Effect of Multistratification and Film Depth on the Visualized Dynamic Sorption Behavior of Perylene in Cellulose Acetate Films by a Confocal Laser Scanning Microscope Technique

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ABSTRACT: The sorption behavior of a fluorescent reagent into a polymer film was visualized by confocal laser scanning microscopy (CLSM), and the effects of the additives, film types, and film depth on the diffusion coefficient (D) of the fluorescence reagent were examined. Perylene and cellulose acetate (CA) were used as a fluorescent reagent and a polymer material, respectively. Perylene dissolved in the additives triethylene glycol diacetate (TEGDA) and glycerol triacetate (GTA) was added to the CA film. Then, the evaluation of two types of CA films, a closed-system cellulose acetate (CCA) sample and an open-system cellulose acetate (OCA) sample, was conducted. At optimized CLSM conditions (with a scanning range at a 20-μm depth from the CA film surface with 1-μm intervals and a scanning speed of 1 fps), the sorption of perylene at the inner CA film was determined. The D values of perylene in the CA film were calculated pursuant to Fick's second law. Higher D values of perylene mixed with TEGDA versus those of perylene mixed with GTA were commonly obtained for the CCA sample (TEGDA: 8.9×10^{-15} m^2/s > GTA: 1.7×10^{-15} m^2/s) and the OCA sample (TEGDA: 11×10^{-15} m^2/s > GTA: 3.3×10^{-15} m^2/s) because of the higher chemical affinity of TEGDA with perylene than that of GTA. Perylene indicated a higher D value and was homogeneously distributed in the case of the OCA sample; we found that diffusivity and distribution of perylene in CA film were largely affected by the multistratification treatment. We also proved that the deeper the film depth was, the lower the diffusivity of perylene was, regardless of the types of additives and films. The factors considered for the film-depth dependence of D were a gradual increase in the diffusion pathway for perylene caused by additive diffusion and the concentration dependence of the perylene D. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1780–1787, 2011

Key words: additives; diffusion; films; fluorescence

INTRODUCTION

The sorption of liquid additives and/or vapor components into polymer materials seriously affects the product quality in many industrial fields, including material engineering and food manufacturing.[1–5] For example, in the manufacturing process of thermoplastics for plastic lapping and rubber materials, plasticizers are added to increase the flexibility, toughness, and/or transparency of the materials.[1,2] In the food industry, serious problems with food quality have been identified that are related to the loss of flavors by sorption into polymer packaging films.[3–5] Multistratification is one of the most effective techniques for preventing the permeation of penetrants through polymer materials.[6]

Numerous studies on the sorption behavior of chemicals into polymer materials have been reported; mainly, these have been done on the basis of their physicochemical properties.[7–11] Since the mid-1980s, aqueous and vaporous penetration methods[12,13] have been widely used to determine the dynamics and physical and chemical parameters of chemicals and/or polymers; for example, the molar volume, solubility parameters, free energy, and free volume have been characterized as a contributors to sorption.[14–16] However, these convenient methods provide no *in situ* information on the real-time distribution behavior of penetrants in polymers.

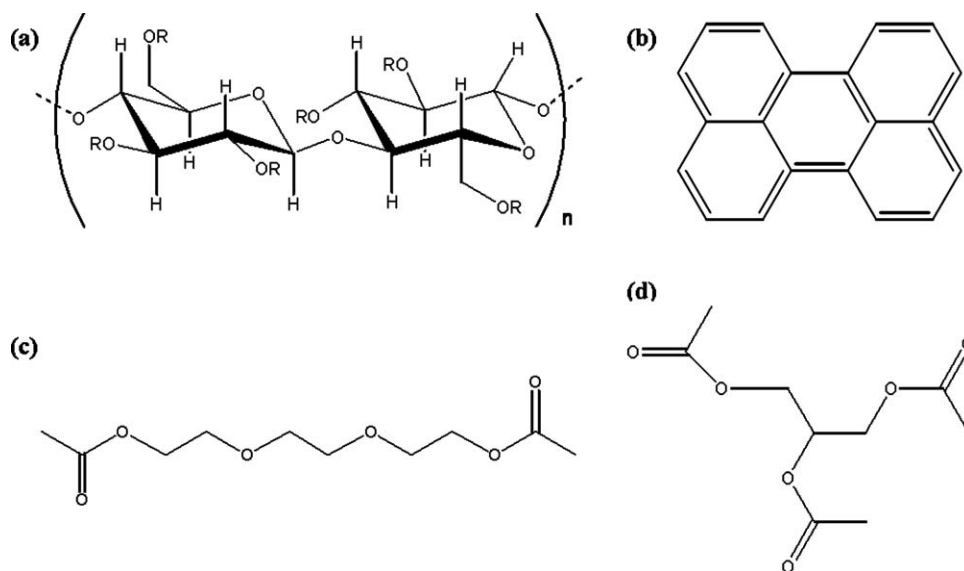*Correspondence to:* T. Hasegawa (takashi.a.hasegawa@jt.com).

