

# Comparative Study of Additives on Visualized Dynamic Sorption Behavior of Perylene in Cellulose Acetate Film by 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 microscope (CLSM), and the effect of additives on the sorption was examined. Perylene and cellulose acetate (CA) were used as a fluorescent reagent and a polymer material, respectively. Perylene dissolved in additives of glycerol triacetate (GTA), triethylene glycol diacetate (TEGDA), 1,3-butylene glycol diacetate (BGDA), paraffin liquid, and poly(ethylene glycol) 200 (PEG) were added onto CA film. At optimized CLSM conditions (scanning range of a 10  $\mu\text{m}$ -depth from the CA film surface with 1  $\mu\text{m}$  intervals and a scanning speed of 1 fps), the sorption of perylene at the inner CA film was determined. Diffusion coefficients of perylene in the CA film were calculated according to Fick's

second law. When perylene was dissolved in TEGDA, the highest diffusion coefficient,  $8.9 \times 10^{-15} \text{ m}^2/\text{s}$ , among the additives was obtained because of high affinity of TEGDA with perylene, whereas the lowest diffusion coefficient was observed in paraffin liquid, which showed a low affinity with perylene. The diffusion coefficients of perylene in GTA, BGDA, and PEG also revealed that physical parameters, such as molecular size and viscosity, of the additives were additional factors affecting the perylene diffusivity in the CA film. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1710–1717, 2010

**Key words:** additives; cellulose diacetate; diffusion; films; fluorescence

## INTRODUCTION

In many industrial fields, such as material engineering and food manufacturing, the sorption of liquid additives and/or vapor components into polymer materials seriously affects product quality. In particular, in the material engineering field, a number of plasticizers have been used for the purpose of increasing flexibility, toughness, and/or transparency without any consideration of their sorption in polymer materials.<sup>1,2</sup>

In past decades, numerous studies on the sorption behavior of chemicals into polymer materials have been reported, mainly on the basis of their physicochemical properties.<sup>3–7</sup> One point of view has been the investigation of the diffusion and distribution of plasticizers themselves in polymer materials,<sup>3–5</sup> and another has been the estimation of the influence of coexisting plasticizers on the sorption behavior of

penetrant compounds.<sup>6,7</sup> In these studies, the sorption amount of penetrant chemicals has been determined by the measurement of a change in weight and/or by extraction of the absorbed penetrants with solvents in the evaluation of the diffusion kinetics of the penetrating chemicals. However, *no in situ* examination of the penetration or distribution of absorbed chemicals has been performed because of the lack of real-time and nondestructive assays. In the field of food industry, serious problems regarding food quality have been identified with regard to the loss of flavors by sorption into polymer packaging films.<sup>8–10</sup> To overcome these problems, we clarified the dynamic sorption behavior of flavors into polymer films.<sup>11–15</sup> It has been clarified that the physical and chemical parameters, such as the molar volume, free energy, free volume, and solubility parameters, of chemicals and/or polymers have been characterized as contributors for flavor sorption<sup>11–13</sup> by determination of the sorption dynamics with our proposed aqueous and vaporous penetration methods.<sup>14,15</sup> However, the proposed convenient penetration methods could not provide any *in situ* information on the real-time sorption behavior of penetrants in polymers.

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In this respect, we newly established an *in situ* determination method for sorption dynamics by applying confocal laser scanning microscope (CLSM) in our previous study.<sup>16</sup> CLSM has been widely used for observation and/or analysis of mass-transfer phenomena in the fields of physiology and pharmacology with the use of fluorescent labeling techniques or fluorescent reagent mixtures.<sup>17–20</sup> Recently, attempts to apply CLSM have been reported in the materials engineering field to evaluate the surface hydrophilicity of polymers,<sup>21</sup> the plasticizing effect of supercritical fluid treatment for polymers,<sup>22</sup> and the biodegradation behavior of the polymer film surface.<sup>23</sup>

In our previous study,<sup>16</sup> we demonstrated an extensive CLSM application for the real-time and nondestructive visualization of sorption behavior; the successive distribution of a fluorescent reagent (perylene) in cellulose acetate (CA) film was visualized without any destruction of the perylene-absorbed CA film.

