1. INTRODUCTION

Drying process of droplets on a flat substrate is a commonly observed phenomenon in our daily life. Because of their important roles in the nature and in industry, drying droplets have been a topic of continued interest for several decades.\(^1\)\(^-\)\(^3\) Recently, the drying process of droplets containing non-volatile materials is focused as an important problem in inkjet printing, which is attracting increasing attention as a key factor in the next-generation fabrication processes for microelectronics\(^4\)\(^-\)\(^6\) and biomaterials.\(^7\)\(^-\)\(^9\) A problem that needs to be considered here is the control of the thickness profiles of the solute films deposited on the substrate after the droplets totally dry up.

When a droplet containing non-volatile materials dries on a substrate, generally observed phenomena are the pinning of the contact line during the drying process and the formation of the solute film having a ring-like profile. These phenomena, commonly known as “coffee ring effect”, were studied by Deegan et al. for colloidal suspension systems.\(^10\)\(^,\)\(^11\) The formation of the ring-like solute deposit is attributable to the outward capillary flow that is driven by the combined actions of the contact line pinning and enhancement of the solvent evaporation in the vicinity of the contact line.\(^12\) The coffee ring effect has been observed and studied in various systems, such as colloidal suspensions\(^13\)\(^-\)\(^15\),\(^24\) polymer solutions\(^16\)\(^-\)\(^18\), and DNA solutions.\(^19\)

For many applications, it is required to realize a flat film without a ring, and how to achieve it is an important challenge. Several approaches have been proposed to suppress the outward flow and to obtain a flat film, such as to control the initial contact angle of the droplet\(^20\)\(^,\)\(^21\), to control the substrate temperature\(^22\), and to use a mixed solvent.\(^23\) For practical applications, the method that can be applied universally independent of the component in the droplet is desired.

In this paper, we report a series of experimental works about the drying process of polymer solution droplets under the geometry that the contact line is strongly pinned. Our works have two objectives:

**Detailed Analysis of Local Polymer Transport**

In the previous experimental works, the evaluation was conducted mainly from the surface profile of droplet and the shape of final deposit. Such measurements are not sufficient to understand the local transport inside the droplet, i.e., the flow...
field and the concentration field of the solute polymer.

These two factors are crucial for evaluating the coffee ring effect dynamically. Although the flow field has been measured by the tracer particle method, no effective method for measuring the solute concentration field has been reported so far.

In chap. 2, we report a new observation method for the polymer concentration field in the drying droplet. In this method, the concentration field can be obtained from the simultaneous measurement of the fluorescence profile of solute polymer and lateral profile of the droplet. We observed that a large spatial inhomogeneity of the polymer concentration grows between the center and edge of the droplet, which is considered to be caused by the outward flow. We also proposed a simple theoretical analysis by comparing the effect of the polymer convection to the polymer diffusion.

Control of Film Profiles

One of the effective methods for controlling the film profile is the use of the Marangoni effect: a flow driven by the gradient of the surface tension $\gamma$. If $\gamma$ near the edge of the droplet is lowered during the drying process, the Marangoni force, which is proportional to the gradient of $\gamma$, will create a flow directed toward the center of the droplet that will suppress the outward flow. This possibility was studied by Hu et al. and Ristenpart et al. for a Marangoni flow driven by the gradient of temperature, the thermal Marangoni effect.

The Marangoni effect is also caused by the gradient of the solute concentration: the concentration Marangoni effect. It was reported that in the droplets of certain polymer solutions in which the surface tension has a negative dependence on the polymer concentration, the concentration Marangoni effect changes the motion of the contact line and the profile of the polymer film.

If a certain material that lowers the surface tension of the liquid is added to the droplet, Marangoni effect can be used for an arbitrary polymer solution. A candidate for such a material is a surfactant. In chap. 3, we report that the addition of surfactants strongly affects the drying and film-formation process of polymer solution droplets. We observed that the addition of a small amount of surfactants makes the profile of a polymer film flatter. We conducted experiments in which we varied parameters such as the polymer concentration, droplet volume, type of surfactant, type of solvent, and surfactant concentration. We discuss how these parameters affect the leveling effect of surfactants and also propose a possible mechanism for this phenomenon.

Another possibility for obtaining a flat film is modifying the film profile after once the film is formed. In chap. 4, we report that the modification of the film profile is possible by switching between the solvent condensation and evaporation. We found that when the polymer dots are exposed to the solvent vapor and are dried again, their profiles change drastically from ring-like to flat. The changes of the dot profile greatly depend on the time for vapor exposure.

2. DYNAMICAL OBSERVATION OF LOCAL POLYMER TRANSPORT

2.1 Experimental Part

The polymer solution was a fluorescent polystyrene (FPS) dissolved in anisole (ANI: Sigma-Aldrich, USA; boiling point, $T_b = 105 \, ^\circ\text{C}$; viscosity, $\eta = 1.03 \, \text{mPa\cdot s}$). Fluorescent polystyrene was synthesized from the copolymerization of styrene (Junsei, Japan) and 4-acrylamidofluorescein (AAm-F; absorbance: 463 nm, emission: 528 nm) into ethanol. The molar ratio for copolymerization was 1:0.003. The weight-averaged molecular weight ($M_w$) of fluorescent polystyrene was measured as 62 kD.

