

Electronic Supplementary Information (ESI)

Manuscript title:

How does the polymer type affect the rate of water evaporation from polymer solutions ?

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S1. Discussion on the resolution and detection limit of the present DIC method

Resolution of the DIC method depends on the slopes of I vs $-dI/dx$ (Fig. 2 (c)) and n vs C (Fig. S2).

The intensities of the images are recorded in 256 steps, from 0 to 255. The minimum slope in Fig. 2

(c) is 6.6×10^2 at $-dI/dx = 0$. Therefore, an increase in intensity by 1 corresponds to an increase in $-$

dI/dx by 1.5×10^{-3} or less. The gap height of the cells for the drying experiments was 0.1 mm, and

this gives the minimum gradient to be detected as $-dn/dx = 1.5 \times 10^{-2} \text{ mm}^{-1}$. The slopes of n vs C

(dn/dC) in Fig. S2 are $1.9 \times 10^{-3} \text{ vol}\%^{-1}$ for PVA and PVP, and $1.5 \times 10^{-3} \text{ vol}\%^{-1}$ for PEG. Using the

relationship $dC/dx = (dn/dC)^{-1}(dn/dx)$, we determined that the minimum resolution of the

concentration gradient detectable using the DIC method was $8 \text{ vol}\% \text{ mm}^{-1}$ for PVA and PVP, and 10

$\text{vol}\% \text{ mm}^{-1}$ for PEG. When the concentration gradient was smaller than those values, the present DIC

method was unable to detect the change in C .

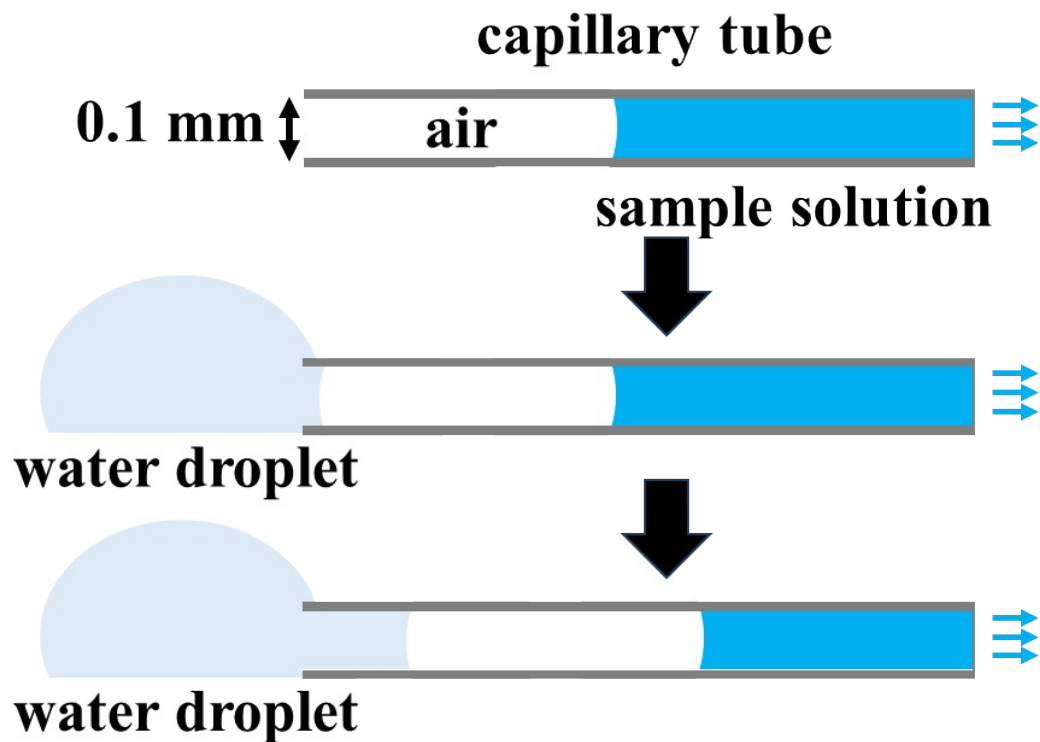


Fig. S1 Schematic of the drying experiment. The sample solution is introduced from the edge on the right (solution side), and then a large droplet of pure water (~ 1 mL) is placed at the left edge (water side). Because of the evaporation of water from the right edge, equivalent amount of water spontaneously comes from the water droplet into the capillary and the position of water-air meniscus on the right edge is maintained.