In this study, we tried to evaluate the effect of various additives on the sorption of fluorescent perylene into CA film by using our established CLSM methodology<sup>16</sup> because additives in polymers may affect the penetration or distribution of perylene because of their collaborative interaction with the CA film and/or penetrant. The additives used to dissolve the penetrant perylene were glycerol triacetate (GTA), triethylene glycol diacetate (TEGDA), 1,3-butylene glycol diacetate (BGDA), paraffin liquid, and poly(ethylene glycol) 200 (PEG), in which GTA, TEGDA, and BGDA are known as plasticizers for CA<sup>24,25</sup> and paraffin liquid and PEG are known as additives of CA filters in the cigarette industrial field.<sup>26,27</sup>

## EXPERIMENTAL

### Materials

CA flakes with a degree of substitution of 2.5 [weight-average molecular weight ( $M_w$ ) =  $1.0 \times 10^5$  g/mol] were product of Daicel Chemical Industries, Ltd. (Osaka, Japan), and were used without further purification. GTA ( $M_w$  = 218.2 g/mol) was purchased from Sigma-Aldrich (Tokyo, Japan). TEGDA ( $M_w$  = 234.3 g/mol), BGDA ( $M_w$  = 174.2 g/mol), and paraffin liquid ( $M_w \approx 395$  g/mol) were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), Daicel Chemical Industries, Ltd., and Nacalai Tesque, Inc. (Kyoto, Japan), respectively. PEG ( $M_w \approx 200$  g/mol) and perylene ( $M_w$  = 252.3 g/mol) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Other reagents were commercially available in extrapure grade, and all of the chemicals were used without further purification.

The structures of the chemicals used in this study are depicted in Figure 1.

### Preparation of CA film

CA film was prepared on a film-making unit consisting of a cover glass and a penicillin cup (Fig. 2) according to the protocol described in our previous article,<sup>16</sup> and the thickness of the prepared CA film was  $95 \pm 5 \mu\text{m}$ .

### Preparation of perylene/additive mixture

Perylene/additive mixture was prepared at room temperature by the dissolution of perylene with an additive to achieve a desired molar ratio of perylene. The molar ratio of perylene to the mixture was defined as equation (1):

$$\text{Molar ratio} = \frac{\text{Amount of perylene(mol)}}{\text{Amount of perylene(mol)} + \text{Amount of additive(mol)}} \quad (1)$$

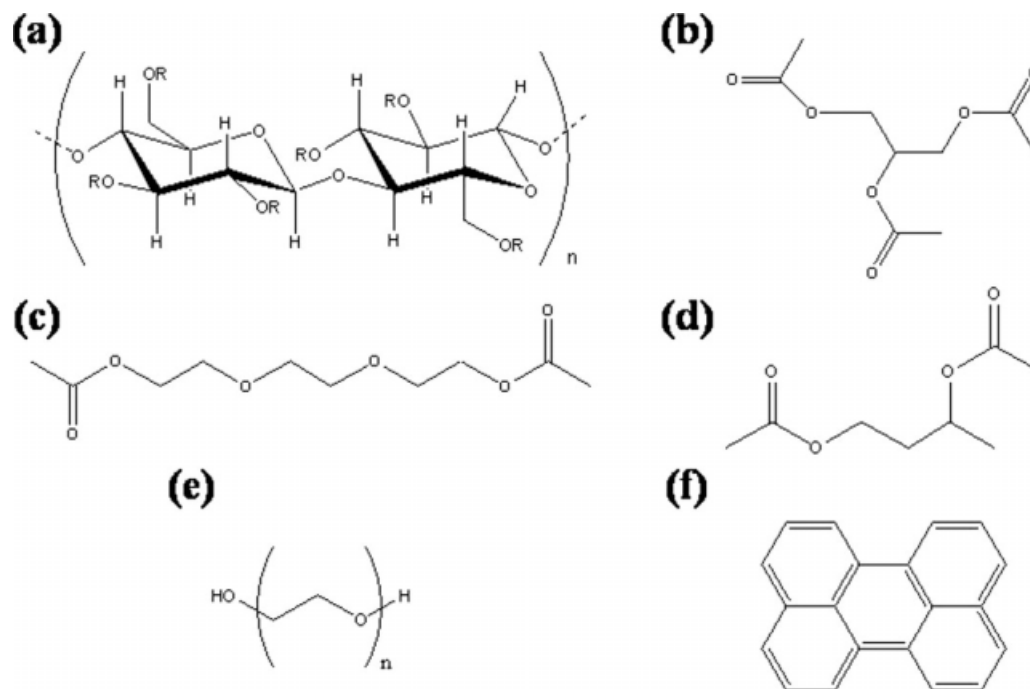
The molar ratio of perylene to GTA, TEGDA, BGDA, paraffin liquid, or PEG for this study was in the range  $2.1 \times 10^{-5}$  to  $13 \times 10^{-5}$ .