Figure 1 Chemical structures of (a) CA (R = CH₃CO or H), (b) perylene, (c) GTA, and (d) TEGDA.

With this in mind, we established an *in situ* determination, that is, a real-time and nondestructive visualization method for sorption dynamics, by applying confocal laser scanning microscopy (CLSM).[17] CLSM has been widely used for the observation and/or analysis of mass-transfer phenomena in the fields of physiology and pharmacology with the use of a fluorescent labeling technique or fluorescent reagent mixture.[18–21] Recently, attempts to apply CLSM have been reported in materials engineering to assess the surface hydrophilicity of polymers,[22] the plasticizing effect of supercritical fluid treatment for polymers,[23] and the biodegradation behavior of polymer film surfaces.[24]

In our previous study,[25] we evaluated the effect of various additives on the sorption behavior of a fluorescent reagent (perylene) into cellulose acetate (CA) films by adopting our established CLSM methodology. The diffusion coefficient (D) of perylene in CA film varied and was dependent on the kind of additives. The diffusivity of perylene was mainly affected by the chemical affinity of the additives with perylene and was additionally affected by the physical properties, such as molecular size and viscosity, of the additives.

In this study, we tried to further ensure the development of the CLSM technique to promote a better understanding of sorption phenomena. The sorption behavior of perylene into closed-system cellulose acetate (CCA) film (bilayer with glass) and an open-system cellulose acetate (OCA) film (monolayer) were investigated and compared according to D values. In the comparison study, both the overall D and its film-depth dependence were evaluated. As additives for the dissolution of perylene, triethylene glycol diacetate (TEGDA) and glycerol triacetate (GTA), known as plasticizers for CA,[26,27] were used.

EXPERIMENTAL

Materials

CA flakes with a degree of substitution of 2.5 [weight-average molecular weight (M_w) = 1.0 × 10⁵ g/mol] were a product of Daicel Chemical Industries, Ltd. (Osaka, Japan) and were used without further purification. Perylene (M_w = 252.3 g/mol), TEGDA (M_w = 234.3 g/mol), and GTA (M_w = 218.2 g/mol) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and Sigma-Aldrich (Tokyo, Japan), respectively. Other reagents were commercially available in extra-pure grade, and all of the chemicals were also adopted without further purification. The structures of the chemicals used in this study are depicted in Figure 1.

Preparation of the CA films

CA flakes were dissolved in acetone to make a 2.0 w/v % solution. The CCA film was prepared on a film-making unit consisting of a cover glass and a penicillin cup (Fig. 2) from an aliquot (200 μL) of CA solution under the protocol explained in the previous report.[17] We prepared the OCA film by putting an aliquot (4 mL) of CA solution into glass Petri dish (diameter = 27 mm) and vaporizing excess acetone for 7 days at room temperature. After it was dried *in vacuo* overnight, the film was peeled off from the Petri dish and fixed between two neodymium magnets (Fig. 3, inner diameter = 23 mm, thickness = 1 mm). The prepared CCA and OCA samples were 95 ± 5 and 60 ± 10 μm thick, respectively.

Preparation of the perylene/additive mixture

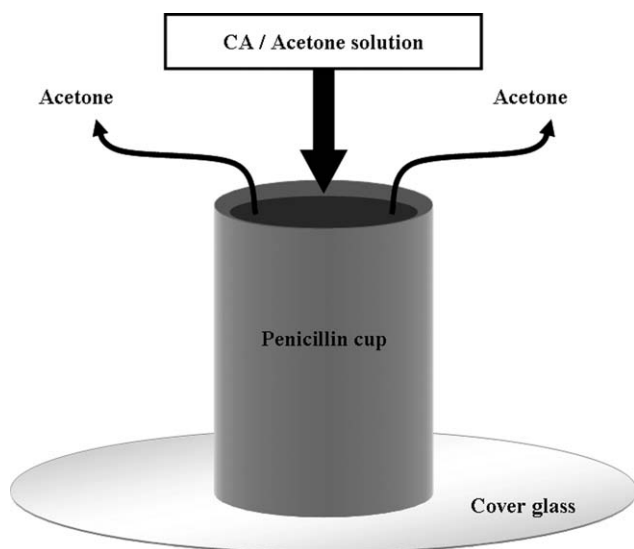We prepared the perylene/additive mixture at room temperature by dissolving perylene with TEGDA or GTA to

Figure 2 Film-making unit used for the preparation of the CCA sample.

achieve a desired molar ratio of perylene. The molar ratio of perylene to the mixture was defined as follows:

$$\text{Molar ratio} = \frac{\text{Perylene amount (mol)}}{\text{Perylene amount (mol)} + \text{Additive amount (mol)}}$$

The molar ratios of perylene with TEGDA and GTA for this study were 9.1×10^{-5} and 8.8×10^{-5}, respectively.