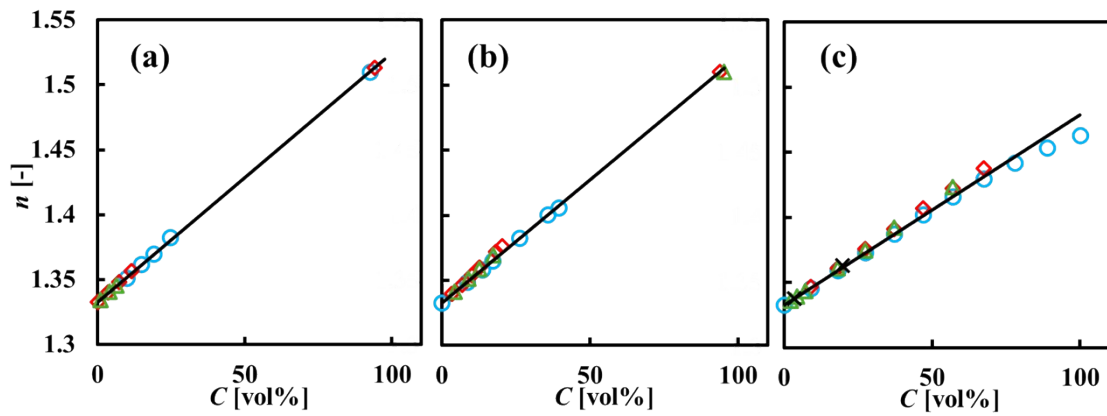


Fig. S2 Refractive index values (n) of (a) PVA, (b) PVP, and (c) PEG plotted against polymer concentrations. The plots of PVA and PVP at $C \sim 100$ vol% are the n values of the dried films and the others are the n values of the aqueous solutions. The solid lines represent $y = ax + n_w$ with $n_w = 1.3327$ (n of pure water) and $a = 1.9 \times 10^{-3}$, 1.9×10^{-3} , and 1.5×10^{-3} vol% $^{-1}$ for (a), (b), and (c), respectively. The symbols indicate the various molecular weights from small to large: \circ , \diamond , \triangle , and \times . (PVA = poly(vinyl alcohol); PVP = poly(vinyl pyrrolidone); PEG = poly(ethylene glycol)).