The substrates was a glass slide (Matsunami, Japan) silanized with silane-coupling agents (3,3,4,4,5,5,6,6,6-nonafluorohexyltrichlorosilane, Shinetsu, Japan). The contact angle of pure anisole on this substrate was ca. 30°. We confirmed that during the drying process of FPS-ANI droplet, the contact line was kept to be pinned until the last stage of drying.

Figure 1 shows the setup for the measurement. The substrate was set on an inverted microscope (Model IX71, Olympus, Japan).
Japan) with a 4 × magnification lens. A droplet of the polymer solution was placed on the substrate with a micropipette, and was dried under an atmospheric condition. The initial volume of each droplet $V_i$ was ca. 0.5 μl. In our experiment, the temperature and humidity were ca. 25 °C and 30 %, respectively. The light from the mercury lamp was filtered and used for excitation ($\lambda$ : 470-490 nm). The emission from the droplet was observed from the bottom through an optical filter ($\lambda$ : 515-550 nm). For the observation of the lateral profile of the droplet, a prism and CCD camera (Model CMOS130-USB2, Fortissimo, Japan) with a magnification lens (Model TS-9 L-CZ8, Fortissimo, Japan) were located on the side of the droplet. White light which was passed through an optical filter (630-700 nm) was used for illumination.

To check the dependence of the fluorescence intensity $I$ on the height $h$ and polymer volume fraction $\phi^{pol}$, we also conducted a supplemental experiment as is shown in fig. 2 (a).

The ANI-FPS solution was sandwiched between two glass plates, which form a rectangular triangle with a fixed aspect ratio $H/R$ ($H = 19.3$ mm, $R = 46.1$ mm). The fluorescence intensity was measured from the bottom as a function of the distance from the apex $x$. By converting $x$ to $h = (H/R)x$, the dependence of $I$ on $h$ was obtained. From the plots of $I$ against $h$, the intensity per unit height of the light path ($I_0 = I/h$) was calculated for various $\phi^{pol}$. The results are shown in fig. 2 (b) and (c). It is confirmed that the dependence of $I$ on $h$ and dependence of $I/h$ on $\phi^{pol}$ are almost linear within the range of height relevant in our experiment ($h \leq 0.3$ mm).

### 2.2 Experimental Results

Figure 3 (a) shows the sequential pictures obtained by the simultaneous measurement of the fluorescence and lateral profiles: the upper are the lateral profiles and the lower are the fluorescence profiles. The initial polymer volume fraction $\phi^{pol}_0$ is 0.02. For the sake of comparison, the time $t$ are normalized by the characteristic drying time $t_f$. $t_f$ is given by the extrapolation of the initial drying rate of the solvent $V$ as

$$t_f = \frac{V(1-\phi^{pol}_0)}{V}.$$  \hspace{1cm} (1)

(Note that $t_f$ is not the same as the actual total drying time. Because the drying rate slows down at the late stage, the actual drying time is slightly longer than $t_f$.) From the fluorescence images, the intensity profiles of the cross sections were measured and plotted in fig. 3 (b).

At an early stage of drying, the fluorescence intensity is highest at the center, and lowest near the edge, which corresponds to the profile of the droplet. As the drying proceeds, although the droplet profile still keeps a spherical cap, the intensity near the central region decreases while

![Fig. 2](image)

**Fig. 2.** (a) Schematic of the supplemental experiment for measuring the dependence of the fluorescence intensity $I$ on the height $h$ and polymer volume fraction $\phi^{pol}$. (b) Plot of $I$ against $h$. (c) Plot of the intensity per unit height $I_0 = I/h$ against $\phi^{pol}$. $I_0$ is normalized by $I_0^{pol} = 0.01$.

![Fig. 3](image)

**Fig. 3.** (a) Images of fluorescence and lateral profile of the droplet in different timesteps $t/t_f$. (b) Cross sections of the intensity profiles in different timesteps $t/t_f$. The radial position $r$ is normalized by the initial radius of droplet $R$. In both figures, the initial polymer volume fraction $\phi^{pol}_0$ is 0.02.
the intensity near the edge increases. The change of the fluorescence distribution indicates that in the drying droplets, there exists a radial polymer transport towards the edge.

As is already confirmed in the supplemental experiment in fig. 2, there exists a linear relationship between the profile of intensity \( I(r, t) \), polymer volume fraction \( \phi(r, t) \) and height \( h(r, t) \) as

\[
\phi^{\text{pol}}(r, t) = C \frac{I(r, t)}{h(r, t)}.
\]

Equation (2) indicates that by dividing the intensity profile \( I(r, t) \) with the height profile \( h(r, t) \) that is obtained from the observation of the lateral view, it is possible to reconstruct the profile of polymer volume fraction \( \phi^{\text{pol}} \). The constant \( C \) is determined from the data that is obtained just after the placement of the droplet where \( \phi^{\text{pol}} \) must be equal to the initial volume fraction \( \phi_i^{\text{pol}} \).