CLSM analysis

The fluorescent spectra of perylene in the CA films were obtained by a CLSM system (CLSM system A1, Nikon Corp., Tokyo, Japan) equipped with a dry objective lens (CFI Plan Apo VC 20×, Nikon). We measured the fluorescence of the CA film itself by settling the CCA and OCA samples on a microscope. We measured the spectra of the perylene/additive mixtures or additives themselves by dropping an aliquot (4 μL) of the solution onto a cover glass settled on a microscope. With a diode laser (408 nm, 290–330 μW) for excitation, fluorescence excited from around the cover glass was detected at room temperature. For the perylene/additive mixtures, the intensity of reflected fluorescence at 450 ± 25 nm was measured from confocal images around the cover glass by the adoption of optical filters.

Visualization of the perylene distribution in the CA films by the CLSM method

Before the perylene penetration measurement by the CLSM method, the air-contact surface of the CA film was determined as a 0-μm depth by transmission

image analysis of the CCA and OCA samples with a halogen lump. The change in the fluorescence intensity of perylene in the CA film during sorption experiments at room temperature was measured by a CLSM system every 3 min after a 4-μL perylene/additive mixture was dropped onto the CA film. Confocal images were obtained by a scanning excitation laser in the cross-sectional region of the CA film with intervals along the z axis. The depth from the air-contact surface of the CA film was 20 μm, with intervals of 1 μm. The confocal imaging area was approximately 640×640 μm^2 on the x–y surface, and the scan speed and flame size were 1 fps and 512×512 pixels, respectively. All other conditions of the CLSM system were the same as mentioned previously. Three replicates of CLSM analysis [Mean $\pm$ Standard deviation (SD)] were performed for this study.

RESULTS AND DISCUSSION

Fluorescence detection of perylene by the CLSM method

As demonstrated in our previous report,[25] the perylene/additive mixtures showed significant perylene-induced fluorescence intensities around 470 and 503 nm, whereas no fluorescence intensities were observed for the additives or CA films (data not shown). This showed that any interference in fluorescence from the additives or CA films could be excluded for *in situ* penetration monitoring of the perylene in the CA films. Likewise, as was the case in our previous study,[25] a good linearity ($r > 0.978$) between the fluorescence intensity and the molar ratio of perylene in each perylene/mixture was obtained in the molar ratio of perylene range from 2.1×10^{-5} to 13×10^{-5} (data not shown).
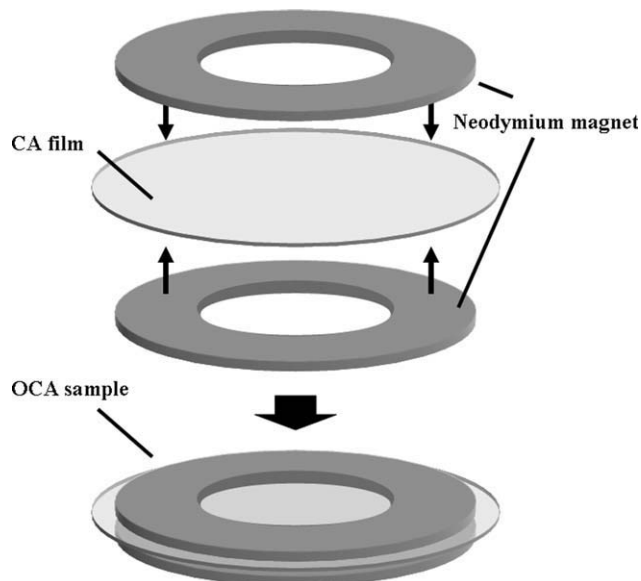