### CLSM analysis

Fluorescent spectra of perylene in the CA film were obtained by a CLSM system (CLSM system A1, Nikon Corp., Tokyo, Japan) equipped with a dry objective lens (CFI Plan Apo VC 20 $\times$ , Nikon Corp.). The fluorescence of the CA film was measured by settling a film sample on a microscope. The spectra of the perylene/additive mixture or additive solution were measured by dropping an aliquot (4  $\mu\text{L}$ ) of the solution onto a cover glass settled on a microscope. A diode laser (408 nm, 290–330  $\mu\text{W}$ ) was used for excitation, and fluorescence excited from around the cover glass was detected at room temperature. For the perylene/additive mixtures, the intensity of the reflected fluorescence at  $450 \pm 25$  nm was measured from confocal images around the cover glass with optical filters.

### Visualization of perylene distribution in the CA film by CLSM method

Before the perylene-penetration measurement by the CLSM method, the air-contact surface of the CA film was determined as a 0  $\mu\text{m}$ -depth by a transmission image analysis of the CA film with a halogen lamp. Changes in the fluorescence intensity of perylene in the CA film during the sorption experiments at



**Figure 1** Chemical structures of (a) CA (R = CH<sub>3</sub>CO or H), (b) GTA, (c) TEGDA, (d) BGDA, (e) PEG, and (f) perylene.

room temperature were measured by a CLSM system every 3 min to 1 h after a 4  $\mu$ L perylene/additive mixture was dropped onto the CA film. Confocal images were obtained by 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 10  $\mu$ m with intervals of 1  $\mu$ m. The confocal imaging area was approximately  $640 \times 640 \mu\text{m}^2$  on the X-Y surface, and scan speed and flame size were 1 fps and  $512 \times 512$  pixels, respectively. All other conditions of the CLSM system were the same as mentioned above. The molar ratio of perylene to each mixture was  $8.8 \pm 0.5 \times 10^{-5}$ . Three replicates of CLSM analysis (Mean  $\pm$  Standard deviation) were performed for this study.

## RESULTS AND DISCUSSION

### Fluorescence detection of perylene by CLSM method

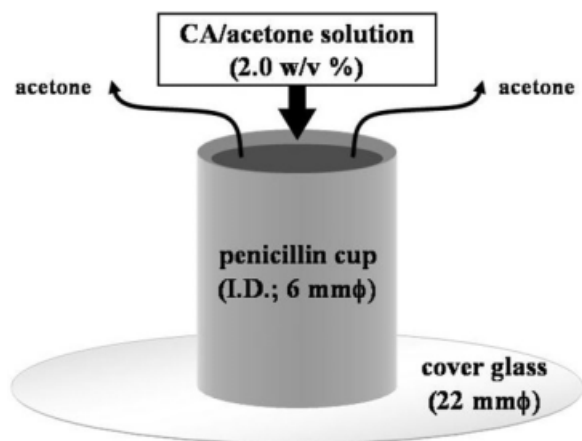
Figure 3 shows the fluorescence spectra of the perylene/additive mixtures, additives, and CA film when excited by a diode laser at 408 nm. The spectra clearly demonstrated that the perylene/additive mixtures showed significant perylene-induced fluorescence intensities around 470 and 503 nm, whereas no fluorescence intensity was observed for the additives and CA film. This indicates that any interference in the fluorescence from the additives or CA film could be excluded for an *in situ* penetration monitoring of perylene in the CA film.

### Linearity for perylene detection by CLSM method

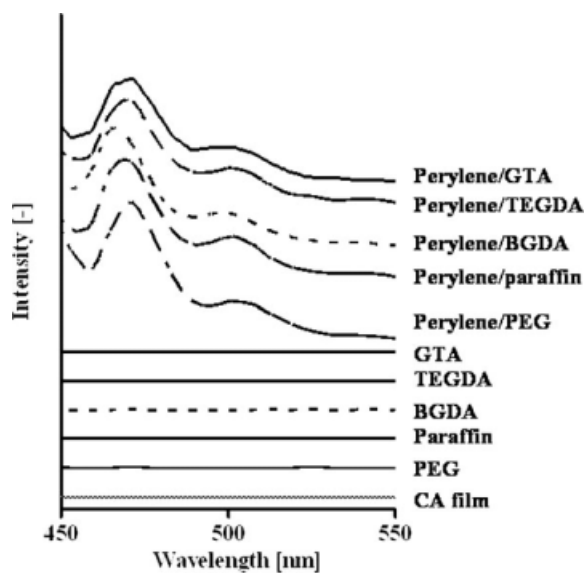
The linearity of the fluorescence intensity with perylene concentration in each mixture was examined as a function of the molar ratio of perylene (Fig. 4). As a result, a good linearity ( $r > 0.978$ ) between the intensity and molar ratio of perylene in each mixture was obtained in the range  $2.1 \times 10^{-5}$  to  $13 \times 10^{-5}$ .