Figure 4 shows the cross sections of the reconstructed polymer volume fraction profiles in different time steps \( \phi^{\text{pol}}(r/R, t/t_i) \). The volume fraction \( \phi^{\text{pol}} \) shown in fig. 4 exceeds the maximum value 1.0. This is because we used eq. (2) for all polymer volume fraction profiles in different time steps. In reality, the linear relation between \( I \) and \( \phi^{\text{pol}} \) breaks down at high \( \phi^{\text{pol}} \). Therefore, the value of \( \phi^{\text{pol}} \) near the contact line is not accurate.

It is clearly observed that a large spatial inhomogeneity of the polymer volume fraction exists in the radial direction. Near the edge, there is a region in which \( \phi^{\text{pol}} \) is considerably higher than the central region: the concentrated region. The concentrated region is visible even at the early time of drying \( (t/t_i = 0.1) \), and grows inward as the drying proceeds. The existence and growth of the concentrated region clearly demonstrates the transport and accumulation of the polymer toward the edge due to the outward flow, i.e., the coffee ring effect. After the droplet totally dries up, the profile of the resulting polymer film was measured and it was confirmed that the polymer film has a ring-like profile: most of the polymer is placed near the edge. The ring-like profile of the polymer film is consistent with the growth of the concentrated region observed in the measurement of the polymer volume fraction field.

To discuss the transport of polymer by the outward flow in detail, the polymer volume fraction near the center of the droplet \( \phi^{\text{pol}}_{c} \) was calculated. Figure 5 shows the plots of \( \phi^{\text{pol}}_c \) against \( t/t_i \). Suppose the ideal case: there is no effect of the convection (outward flow) and all polymer stays at the initial position during the entire drying process. In that case, \( \phi^{\text{pol}} \) is kept to be spatially uniform and the time dependence of \( \phi^{\text{pol}} \) is given by

\[
\phi^{\text{pol}}(t) = \frac{\phi^{\text{pol}}_{\text{sur}}}{1 - \phi^{\text{pol}}(1 - t/t_i)}.
\]

This case is also plotted in Fig. 5 by a green solid line. On the contrary, in the experimental data, the increase of \( \phi^{\text{pol}}_c \) delays greatly compared to the ideal case. \( \phi^{\text{pol}}_c \) does not increase until the late stage of drying \( (t/t_i \approx 0.8) \). This result indicates that during the drying process, most of the polymer that is initially located near the center is transported to the edge.

To check the effect of the evaporation rate, the same measurement was conducted for the droplets dried in a small box which is saturated with ANI vapor. In this box, the

![Fig. 4](image_url)  
**Fig. 4.** Cross sections of the profiles of polymer volume fraction in different timesteps \( t/t_i \). The radial position \( r \) is normalized by the initial radius of droplet \( R \). The initial polymer volume fraction \( \phi^{\text{pol}}_i \) is 0.02.

![Fig. 5](image_url)  
**Fig. 5.** Plot of the polymer volume fraction in the central region \( \phi^{\text{pol}}_c \) against \( t/t_i \). The initial polymer volume fraction \( \phi^{\text{pol}}_i \) is 0.02. The experimental data are shown as points (two cases are shown: dried in atmosphere and in a small box). The solid line indicates the case that the droplet keeps its volume fraction spatially uniform.
The evaporation rate was lowered about 1/3 of the atmospheric condition. The result of the $\phi_v^{pol}$ against $t/t_i$ is plotted in fig. 5. It is observed that in the case of drying in the box, $\phi_v^{pol}$ starts to increase at an earlier stage and the data points go closer to the curve of the ideal case.

### 2.3 Discussion

The growth of the concentrated region near the edge and the delay of the increase of polymer volume fraction in the central region can be discussed in terms of the competition between the convection of the polymer by the outward flow and the diffusion of the polymer. In the drying droplet of polymer solution, the governing equations are the local conservation of the solvent:

$$\frac{\partial h}{\partial t} + \nabla \cdot \bar{Q} = \frac{\bar{J} \cdot \bar{n}}{\rho},$$  \hspace{1cm} (4)

and the polymer:

$$\frac{\partial}{\partial t}(\phi^{pol} h) + \nabla \cdot \phi^{pol} \bar{Q} = \nabla \cdot (Dh \nabla \phi^{pol}).$$  \hspace{1cm} (5)

Here, $\bar{V} = (\partial/\partial t, \partial/\partial y)$, $h(\bar{r}, t)$ is the height of the droplet surface, $\bar{J}$ is the evaporative flux of the solvent per unit area, $\bar{n}$ is a unit vector normal to the surface, $\rho$ is the solvent density, and $D$ is the diffusion coefficient, where $\bar{r} = (x, y)$ is a two-dimensional vector. The volume flux $\bar{Q}$ is an integration of the velocity field in vertical direction:

$$\bar{Q}(\bar{r}, t) = \int_{0}^{1} \bar{u}(\bar{r}, z, t) \, dz$$  \hspace{1cm} (6)

Given the appropriate profile of the evaporative flux $\bar{J}$ and the initial profile of the droplet $h$, detailed analysis is possible using a numerical simulation. Here we make a simple analysis. Suppose that at the edge of the droplet, the fluid of volume $J$ is taken out per unit time per unit surface area. For the contact line to be kept pinned, this volume has to be supplied by the outward flow from the center. The conservation of volume at the region is expressed as

$$\pi R^2 J \approx \pi RHU,$$  \hspace{1cm} (7)

where $R$ and $H$ are the radius and height of the droplet and $U$ is the characteristic velocity of the outward flow. Therefore, $U$ is estimated from $J$ as

$$U \approx \frac{R}{H} J.$$  \hspace{1cm} (8)

In our experimental system, $|dV/dt| = \pi R^2 J \approx 1.0 \text{ nL/s}$, $R \approx 1.0 \text{ mm}$, and $H \approx 0.3 \text{ mm}$. So $U$ is calculated as $U \approx 10^{-6} \text{ m/s}$.