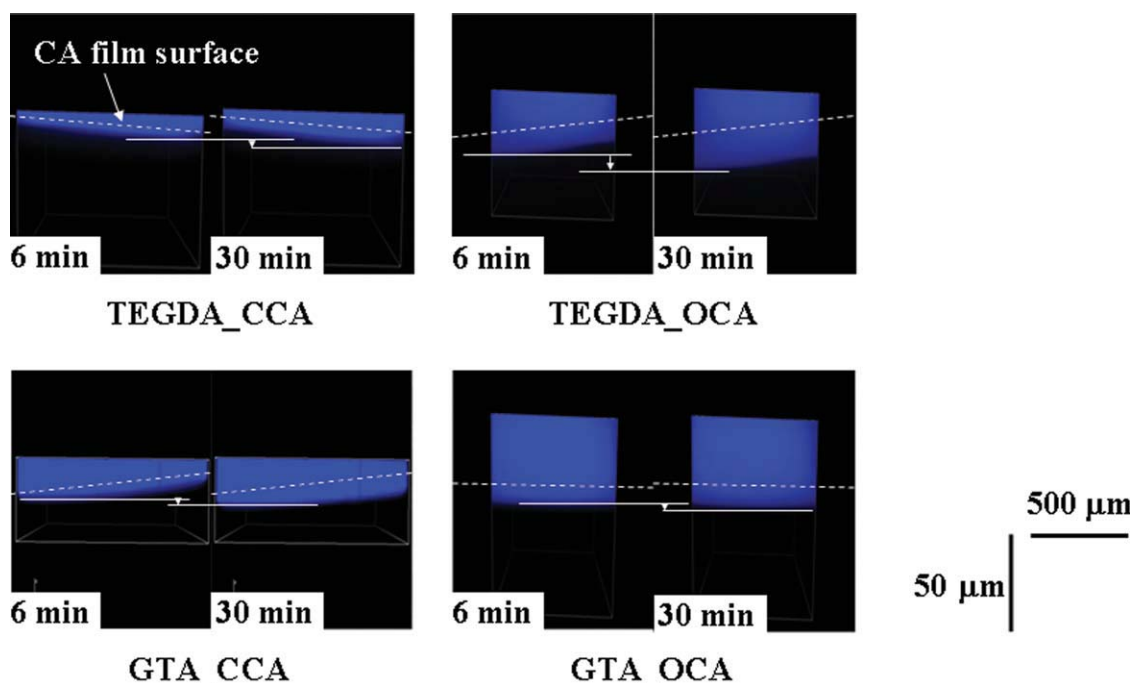**Figure 3** OCA sample fixed between neodymium magnets.

Figure 4   Time-course cross-sectional chemical images (x–z surface) of the CCA and OCA samples.

Monitoring of the sorbed perylene in the CA films by the CLSM method

Three-dimensional chemical images of the CA films treated with perylene/additive mixtures were reconstructed by the chemical images of the x–y surface obtained at several depths of the CA film. Cross-sectional chemical images (x–z surface) of the CCA and OCA samples at 6 and 30 min after the addition of the perylene/additive mixtures are shown in Figure 4. Although there was some influence of asperity or slant on the air-contact surface of the CA films, the blue color derived from the fluorescence intensity of perylene was detected in each image. It was clear that the blue color expanded to a deeper area over time after the addition of the mixtures in each CA film sample. These results indicate that the sorption of the perylene/additive mixture proceeded progressively from the top of the CA film to the inside of the film. With respect to the effect of the additives on the perylene penetration, the change was higher for the perylene/TEGDA mixture in both CCA and OCA samples. Intriguingly, the perylene penetration behavior in the OCA sample became more intense than in the CCA sample, especially for perylene/TEGDA mixture.

Effect of the additives and CA film type on D of perylene

To quantify this behavior, the fluorescence intensities derived from perylene in the CA film were calculated as an average of each pixel in the x–y

surfaces. Approximately 4.0×10^4 square μm areas were selected from the observation areas for analysis. Figures 5–8 show the changes in the intensities in each depth of the CA films, in which the intensity was averaged through three replicates. On the horizontal axis, the 0-μm depth indicated the air-contact surface of the CA film. We standardized the
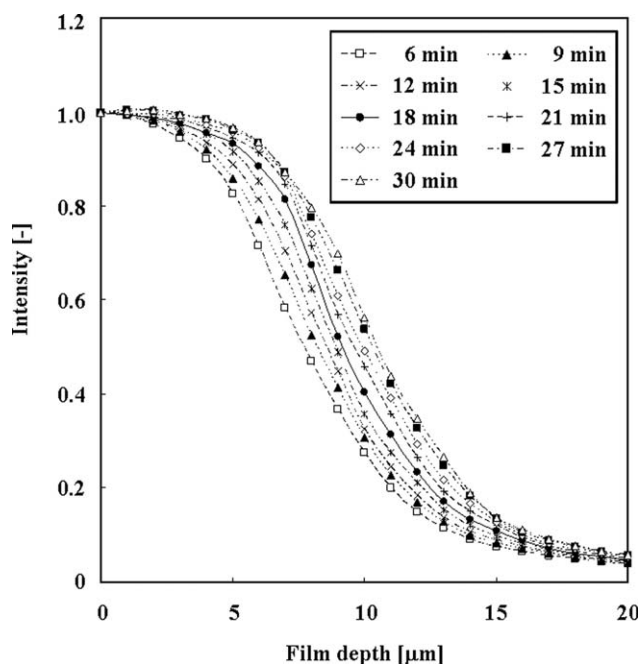

