/CDD-512-TKM-1). We employed Hv geometry in which the optical axis of the analyzer was set perpendicular to that of the polarizer [6,25,27]. The input data from the CCD camera was digitized by an ST-13X controller and was stored in a personal computer for further analysis. For the background subtraction, the Hv scattering intensity of the molten state of PVDF specimen was subtracted from that of the crystallized specimen. The microscope observation and light scattering measurement were carried out at fixed temperature. Then, subsequent observation and measurement were carried out at higher temperature. In this way, the isothermal observations and measurements were repeated at appropriate temperature intervals in the heating and cooling processes.

The dielectric measurements of the crystallized film specimen were performed at 100 °C with a Solartron SI 1260 Impedance/Gain-Phase Analyzer equipped with an impedance transformer (SI 1296 Dielectric Interface, Solartron) at a frequency, f , ranging from 10^2 Hz to 10^6 Hz under air at ambient pressure. The angular frequency, ω , was obtained by $\omega = 2\pi f$.

3. Results and discussion

Fig. 2 shows the *in-situ* observation of the crystallized PVDF ($T_c = 120$ °C) by using optical microscope in the heating process (a) under air at ambient pressure and (b) under CO₂ at 10 MPa. Spherulite having a size of several μm is seen. Change of the spherulite structure was not observed up to the vicinity of the melting temperature in the heating process under air at ambient pressure. The contrast of the spherulite became lower when the temperature was raised to 160 °C and the structure disappeared completely at 180 °C (Fig. 2a). Similar structure change was observed under CO₂, but the structure disappeared at lower temperature under CO₂ than that under air at ambient pressure; e.g., the structure disappeared completely at 174 °C under CO₂ at 10 MPa (Fig. 2b). The temperature in which the structure disappears completely was defined as melting temperature. The melting temperature thus obtained is shown by open squares in Fig. 3. The melting temperature decreases with increasing CO₂ pressure. This indicates that the melting temperature depression occurs in the crystallized PVDF under CO₂. The structure change in the heating process was quantitatively discussed by the results of Hv light scattering measurements, as in the following.

Fig. 4 shows the Hv light scattering patterns of the crystallized PVDF ($T_c = 120$ °C) at various temperatures in the heating process (a) under air at ambient pressure and (b) under CO₂ at 10 MPa. Four-leaf clover type pattern was observed, suggesting that spherulites are formed and crystallites are regularly arranged along the radial direction [6,27]. The change of the scattering intensity was larger and the scattering pattern disappeared at lower temperature under CO₂ than those under air at ambient pressure.

In order to quantitatively evaluate the change of the Hv light scattering intensity in the heating process, we employed the

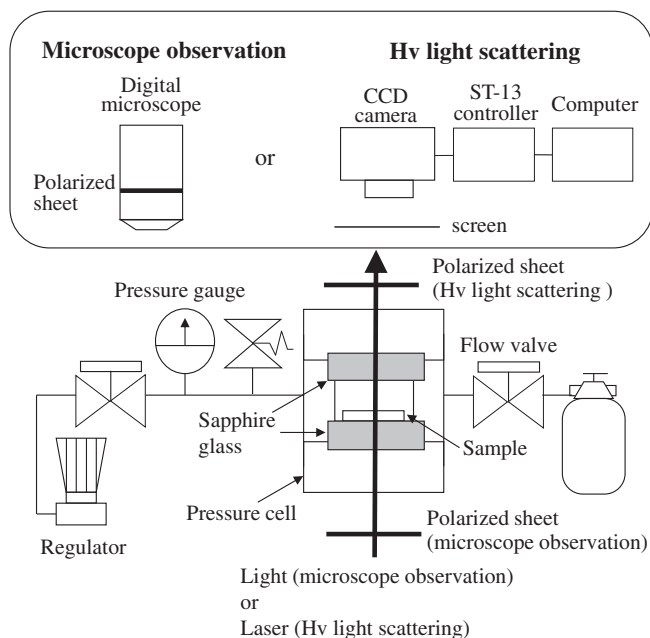


Fig. 1. Schematic illustration of the instrumental setup for both the *in-situ* microscope observation and light scattering measurement.

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