Now the characteristic flow velocity has been obtained, let us compare the magnitude of the polymer transport by the outward flow to the polymer diffusion. This is possible by calculating the Peclet number:

$$Pe = \frac{UR}{D}.$$  \hspace{1cm} (9)

Here we chose the radius of the droplet $R$ as the size of the system. Substituting the experimental values $D = 2.0 \times 10^{-11} \text{ m}^2/\text{s}$, Peclet number is calculated as $Pe \approx 50$. This result indicates that in the drying droplets, the effect of the convection dominates the system and the inhomogeneity of $\phi^{pol}$ grows between the center and the edge, which is consistent with our experimental results.

Equation 9 also indicates a possibility that in the case the polymer diffusion competes with the transport by the outward flow, the polymer distribution becomes spatially uniform. In fact in the drying droplets confined in a small box where the Peclet number is ca. 15, it was observed $\phi_v^{pol}$ starts to increase at an earlier stage.

### 3. CONTROLLING DRYING AND FILM FORMATION PROCESSES WITH A SMALL AMOUNT OF SURFACTANT \(^{35}\)

#### 3.1 Experimental Part

The polymer solution is monodispersed polystyrene (PS; Sigma-Aldrich, USA; $M_w = 2460$ Da) dissolved in dipropylene glycol methyl ether acetate (DPMA; Sigma-Aldrich, USA; $T_b = 200 \text{ °C}$, $\eta = 1.7 \text{ mPa} \cdot \text{s}$, $\gamma = 28.3 \text{ mN/m}$). This solution is the same as that used by Jung et al. \(^{36}\) and its basic properties (surface tension $\gamma$, viscosity $\eta$, diffusion coefficient $D$) are mentioned in their paper. Solutions having three different initial polymer concentrations by weight - $c_{pol}^0 = 5\%$, 10\%, and 20\% (initial volume fractions $\phi_v^{pol} = 0.046$, 0.093, and 0.188) - were used.

For the surfactant, two types of surfactants - fluorosurfactant F470 and F489 (DIC, Japan) - were used. The surface tension $\gamma$ of DPMA was measured using a Du Noüy tensiometer (Itoh Seisakusyo, Japan) against the concentration of the surfactant by weight $c_{sur}^{pol}$, and it is plotted in fig. 6. For both F470 and F489, $\gamma$ decreases sharply at a low concentration, 0% $\leq c_{sur}^{pol} \leq 0.5\%$. In this region, the slope $|\partial \gamma/\partial c_{sur}^{pol}|$ of F489 is larger than that of F470. At a high concentration, the slope decreases but $\gamma$ still continues to decrease. In most cases in our experiments, the initial concentration of the surfactant by weight $c_{sur}^{pol}$ was set as 0.05\%; except for the experiment about the dependence of $c_{pol}^{sur}$. 


To avoid the complication due to the de-pinning of the contact line, we used glass slides patterned with circular bank structures as substrates. The schematics of the substrate are shown in fig. 7 (a) and (b). The internal radius of the bank is 100 µm, and the width and the height are 30 µm and 2.2 µm. The top surface of the bank is made lyophobic: the advancing contact angle of the DPMA $\theta_A$ is $\theta_A \geq 50^\circ$. The remainder of the substrate is lyophilic: $\theta_A \leq 10^\circ$.

Figure 7 (c) shows a schematic of the experimental system. The polymer solution was ejected from a microdispenser system (MD-K-140, Microdrop Technologies, Germany) onto a substrate. To adjust the position of droplet ejection and to observe the lateral profile of the droplet, a CCD camera (Model CMOS130-USB2-3, Fortissimo, Japan) with a magnification lens (Model TS-9 L-CZ8, Fortissimo, Japan) was set at the side of the nozzle. The initial volume of the droplet was set as $V_i = 350$ pl, 500 pl, and 750 pl within an accuracy of ±50 pl. In our experimental condition (temperature was ca. 22 °C, relative humidity was 50 ± 5 %), the respective total drying times of these droplets were ca. 4 min, 6 min, and 8 min.

After the droplet totally dried up, the three-dimensional (3D) surface profile of the polymer film was measured using an optical surface profiler (Wyko NT9100, Veeco, USA) with a 20 × objective lens.