Figure 5   Relationship between the depth of the CCA sample and I_s at several times after the addition of the perylene/TEGDA mixture.
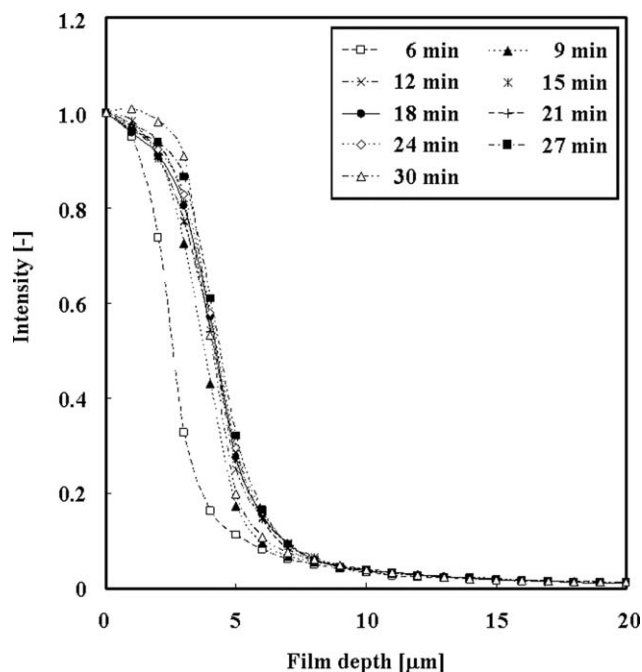
Figure 6 Relationship between the depth of the CCA sample and I_s at several times after the addition of the perylene/GTA mixture.

fluorescence intensities in each depth by subtracting the CA-based intensity and subsequently dividing the obtained intensity by that of the 0-µm depth at each time. Consequently, the standardized intensity (I_s) of each CA film depth increased progressively from 6 to 30 min after the addition of the mixtures.
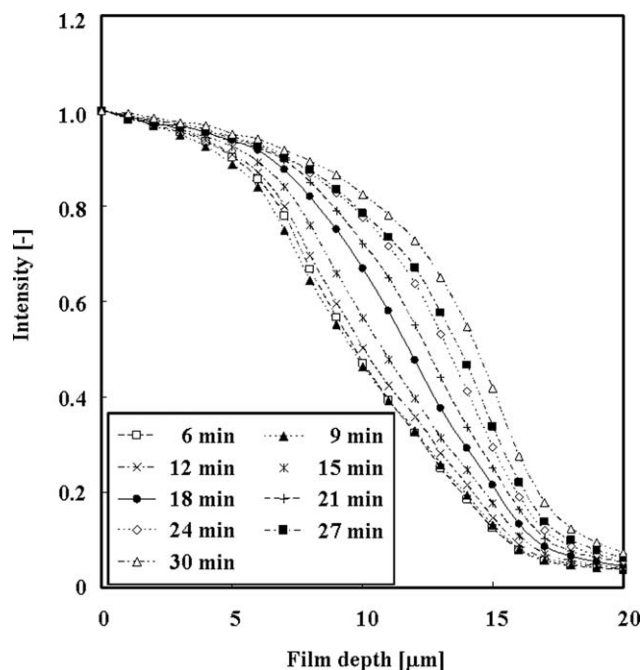

Figure 7 Relationship between the depth of the OCA sample and I_s at several times after the addition of the perylene/TEGDA mixture.
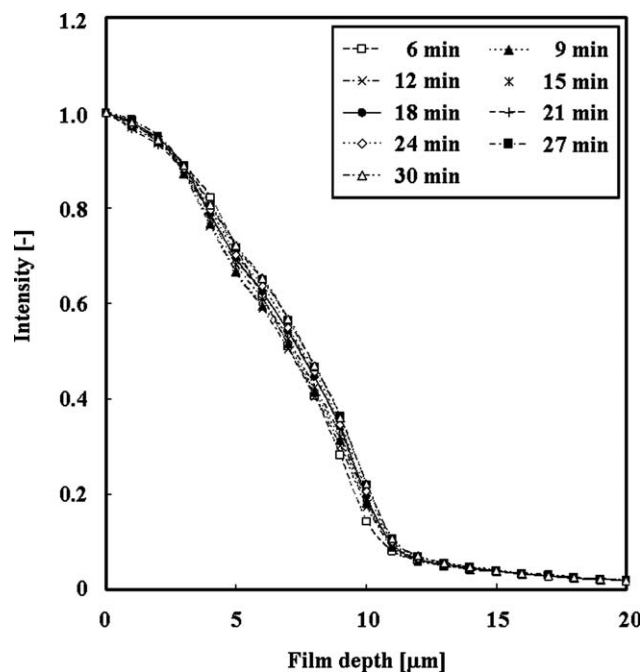

Figure 8 Relationship between the depth of OCA sample and I_s at several times after the addition of the perylene/GTA mixture.