### Monitoring of sorbed perylene in CA film by CLSM method

Chemical images at 0, 4, and 8  $\mu$ m-depths of the CA film treated with perylene/additive mixtures 3 min

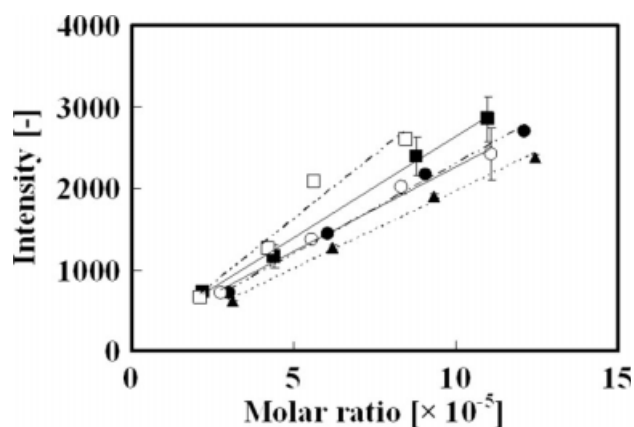


**Figure 2** Film-making unit used for the preparation of the CA film.

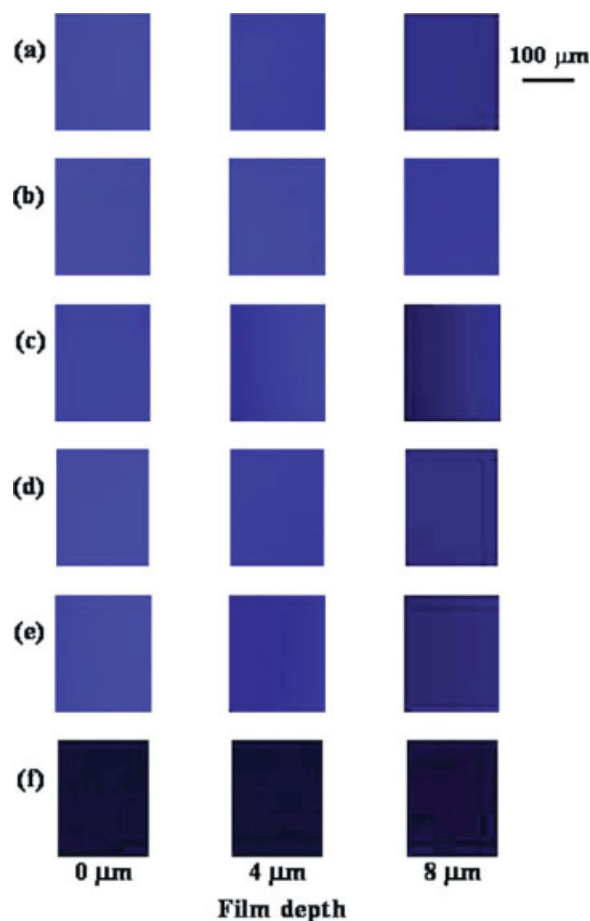


**Figure 3** Fluorescence spectra of the perylene/additive mixtures, additives, and CA film excited by a 408-nm diode laser.

after the addition onto the film are shown in Figure 5 in addition to the time-course images obtained at 21 and 30 min after the addition (in Figs. 6 and 7, respectively). Considering the influence of asperity on the air-contact surface of CA film, we selected approximately  $4.0 \times 10^4 \mu\text{m}^2$  areas from the observation areas for analysis. Blue color derived from the fluorescence intensity of perylene was detected in each image. It was clear that the higher the depth of the film was, the darker the blue color induced by the sorbed perylene was. From the results in Figures 5–7, we found that the brightness of the blue color became greater over time after the mixture addition (t), especially for GTA, TEGDA, and BGDA. These results show that the sorption of the perylene/addi-



**Figure 4** Relationship between the concentration and fluorescence intensity of perylene mixed with additives: (■) GTA, (●) TEGDA, (○) BGDA, (□) paraffin liquid, and (▲) PEG.