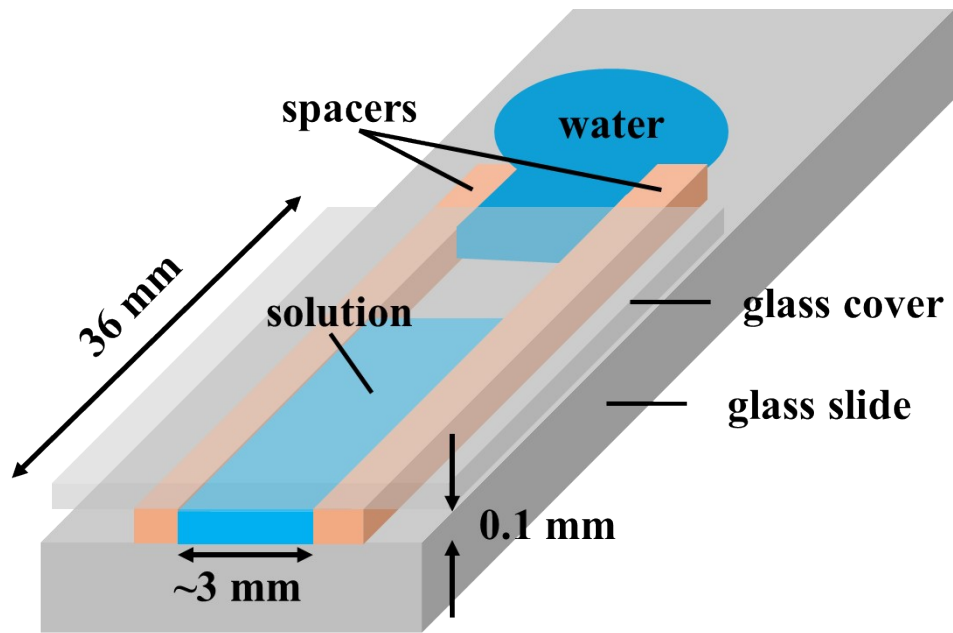


Fig. S3 Schematic image of the unidirectional cell used in the drying experiments.

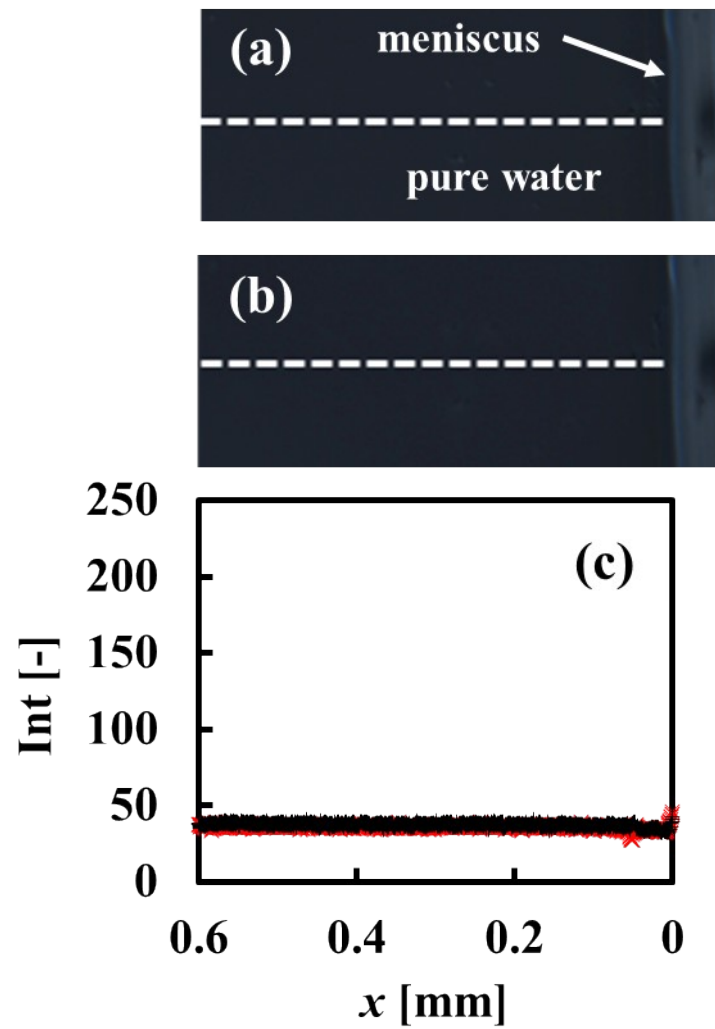


Fig. S4 DIC images of pure water (a) at the beginning of drying and (b) 30 min after (a). (c) Intensity profiles measured along the dashed white lines in (a) (black) and (b) (red). No change was observed.

The range of y-axis is the same as those of Fig. 5 (g-i). (DIC = differential interference contrast).