With regard to the CCA samples (Figs. 5 and 6), I_s increased by a factor of 0.34 at a 8-µm depth and 0.22 at a 4-µm depth in the perylene/TEGDA and perylene/GTA mixtures, respectively. For the OCA samples (Figs. 7 and 8), on the other hand, each increment was a factor of 0.26 at a 14-µm depth and 0.20 at a 9-µm depth in the perylene/TEGDA and perylene/GTA mixtures, respectively.

From the results shown in Figures 5–8, D of perylene was calculated based on Fick's second law, as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial}{\partial x}\left(\frac{\partial C}{\partial x}\right)$$

where C is the concentration of perylene, t is the time by postaddition of the mixture, and x is the film depth. The left side of the equation was obtained as the slope of I_s versus t in each depth of film because the intensity had a good linearity for the molar ratio of perylene. Then, the second term on the right side was calculated as the slope of a change of I_s in a 2-µm depth range ($\partial I_s/\partial x$) versus the film depth. Finally, D was calculated as the coefficient of both sides of the equation for each depth of film and averaged. A detailed scheme for the calculation of D was presented in our previous report.[25] Figure 9 shows the D values of perylene in the CA films when they were mixed with additives. For the CCA samples, the D values were calculated in the 10–13 and 3–8 µm depth range in the perylene/TEGDA and perylene/GTA mixtures,
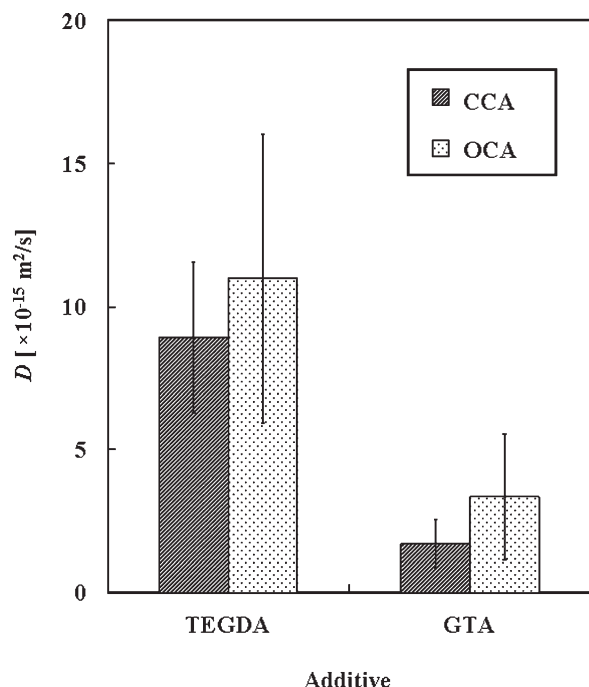
Figure 9 D values of perylene in the CCA and OCA samples when mixed with TEGDA or GTA. The data are the Mean $\pm$ SD (Number of repetitions $n = 3$).

respectively. For the OCA samples, the D values were calculated in the 14–17 and 9–11 μm depth ranges in the perylene/TEGDA and perylene/GTA mixtures, respectively. The D value varied depending on the kind of additives and the CA film type. In both the CCA and OCA samples, the D values of perylene in the CA films when they were mixed with TEGDA (CCA: $8.9 \pm 2.6 \times 10^{-15}$ m²/s, OCA: $11 \pm 5.1 \times 10^{-15}$ m²/s) were higher than those when they were mixed with GTA (CCA: $1.7 \pm 0.83 \times 10^{-15}$

m²/s, OCA: $3.3 \pm 2.2 \times 10^{-15}$ m²/s). Regardless of the kind of additives, the D values of perylene in the CA film became higher for the OCA samples (TEGDA: $11 \pm 5.1 \times 10^{-15}$ m²/s, GTA: $3.3 \pm 2.2 \times 10^{-15}$ m²/s) than for the CCA samples (TEGDA: $8.9 \pm 2.6 \times 10^{-15}$ m²/s, GTA: $1.7 \pm 0.83 \times 10^{-15}$ m²/s).

In our previous study,[25] we evaluated the effect of various additives on the sorption behavior of perylene into CCA samples and verified that D of perylene in CA films was affected by the physico-chemical properties of the additives. The higher D value of perylene mixed with TEGDA (8.9×10^{-15} m²/s) versus that perylene mixed with GTA (1.7×10^{-15} m²/s) was attributed to the higher chemical affinity of perylene with TEGDA on the basis of the estimation with solubility parameters. Similarly, in the case of the OCA sample, as the previously discussed results in this study suggest, the order of the D value of perylene was TEGDA mixture (11×10^{-15} m²/s) > GTA mixture (3.3×10^{-15} m²/s); this order was attributed to the difference in the chemical affinities of the perylene with additives.