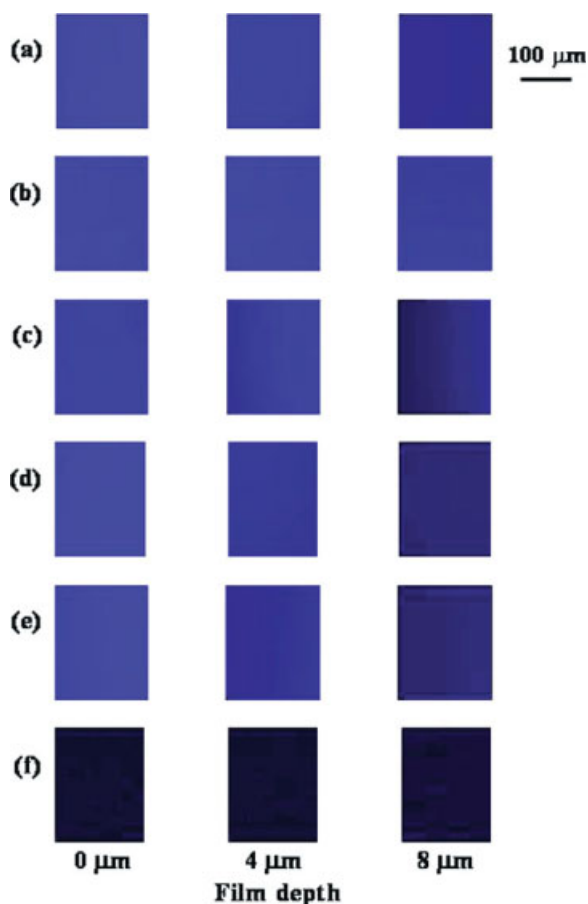


**Figure 5** Chemical images of the CA film at several depths 9 min after the addition of perylene/additive mixtures: (a) perylene/GTA, (b) perylene/TEGDA, (c) perylene/BGDA, (d) perylene/paraffin liquid, (e) perylene/PEG, and (f) a control (without addition).

tive mixture proceeded from the top of the CA film to inside the film progressively over time. The brightness and its change were highest for the perylene/TEGDA mixture.

To quantify this behavior, the fluorescence intensity was calculated as an average of each pixel in a given analytical area for the perylene/additive mixture. Figure 8 shows the changes in the intensities in each depth of CA film, in which the intensity was averaged through three replicates of CLSM analysis. On the horizontal axis, the  $0\mu\text{m}$ -depth indicated the air-contact surface of CA film. The fluorescence intensities in each depth were standardized by the subtraction of the CA-based intensity and subsequently division of the obtained intensity by that of the  $0\mu\text{m}$ -depth for each time. As a result, the change in intensity over time was largest in the perylene/TEGDA mixture. In particular, the standardized intensity ( $S_i$ ) in the perylene/TEGDA mixture increased by a factor of 0.37 at an  $8\text{-}\mu\text{m}$  depth from 3 to 30 min after the addition of the mixture. The





**Figure 6** Chemical images of the CA film at several depths 21 min after the addition of perylene/additive mixtures: (a) perylene/GTA, (b) perylene/TEGDA, (c) perylene/BGDA, (d) perylene/paraffin liquid, (e) perylene/PEG, and (f) a control (without addition).

perylene-induced intensities also clearly increased when GTA and BGDA were used in the mixtures, and their increment was a factor of 0.24 at a 4- $\mu\text{m}$  depth and 0.12 at a 3- $\mu\text{m}$  depth, respectively. For paraffin liquid and PEG, on the other hand, the changes in the intensities were as little as 0.01 at any film depth ( $x$ ), although the intensities were detected within almost a 9- $\mu\text{m}$  depth of the CA film.

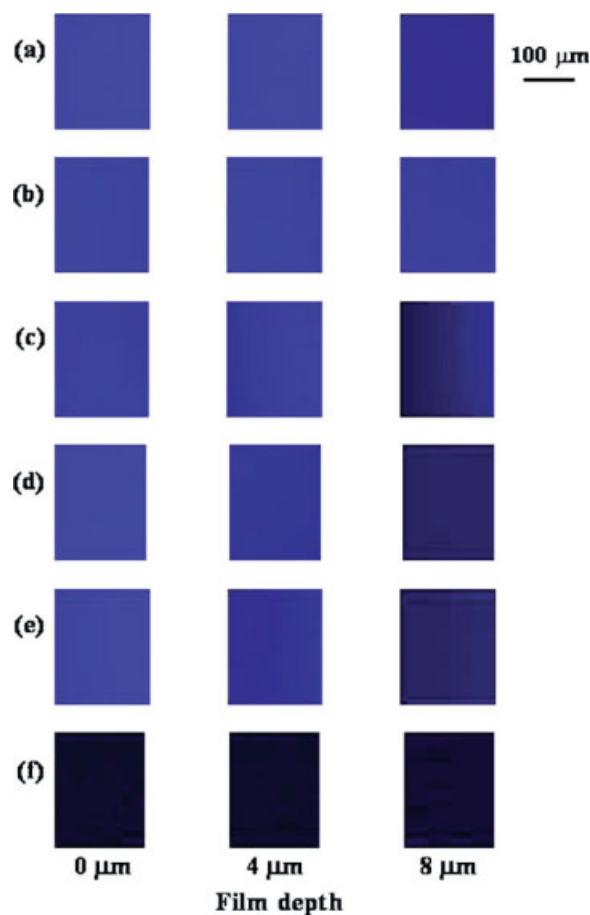
#### Calculation of diffusion coefficient ( $D$ ) of perylene in CA film