3.2 Experimental Results

Figure 8 shows the 3D profile of the polymer film formed after the droplet totally dries up. Figure 8 (a) shows the data for the droplet of a polymer solution with no surfactant, and fig. 8 (b), that for the droplet of a polymer solution containing the surfactant F489 ($c_{i,sur} = 0.05 \%$). In both droplets, the initial polymer concentration is $c_{i,pol} = 10 \%$ and the initial volume of the droplet is $V_i = 750$ pl.

Although the amount of the surfactant is relatively small compared with the amount of the solute polymer, the obtained film profile is totally different in these two cases. With no surfactant, most of the polymer is found near the edge and the resulting polymer film has a ring-like profile. On the other hand, with the surfactant F489, a large amount of the polymer is found near the central region, and as a whole, the film has a flat profile. In other words, the addition of F489 “levels” the profile of the polymer film.

To determine the dependence on the initial polymer concentration $c_{i,pol}$ and the initial volume $V_i$, the profiles of the films formed from droplets of various $c_{i,pol}$ and $V_i$ values...
were measured in the same manner. Figure 9 shows the cross sections of the polymer films of these droplets. Here, the data for the droplets with no surfactant ((a), (d), and (g)), droplets containing the surfactant F470 ((b), (e), and (h)), and droplets containing the surfactant F489 ((c), (f), and (i)) are compared.

The leveling effect is commonly observed irrespective of the parameters $c_i^{\text{pol}}$ and $V_i'$. With no surfactant, the polymer is almost localized near the edge and a film with a ring-like profile appears. On the other hand, with the addition of surfactants, most of the polymer is localized in the central region and the polymer film has a flatter profile. (In the case of $c_i^{\text{pol}} = 20 \%$, $V_i' = 750 \mu l$, the profile of the polymer film is flat even without the addition of surfactants. In this case, the viscosity of the liquid and the initial contact angle are large.

This makes the velocity of the outward flow lower, and most of the polymer remains near the center. Comparing the results of different surfactants, the polymer film becomes flatter in the case with F489 than with F470. We also confirmed that the leveling effect is observed in the droplets of different solvent: PS-Acetophenon (ACE; Sigma-Aldrich, USA; $T_0 = 202 \, ^\circ\text{C}$, $\eta = 1.7 \, \text{mPa}\cdot\text{s}$, $\gamma = 38.8 \, \text{mN/m}$).

To determine the dependence on the surfactant concentration $c_i^{\text{sur}}$, the profiles of the films formed from droplets having various $c_i^{\text{pol}}$ were measured. In this measurement, F489 was used for the surfactant and the initial polymer concentration $c_i^{\text{pol}}$ was fixed to be 10 %. To evaluate the results quantitatively, the volume of the polymer that resides in the central region $V_i^{\text{pol, center}}$ was calculated from the film profile. Here, $V_i^{\text{pol, center}}$ is the volume of the polymer existing within the range $0 \leq r \leq R/2$. For the sake of comparison, $V_i^{\text{pol, center}}$ is normalized by the total volume of the polymer of film in the entire region $V_i^{\text{pol, total}}$.

Figure 10 shows the plot of $V_i^{\text{pol, center}}/V_i^{\text{pol, total}}$ against $c_i^{\text{sur}}$.

It is seen that the magnitude of the leveling effect depends on the surfactant concentration $c_i^{\text{sur}}$. In fig. 10, three distinct regions are observed for the leveling effect in $c_i^{\text{sur}}$.

(a) Very dilute case ($c_i^{\text{sur}} \leq 0.002 \%$): the leveling effect is quite small and the film profile is similar to that in the case without a surfactant.

(b) Dilute case (0.002 % $\leq c_i^{\text{sur}} \leq 0.05 \%$): the leveling effect becomes more prominent as $c_i^{\text{sur}}$ increases.

(c) Concentrated case (0.05 % $\leq c_i^{\text{sur}}$): the leveling effect is almost saturated. $V_i^{\text{pol, center}}/V_i^{\text{pol, total}}$ does not change with the increase of $c_i^{\text{sur}}$.

### 3.3 Discussion

The leveling effect can be explained by the model illustrated in fig. 11. As drying proceeds, due to the outward flow and the enhancement of the solvent evaporation near the contact line, the concentrations of the polymer and the surfactant near the edge become higher than those in the center. Accordingly, the surface tension $\gamma$ near the edge becomes lower than that in the center. The radial gradient of the surface tension, i.e.,

![Fig. 9](image-url)  
**Fig. 9.** Cross sections of the profiles of the polymer films formed after drying. The solid, dashed, and dotted lines indicate the data for $V_i' = 350 \mu l$, 500 $\mu l$, and 750 $\mu l$. The initial polymer and surfactant concentrations are (a) $c_i^{\text{pol}} = 5 \%$ without surfactant, (b) 5 % with F470 ($c_i^{\text{sur}} = 0.05 \%$), (c) 5 % with F489 (0.05 %), (d) 10 % without surfactant, (e) 10 % with F470 (0.05 %), (f) 10 % with F489 (0.05 %), (g) 20 % without surfactant, (h) 20 % with F470 (0.05 %), and (i) 20 % with F489 (0.05 %).