Regardless of the kind of additive, the D values of perylene in the OCA samples were higher than those in the CCA samples. Figure 10 represents the shift of I_s at each depth of the CCA and OCA samples 1, 2, and 24 h after the addition of the perylene/TEGDA mixture. With the exception that the cross-sectional region for scanning was 0–40 μm deep from the air-contact surface of the CA film, the experimental conditions and analytical protocols were same as mentioned previously. As for the CCA sample, we did not investigate a progressive penetration of perylene into the CA film but a swing-over of perylene penetration to some extent after 1 h. The I_s values at 1, 2, and 24 h after the
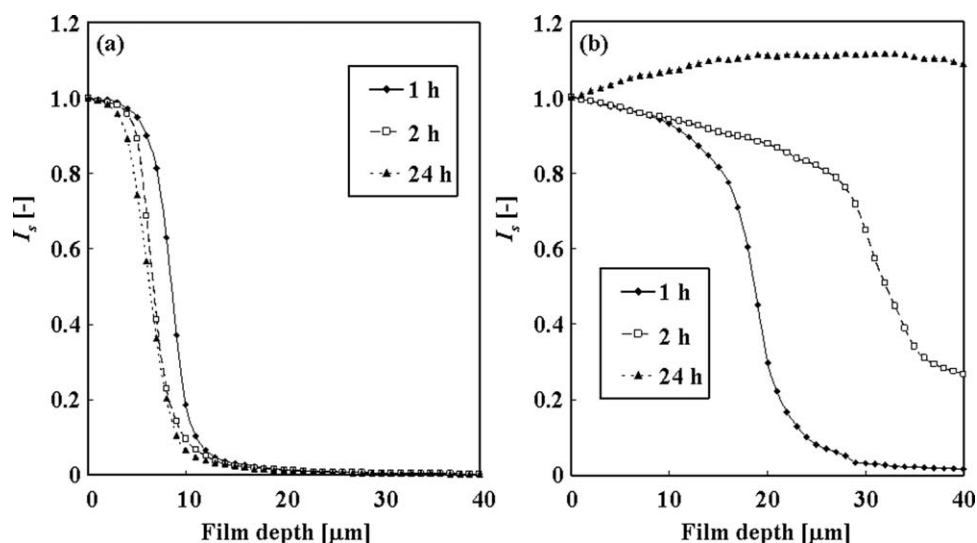

Figure 10 Relationship between the depth of the CA film and I_s at several times after the addition of the perylene/TEGDA mixture: (a) CCA and (b) OCA.
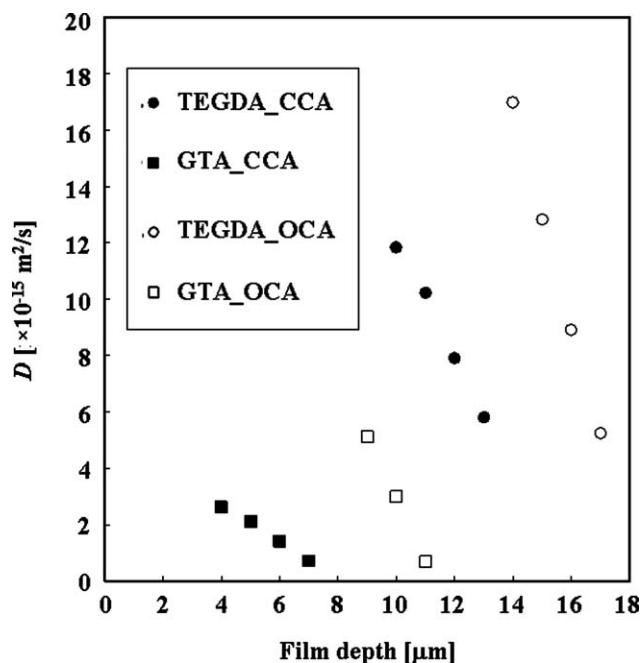
Figure 11 Relationship between the CA film depth and D of perylene.

addition of the perylene/TEGDA mixture were 0.015, 0.014, and 0.012 at a 20-μm depth and 0.0034, 0.0035, and 0.0033 at a 40-μm depth, respectively. This result indicates that the perylene penetration came to equilibrium around 1 h after the addition of the mixture, and the distribution ratio of perylene at a 40-μm depth was 0.3% compared with the air-contact surface (0-μm depth) of the CA film. For the OCA sample, on the other hand, the penetration of perylene into the CA film was progressing even at 24 h after the addition of the mixture. The I_s values at 1, 2, and 24 h after the addition of the perylene/TEGDA mixture were 0.30, 0.88, and 1.1 at a 20-μm depth and 0.017, 0.27, and 1.1 at a 40-μm depth, respectively. This result indicates that perylene was homogeneously distributed in the OCA sample by 24 h after the addition of the mixture, in contrast to the CCA sample.