From the results shown in Figure 8,  $D$  of perylene was calculated on the basis of Fick's second law, which is given as equation (2):

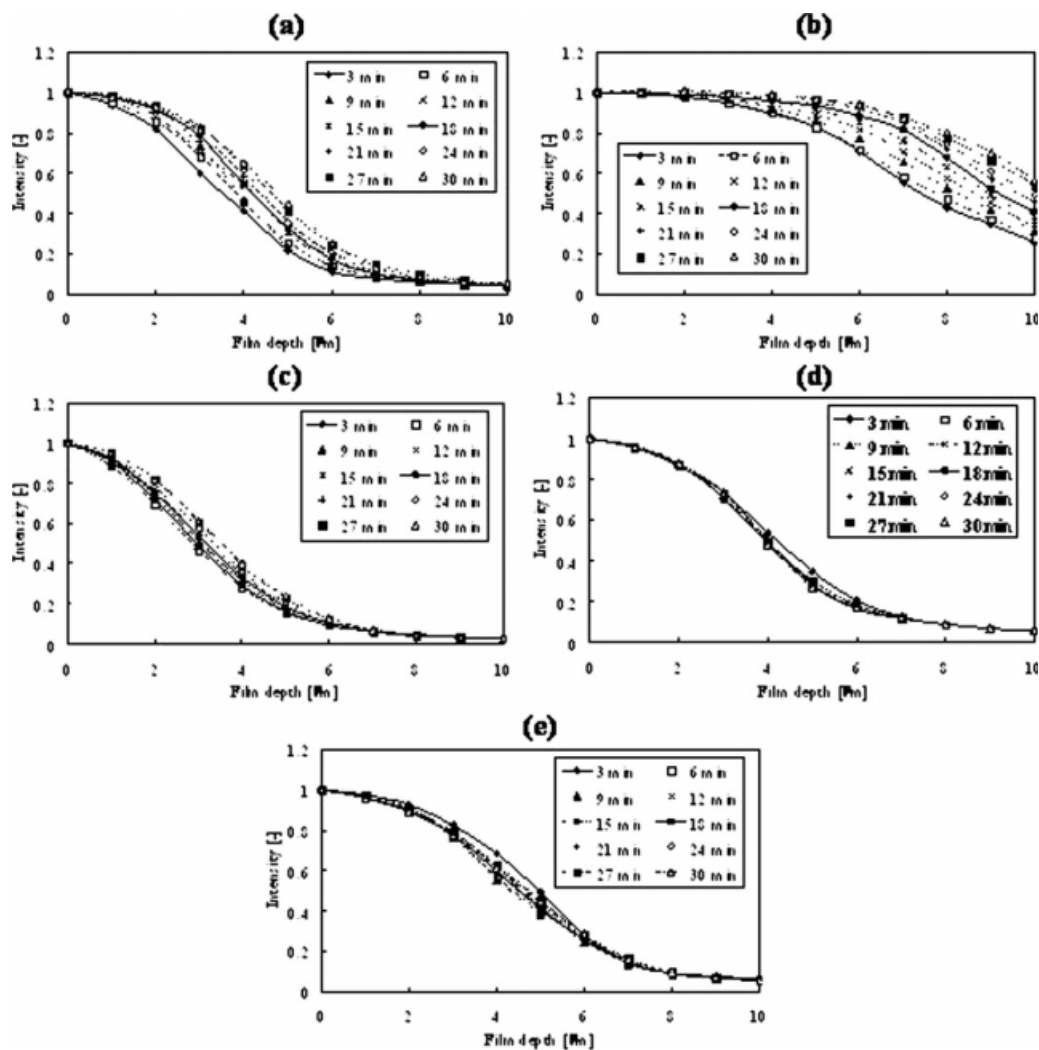
$$\frac{\partial C}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right) \quad (2)$$

where  $C$  is the concentration of perylene. The left side of the equation was obtained as the slope of  $S_i$  versus  $t$  in each depth of film because the intensity had a good linearity for the molar ratio of perylene