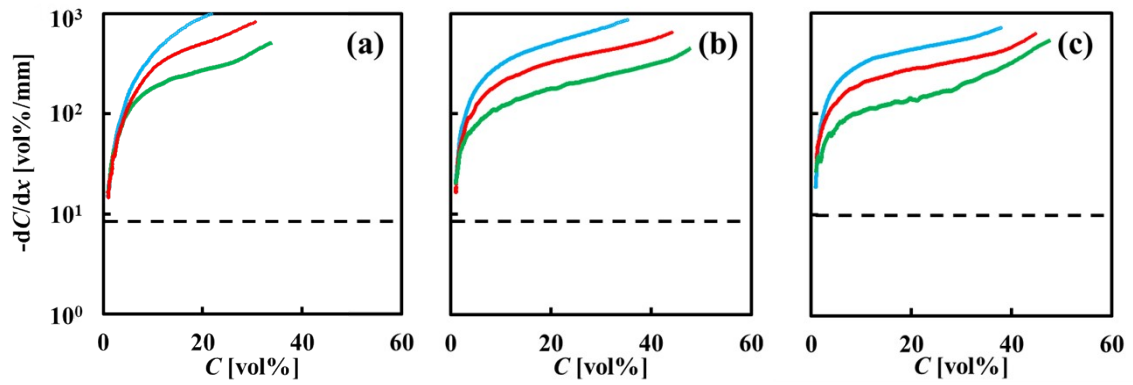


Fig. S5 Concentration gradients of (a) PVA ($M_w = 1.8 \times 10^4$ g/mol, $C_0 = 0.80$ vol%), (b) PVP ($M_w = 3.6 \times 10^5$ g/mol, $C_0 = 0.83$ vol%), and PEG ($M_w = 4 \times 10^5$ g/mol, $C_0 = 0.89$ vol%). The drying times were 10 min (blue), 20 min (red), and 60 min (green). The corresponding concentration profiles are shown in Fig. 6 (d–f). The dashed lines show the detection limit of each polymer.

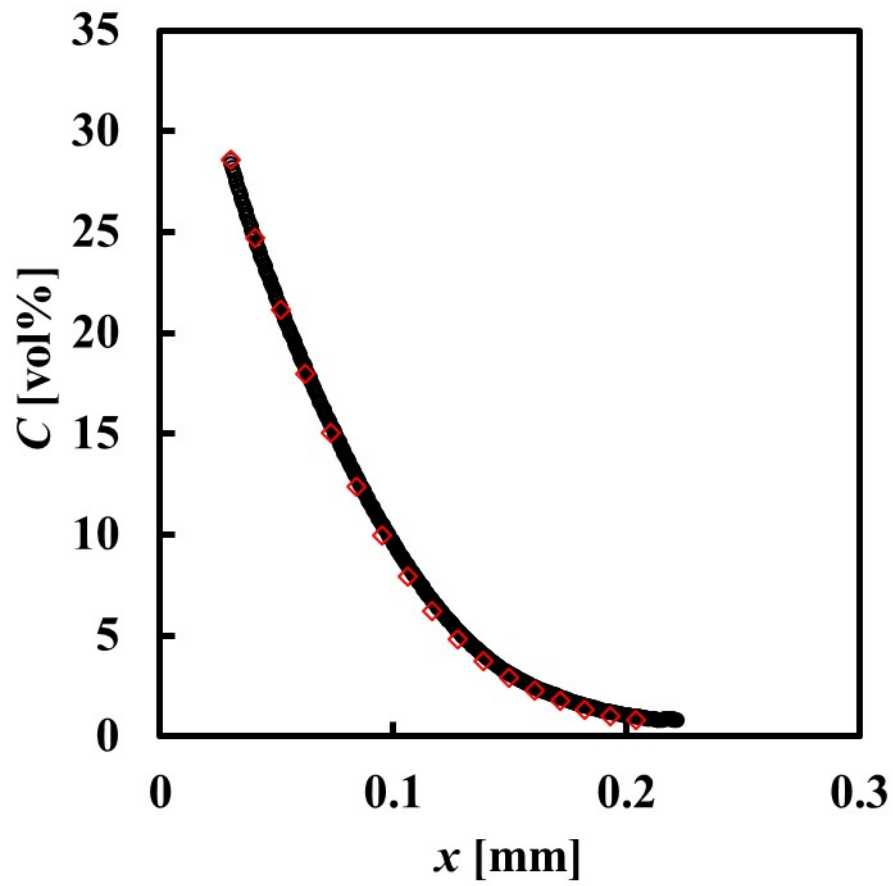


Fig. S6 Comparison of measured (black) and calculated (red) PVA ($M_w = 1.8 \times 10^4$ g/mol)

concentration profiles at $t = 60$ min. The calculation was carried out for the data with

$$(\partial C / \partial t) / \nu (\partial C / \partial x) \text{ ratios} < 10^{-2}.$$