Studies on gas permeation through polymer films have revealed that the permeability of the multilayer is not always correspondent to the multiplication of those of each consisting monolayer[28] or that the permeability of the multilayer differs, depending on the side of coating layer (inside or outside).[29] With the cover glass of the CCA sample considered a coating layer of the CA film, these results suggest that D and the distribution of perylene in the CA films largely varied with the multistratification treatment.

Film-depth dependence of D of perylene in the CA films

To promote more understanding of the sorption behavior of perylene into CA films, the D values at

each film depth were calculated pursuant to Fick's second law. Figure 11 describes the relationships between the film depth and D of the CCA and OCA samples. It was greatly interesting that these results showed clearly that there were strong negative correlations between the two; that is, the deeper the film depth was, the lower the diffusivity of perylene was, regardless of the types of additives and films. As is well known, Fick's second law is based on the hypothesis that although the concentration gradient of penetrant to film depth transforms over a time course, the rate of its transformation is constant, and D is obtained as a constant number. These results, however, contradict this hypothesis. Comparing the slopes obtained approximate linearization, we found that the absolute values of the OCA samples (TEGDA: 3.9×10^{-15}, GTA: 2.2×10^{-15}) were higher than those of the CCA samples (TEGDA: 2.0×10^{-15}, GTA: 0.64×10^{-15}). This means that the influence of the film depth increase with decreasing diffusivity was larger for the OCA samples than for the CCA samples.

As factors causing the film-depth dependence of D, two viewpoints were considered. The first factor was the effect of the additives mixed with perylene. With respect to the diffusion of penetrant in the polymer materials, the free volume theory was proposed in 1960s,[30] and recently, it has been generally thought that amorphous portion in polymer material is the dominant diffusion pathway.[31–37] It was considered that with the diffusion of TEGDA or GTA, the amorphous portion, that is, the diffusion pathway for perylene[27], gradually increased due to the CA solubility[27] of additives. As a result, the D value of perylene in the superficial part of the CA film was higher than that of the deep part. The second factor was the concentration dependence of D. It has been reported that the higher the concentration of penetrant in an experimental system is, the higher the D of penetrant in the polymer materials will be.[38,39] In polymer materials, the concentration of penetrant should vary with the distance from the liquid/solid or vapor/solid boundaries. We considered that the aforementioned film-depth dependence of the D value directly indicated the concentration dependence of D in the CA films. As for the CCA sample, perylene had a lower D value than that obtained previously (3.8×10^{-15} m^2/s $< 8.9 \times 10^{-15}$ m^2/s) when mixed with TEGDA at a lower molar ratio ($0.28 \times 10^{-5} < 9.1 \times 10^{-5}$). Moreover, this result proves that D of perylene was dependent on the concentration.

CONCLUSIONS

In this study, the effects of the kinds of additives, TEGDA or GTA, and film types, CCA or OCA, on the sorption behavior of perylene into CA films

were evaluated. Through dynamic monitoring of the perylene penetration by a CLSM methodology, the overall D values of perylene in CA films and its film-depth dependence were calculated according to Fick's second law.

The higher chemical affinity of TEGDA with perylene versus that of GTA commonly caused a higher D of perylene for both the CCA sample (TEGDA: 8.9×10^{-15} m^2/s > GTA: 1.7×10^{-15} m^2/s) and OCA sample (TEGDA: 11×10^{-15} m^2/s > GTA: 3.3×10^{-15} m^2/s). What is really interesting was that perylene had a higher diffusivity in the OCA sample than in the CCA sample beyond the types of additives. In conclusion, we simultaneously clarified that when it was mixed with TEGDA, perylene appeared homogeneously distributed in the OCA sample by 24 h after the mixture addition ($I_s = 1.1$ at a 40-μm depth of CA film) as opposed to CCA sample ($I_s = 0.0033$ at the same depth). These results demonstrate that D and the distribution of perylene in the CA films largely varied with the multistratification treatment.

From the results on the film-depth dependence of D, as were greatly interesting, it was clear that the greater the film depth was, the lower the diffusivity of perylene was, regardless of types of additives and films. Although this finding contradicted the hypothesis of Fick's second law, a gradual increase in the diffusion pathway for perylene caused by additive diffusion and the concentration dependence of the perylene D values were considered factors.

The aforementioned results and findings could be directly achieved because of the advantages of the CLSM system, that is, a real-time and nondestructive visualization method for sorption dynamics. It was proven that our proposed CLSM methodology should be beneficial for the promotion of a better understanding of sorption behavior.

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