![Fig. 10](image-url)  
**Fig. 10.** Relative polymer volume in the central region $V_i^{\text{pol, center}}/V_i^{\text{pol, total}}$ against the concentration of the surfactant (F489) $c_i^{\text{sur}}$. Here, $c_i^{\text{pol}}$ is fixed at 10 % and different symbols indicate the different initial volumes $V_i$ (500 $\mu l$ and 750 $\mu l$).
the Marangoni force $V\gamma$, causes the Marangoni flow directed toward the center. The transport of the polymer by the outward flow is thus suppressed by this flow, and the final profile of the film becomes flatter.

The magnitude of the Marangoni force $|V\gamma|$ depends on two quantities,

$$|V\gamma| = \left| \frac{\partial \gamma}{\partial c_{\text{sur}}} \right| |\nabla c_{\text{sur}}|,$$

(10)

where $\partial \gamma/\partial c_{\text{sur}}$ denotes the slope of the surface tension decreasing against the surfactant concentration and $\nabla c_{\text{sur}}$, the local gradient of the surfactant concentration. As $|\nabla c_{\text{sur}}|$ and $|\partial \gamma/\partial c_{\text{sur}}|$ increase, the resulting Marangoni force increases and the leveling effect becomes more prominent.

We compare this conjecture with the experimental results. In fig. 9, it is observed that the surfactant F489 makes the profiles of the polymer films flatter than F470. From the fact that $|\partial \gamma/\partial c_{\text{sur}}|$ of F489 is larger than that of F470, these results confirm that the larger $|\partial \gamma/\partial c_{\text{sur}}|$ causes the larger Marangoni force.

The gradual transition of the leveling effect at low $c_{i}^{\text{sur}}$ shown in fig. 10 can be explained in terms of the dependence of $|V\gamma|$ on $|\nabla c_{\text{sur}}|$. As is explained in ref.\textsuperscript{18}, the concentration field of the surfactant depends on its initial concentration. At very low $c_{i}^{\text{sur}}$ ($c_{i}^{\text{sur}} \leq 0.002 \%$), the local gradient of $c_{\text{sur}}$ in the droplet is relatively small and the resulting Marangoni flow is not sufficient to suppress the outward flow. As $c_{i}^{\text{sur}}$ increases ($0.002 \% \leq c_{i}^{\text{sur}} \leq 0.05 \%$), the Marangoni flow competes with the outward flow, and the leveling effect starts to be observed.

In fig. 10, it is seen that $V_{\text{pol}}^{\text{center}}/V_{\text{pol}}^{\text{total}}$ is saturated at high $c_{i}^{\text{sur}}$ ($0.05 \% \leq c_{i}^{\text{sur}}$). We compare the values of $V_{\text{pol}}^{\text{center}}/V_{\text{pol}}^{\text{total}}$ in this region with the values of the ideal case of the leveling effect, i.e., the case in which the Marangoni flow completely suppresses the outward flow and the polymer concentration is kept to be spatially uniform during the entire drying process.

In the case of $V_{i} = 750 \text{ pl}$ and $c_{i}^{\text{pol}} = 10 \%$, $V_{\text{pol}}^{\text{center}}/V_{\text{pol}}^{\text{total}}$ in the ideal case is ca. 0.26, which is nearly identical to the experimental values at high $c_{i}^{\text{sur}}$. This indicates that a small amount of surfactant can level the film profile almost ideally.

The magnitude of the Marangoni force that is required to suppress the outward flow can be estimated by solving the Stokes equation in the drying droplet. In our experiment, the aspect ratio of the droplet $H/R$ is sufficiently small. Therefore, the lubrication approximation can be applied for the calculation of the velocity field $\vec{u}(\vec{r}, z, t)$ and flux rate $\vec{Q}(\vec{r}, t)$. $\vec{Q}(\vec{r}, t)$ is expressed as$^{3,37}$

$$\vec{Q}(\vec{r}, t) = \frac{h^{3}}{3\eta} \nabla (\gamma H^{2} h) + \frac{h^{2}}{2\eta} \nabla \gamma.$$

(11)

The first term of eq. (11) indicates the contribution of the local gradient of the Laplace pressure, which is the driving force of the outward flow. The second term indicates the contribution of the Marangoni force.

The magnitude of the first and second terms can be estimated as$^{37}$

$$Q_{\text{ca}} \sim \frac{\eta H^{4}}{\eta R} (1 + \frac{\Delta \gamma}{\gamma}), \quad Q_{\text{sl}} \sim \frac{\Delta \gamma H^{2}}{\eta R},$$

(12)

where $\Delta \gamma$ is the difference between the surface tension of the center and the edge of the droplet. The ratio of these two terms for small $\Delta \gamma/\gamma$ is given by

$$\frac{Q_{\text{sl}}}{Q_{\text{ca}}} = \frac{R^{2} \Delta \gamma}{H^{2} \gamma}.$$  

(13)

Substituting the experimental values, e.g., $H = 20 \mu m$, $R = 100 \mu m$, $\gamma = 30 \text{ mN/m}$, $\Delta \gamma$ that satisfies $Q_{\text{sl}}/Q_{\text{ca}} = 1$ is calculated to be ca. 1.2 mN/m. This indicates that in small $H/R$, a small Marangoni force is sufficient to suppress the outward flow and to level the film. If the droplet contains F489 ($c_{i}^{\text{sur}} = 0.05 \%$), this condition is satisfied if there is a 0.1 $\%$ difference between $c_{\text{sur}}$ of the center and the edge of the droplet, which is plausible in the actual system.