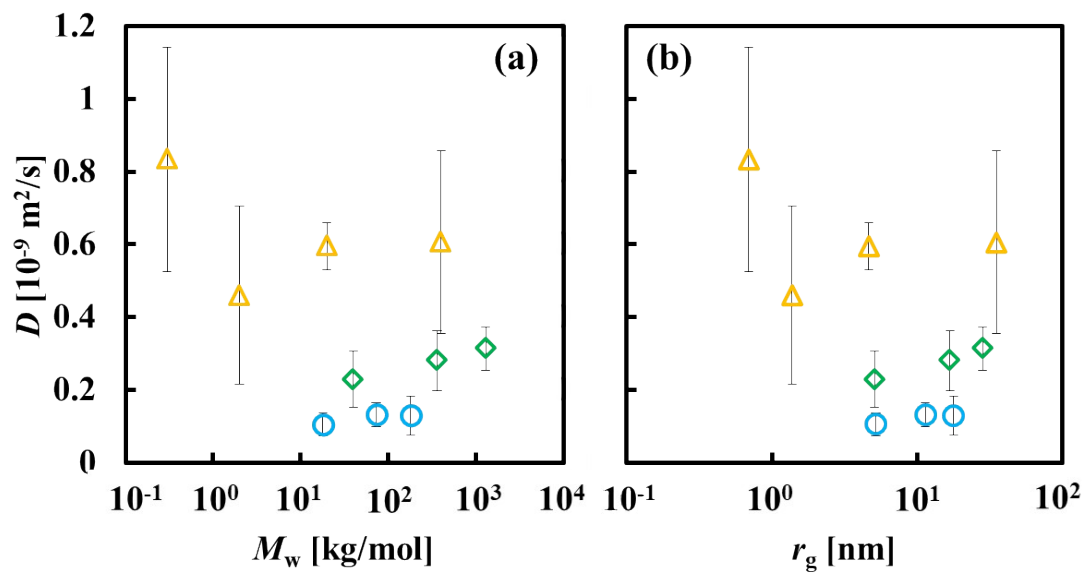


Fig. S7 Estimated diffusion constants of the examined polymers are plotted by (a) M_w and (b) radius

of gyration r_g . Solute types are PVA (\circ), PVP (\diamond), and PEG (\triangle).