(Fig. 4). Then, the second term of the right side was calculated as the slope of a change of  $S_i$  in the 2- $\mu\text{m}$ -depth range,  $\partial S_i / \partial x$ , versus  $x$ . Finally,  $D$  was calculated as the coefficient of both sides of the equation for each depth of film and averaged. Considering good agreement with Fick's second law, the calculation was performed in a particular  $x$  range where both  $S_i$  to  $t$  and  $\partial S_i / \partial x$  to  $x$  relations had linearity. As was the case for the perylene/GTA mixture (shown in Figs. 9 and 10), a high linearity ( $r > 0.969$ ) was obtained in each mixture, and  $D$  was calculated in the range 3–8  $\mu\text{m}$  of depth of the CA film for the mixtures with GTA, BGDA, paraffin liquid, and PEG. For the perylene/TEGDA mixture, additional analysis was performed within a 30  $\mu\text{m}$ -depth of film with 1- $\mu\text{m}$  intervals (data not shown), and  $D$  was calculated in the 10–13  $\mu\text{m}$ -depth range. Figure 11 shows the  $D$  values of perylene in the CA film when it was mixed with additives. The value varied depending on the additives and became highest in the mixture with TEGDA ( $8.9 \times 10^{-15} \text{ m}^2/\text{s}$ ). The order was TEGDA  $>$  GTA ( $1.7 \times 10^{-15} \text{ m}^2/\text{s}$ )  $>$  BGDA ( $1.3 \times 10^{-15} \text{ m}^2/\text{s}$ )



**Figure 7** Chemical images of the CA film at several depths 30 min after the addition of perylene/additive mixtures: (a) perylene/GTA, (b) perylene/TEGDA, (c) perylene/BGDA, (d) perylene/paraffin liquid, (e) perylene/PEG, and (f) a control (without addition).



**Figure 8** Relationship between the depth of the CA film and fluorescence intensity at several times after the addition of perylene/additive mixtures: (a) perylene/GTA, (b) perylene/TEGDA, (c) perylene/BGDA, (d) perylene/paraffin liquid, and (e) perylene/PEG.

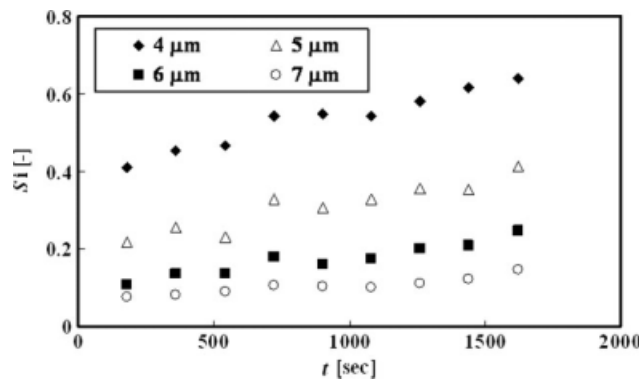
> PEG ( $0.54 \times 10^{-15} \text{ m}^2/\text{s}$ ) > paraffin liquid ( $0.34 \times 10^{-15} \text{ m}^2/\text{s}$ ) in descending order; this indicated that the additives greatly affected the diffusion behavior of perylene in the CA film.

**Effects of chemical and physical parameters on  $D$  value of perylene**

The previous results suggest that the sorption behavior of perylene in the CA film was largely affected by the physicochemical properties of the additives. With regard to the sorption of compounds into polymer materials, the physical and chemical parameters, such as molar volume, free energy, free volume, and solubility parameters, of compounds and/or polymers determine the dynamics.<sup>11-13</sup> When one takes particular note of the solubility parameter, the affinity of a compound with a polymer material and/or another compound

is explained by two-dimensional distance ( $\delta_c$ ) defined as equation (3).<sup>11</sup>

$$\delta_c = \left[ (\delta_{1np} - \delta_{2np})^2 + (\delta_{1p} - \delta_{2p})^2 \right]^{1/2} \quad (3)$$