4. CONTROLLING FILM PROFILES BY SWITCHING BETWEEN EVAPORATION AND CONDENSATION$^{38}$

4.1 Experimental Part

The polymer films were fabricated from the drying droplets of polymer solution. The polymer solution and fabrication process are same as the experiment in chap. III. The polymer solution is monodispersed polystyrene (PS) dissolved in dipropylene glycol methyl ether acetate (DPMA). The initial
polymer concentration by weight $c_{\text{pol}}$ was set as 10%. The polymer solution droplets were ejected from a microdispenser system onto a substrate which has circular bank structures. The volumes of the droplets $V_i$ were set as 400 pl and 800 pl within an accuracy of ± 50 pl. The droplets were dried in an atmospheric condition (temperature and humidity were 23 °C and 45 %, respectively). To make the films completely dried, the films were dried for more than 1 day. Then the films were exposed to the vapor of DPMA. The substrate was placed on a pedestal which is located in the petri dish. The bottom portion of the petri dish was filled with DPMA and a lid was placed on the top to keep the vapor pressure of the solvent high. The time for the of vapor exposure $t_e$ was changed from 1 min to 100 min. After the vapor exposure, the films were dried in an atmospheric condition again, and the three-dimensional (3D) profiles of the polymer films were measured using an optical surface profiler (Wyko NT9100, Veeco, USA) with a 20 × objective lens.

4.2 Experimental Results

Figure 12 shows variations of the dot profiles (3D profiles and cross sections are shown) before and after the vapor exposure, and their dependences on the exposure time $t_e$. Figure 12 (a) is the initial dot profile, (b), (c), and (d) are profiles after the dots are exposed to solvent vapor and are dried again. The exposure time $t_e$ are (b) 3 min, (c) 10 min, and (d) 100 min, respectively.

The film profile drastically changes after the vapor exposure, and the change of the profile depends on the exposure time $t_e$. Even for a short exposure time ($t_e = 3$ min), more polymer is found in the central region and the film becomes flatter than the original profile. This behavior: the leveling of the film, becomes more prominent with the increase of the exposure time $t_e$. In the case of $t_e = 10$ min, the film profile is almost completely flat. However, for further exposure ($t_e > 10$ min), the film goes back to ring-like again. In the case of $t_e = 100$ min, the film profile is almost same as the original profile. We observed that the film profile remains essentially the same for further increase of the exposure time.

For a quantitative analysis, the volume of the polymer that resides in the central region relative to the total volume $V_{\text{center, pol}}/V_{\text{total, pol}}$ was calculated from the cross sections of the profile. Figure 13 shows the plot of $V_{\text{center, pol}}/V_{\text{total, pol}}$ against the exposure time $t_e$. Here, data of two different initial volume $V_i$ (400 pl and 800 pl) are plotted. In both $V_i$, it is observed that there exists an optimal vapor exposure time $t'_e$ to obtain a flat film. $t'_e$ was between 6 and 10 min. For a longer or shorter exposure time, the film profile deviates from flat to ring-like.

4.3 Discussion

The change of the film profile is considered to be caused by the mechanism that is illustrated in fig. 14 (a). When the polymer film is exposed to solvent vapor, the solvent vapor condenses into the film. As the solvent condensation proceeds, the polymer concentration $c_{\text{pol}}$ in the dot decreases and the film changes from a glassy state to a fluid polymer solution, i.e., the film re-fluidizes. Since the thickness of the
film $h$ is considerably small ($h \approx 2 \, \mu m$), the re-fluidization is considered to take place uniformly across the dot. The diffusion time in the dot, $h^2/D$ is estimated to be less than a second for $D = 2 \times 10^{-11} \, m^2/s$, which is considerably short. Therefore, the speed of the condensation is determined by the diffusion of solvent in the vapor phase. The re-fluidization of the polymer film caused by the condensation of solvent vapor was previously observed in the dewetting of polymer films $^{30,40}$ and in the Plateau-Rayleigh instability in polystyrene troids $^{41}$. Here we explain this phenomenon is also effective to modify the profiles of polymer films.

Since the curvature of the polymer film is inhomogeneous between the center and edge, the local gradient of the curvature causes the gradient of the Laplace pressure $\nabla p$. As the film becomes fluid, $\nabla p$ drives a flow from the edge to center. Finally, the curvature becomes uniform in the entire region of the film, and the surface profile becomes a spherical cap.

When the film is put back to the atmosphere, the solvent that condenses in the film starts to evaporate again. However, the polymer concentration of the film at that moment is considerably higher than the initial concentration at the first drying stage $c_{pol}^0$. The solution becomes glassy at a very early moment of the second drying stage, thus the polymer transport by the outward flow rarely occurs. In fact Jung et al. reported that if the initial polymer concentration of the droplet is considerably high ($c_{pol}^0 \geq 20 \%$), the effect of the outward flow is small and much polymer resides in the central region. $^{36}$ As it is illustrated in fig. 14 (b), to obtain a flat dot, the optimum result is expected in the case that the vapor exposure is stopped at the moment $t_i'$ that the flow levels the entire region of the dot (picture (ii)). For a shorter exposure time $t_i < t_i'$, the re-fluidization process stops before the film is leveled sufficiently (picture (i)). For a longer exposure time $t_i > t_i'$, the solvent condensation still continues after the film is leveled, i.e., the film is too much diluted by the solvent vapor.