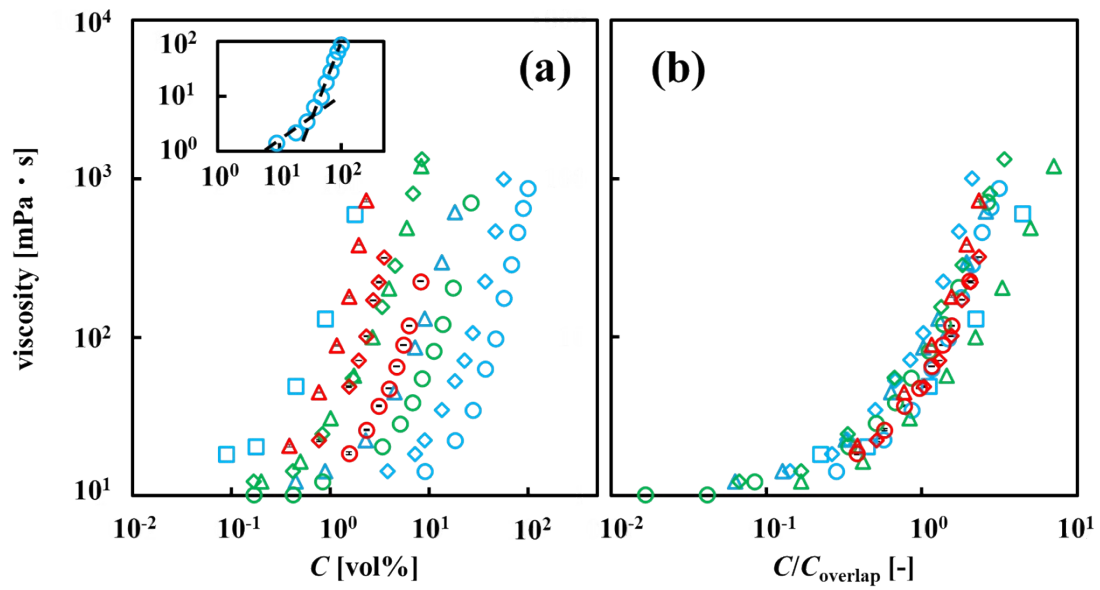


Fig. S8 (a) Viscosities of the polymer solutions versus the solute concentration (C) values. The data pertaining to PVA are shown in red, those pertaining to PVP are shown in green, and those pertaining to PEG are shown in blue. The symbols indicate the various molecular weights from small to large: ○, ◇, △, and □; (b) shows the same data in (a) plotted against the normalized concentrations C/C_{overlap} . We defined the value of C_{overlap} as the intersection of the two dashed lines shown in the inset of (a).

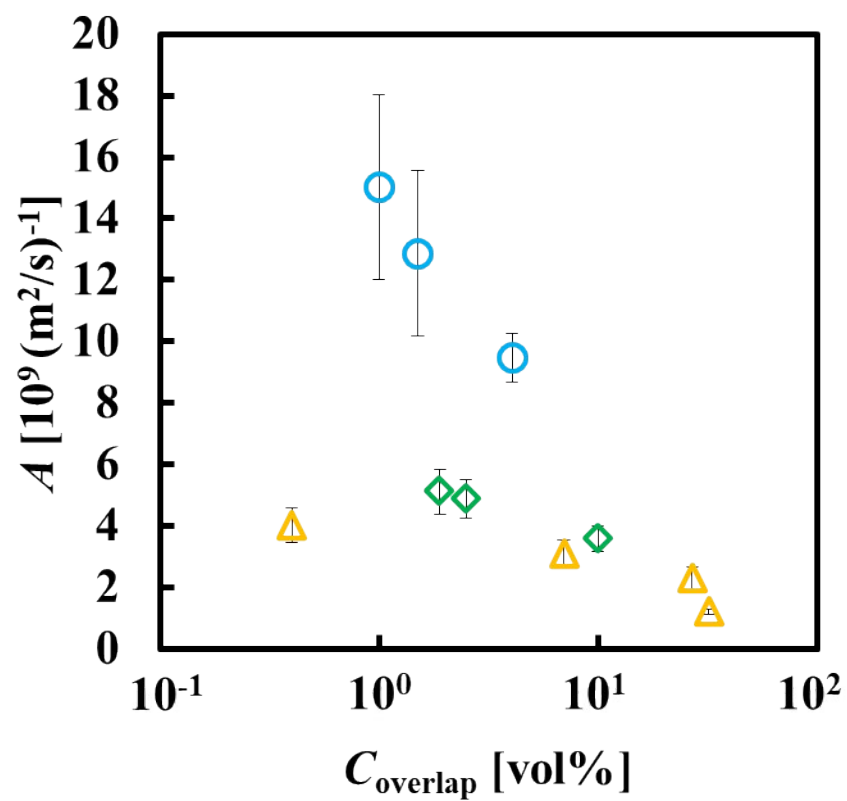


Fig. S9 Correlation between C_{overlap} and A . Solute types are PVA (\circ), PVP (\diamond), and PEG (\triangle).