As the film is put back to the atmosphere, the outward flow occurs again during the second drying stage and the polymer is transported to the edge (picture (iii)).

The leveling of the polymer dot during the condensation-evaporation processes can be discussed by solving the equations of the local conservation of the fluid and polymer shown in eqs. (4) and (5). Here, the symbol of $J = (\vec{J}, \vec{n})/\rho$ changes between the condensation and negative for the evaporation. The volume flux $\bar{Q}(\vec{r}, t)$ is obtained from the Stokes equation under the lubrication approximation as

$$\bar{Q}(\vec{r}, t) = \frac{h^3 \gamma}{3 \eta} \nabla^2 h,$$

where $\gamma$ and $\eta$ are the surface tension and viscosity.

Here we make a simple analysis based on the theory for the leveling of a liquid film. $^{42}$ In the present system, the polymer film can be regarded as a thin liquid film having a roughness whose wave length is comparable to the film radius $\lambda \approx R$. The characteristic time $\tau$ for this roughness to be leveled by the capillary flow has a form

$$\tau \sim \frac{\eta R^4}{h_0^3},$$

where $h_0$ is an average thickness of the dot. By substituting the experimental values: $R = 100 \, \mu m$, $h_0 = 2 \, \mu m$ (since $J$ could not be obtained experimentally, we used the thickness before the condensation-evaporation processes), and $\gamma = 30 \, mN/m$, the value of the viscosity $\eta$ that makes $\tau$ comparable to the optimal exposure time in our experiment ($t_i, 100 \, s$) is obtained as ca. 300 mPas. In our solution: PS($M_w = 2460 \, Da$)-DPMA, this condition is satisfied when the polymer concentration of the film decreases to $c_{pol}^0 \approx 60 \%$. This is the estimated polymer concentration of the film just after the optimal vapor exposure, which is considerably higher than the initial polymer concentration at the first drying stage ($c_{pol}^0 = 10 \%$).

Equation 15 implies that the rheological property of the
polymer solution greatly affects the optimal exposure time \( t' \). For the polymer solution with a larger molecular weight, the viscosity increases more rapidly against \( c^{1/2} \). For that solution, it is assumed that longer exposure time is required to obtain a flat film. To confirm this conjecture, we conducted the same experiment using PS having larger molecular weight \( (M_w = 29300 \text{ Da}) \). In this case, the leveling of the film profile was also observed, but its time dependence was different. For \( t_e = 10 \text{ min} \) (the optimal exposure time in the case of \( M_w = 2460 \text{ Da} \)), the film profile has almost no difference from the original profile. The optimal exposure time \( t'_e \) shifted to ca. 60 min, which is consistent with our conjecture.

5. CONCLUSION

In this paper, we have reported a series of experimental works for understanding and controlling the drying processes of polymer solution droplets with a pinned contact line. For the analysis of the polymer transport, we have established a new observation method for the polymer concentration (volume fraction) field via the simultaneous measurement of the fluorescence and lateral profile. We have observed that a highly concentrated region is created in the vicinity of the contact line, while the polymer concentration in the central region does not increase until the late stage of drying. The experimental results can be understood in terms of the competition between the polymer convection and diffusion.

For the control of the polymer film, we have proposed two methods. The first method is to add a small amount of surfactants. We have observed that a small amount of surfactants drastically changes the profile of the polymer film from ring-like to flat irrespective of the polymer concentration and initial volume of the droplet. The leveling effect is considered to be caused by the inward Marangoni flow that is driven by the accumulation of the surfactant near the edge. The second method is to switch between the solvent evaporation and condensation. When the polymer film is exposed to solvent vapor and is dried again, the film profile changes from ring-like to flat. We have found that there exists an optimal exposure time \( t'_e \) to obtain a flat film, and proposed a simple theoretical model for predicting \( t'_e \).

Finally, we close this paper by mentioning some future problems. The first problem is the dynamics of drying droplets with a moving contact line. It was reported that in some specific systems, the contact line moves at a certain stage of drying.\(^{41-45}\) For those cases, predicting the solute transport is far more difficult because the flow field is now coupled with the motion of the contact line. Constructing an effective model for those cases, which also explains the critical condition of the contact line pinning, is thus expected.

The second problem is the formation of the skin layer at the liquid surface.\(^{46}\) Theoretically, the formation of the skin layer is understood in terms of the competition between the evaporative flux and diffusion of solute.\(^{47,48}\) However, the experimental evaluation has not been achieved so far due to the difficulty of the local measurement in the vicinity of the liquid surface. The direct observation of the skin layer would be possible by an optical microscopy or rheological measurement with a good vertical resolution.\(^{49,50}\)

REFERENCES