**Figure 9** Relationship between  $t$  and  $S_i$ .

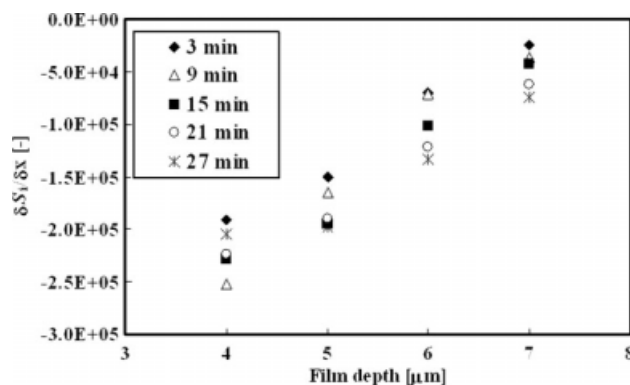


Figure 10 Relationship between  $x$  and the change in  $S_i$ .

where  $\delta_t$  is the total solubility parameter value and  $\delta_{np}$  and  $\delta_p$  are the nonpolar and polar components of  $\delta_t$ , respectively. The smaller  $\delta_c$  is, the higher the affinity is. Table I shows the solubility parameter values of perylene, additives and CA. The solubility parameter values of CA were as previously reported,<sup>28</sup> and those of other compounds were calculated with the computational software Molecular Modeling Pro (version 6.0.1, ChemSW, Inc., Fairfield, CA). The  $\delta_c$  values of the additives from perylene and CA were calculated with the equation (3), and Figure 12 shows an index of chemical affinities,  $1/\delta_c$ . The chemical affinities of the additives with perylene or CA would have affected the perylene–additive compatibility or sorption of the additive itself into the CA film.

It was considered that the highest  $D$  value in the perylene/TEGDA mixture was due to the high affinity of perylene with TEGDA. In contrast, the lowest  $D$  value in the perylene/paraffin liquid mixture was caused by the low affinity of perylene with both paraffin liquid and the CA film. For GTA, BGDA, and PEG, the difference in  $D$  could not be explained only by chemical affinities. Although the  $1/\delta_c$  values from CA were almost the same, the  $1/\delta_c$  values

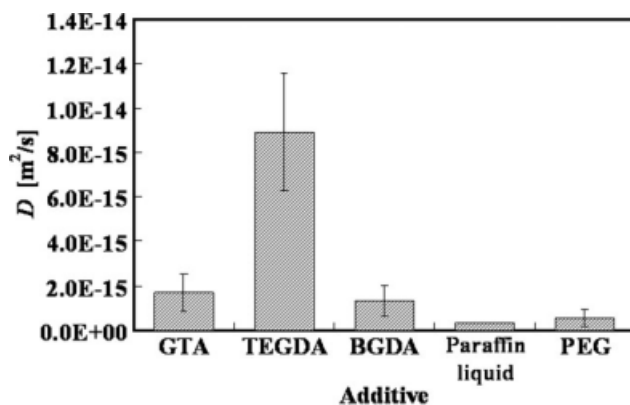


Figure 11  $D$  values of perylene mixed with additives in the CA film.

TABLE I  
Solubility Parameters of the Compounds

Compound	Solubility parameter ( $\text{MPa}^{1/2}$ )		
	$\delta_t$	$\delta_{np}$	$\delta_p$
Perylene	26.0	26.0	1.3
GTA	27.2	26.3	6.8
TEGDA	25.9	25.3	5.7
BGDA	18.9	18.4	4.1
Paraffin liquid	16.7	16.7	0
PEG	22.5	22.0	4.5
CA	25.1	21.6	12.7

from perylene were  $\text{PEG} > \text{GTA} > \text{BGDA}$  in descending order. This order did not agree with that of  $D$  shown in Figure 11; namely, the  $D$  value of perylene in CA added with PEG was lower than the expected value.

The physical parameters, such as the molecular size and viscosity ( $\eta$ ), of the chemicals were then taken into consideration as external affecting factors. When considering the sorption of additives into the CA film, the diffusion coefficient of the additive ( $D'$ ) may have been influenced by its molecular diameter ( $d$ ) and  $\eta$ . The relationships of those parameters are given by the Stokes–Einstein equation, as equation (4):

$$D' = \frac{kT}{3\pi d\eta} \quad (4)$$

where  $k$  and  $T$  are Boltzmann's constant and the absolute temperature, respectively. Table II shows the sphere-equivalent  $d$  and  $\eta$  values of the additives. The sphere-equivalent  $d$  values were calculated by Molecular Modeling Pro. The  $\eta$  values were measured at 25°C with a digital viscometer (DVL-BII, Toki Sangyo Co., Ltd., Tokyo, Japan). As a result,  $D$  of PEG in the CA film was calculated to be lower than those of GTA and BGDA because of the higher  $\eta$  value of PEG. Thus, the lower  $D$  of perylene in PEG (Fig. 11) was caused by the poor

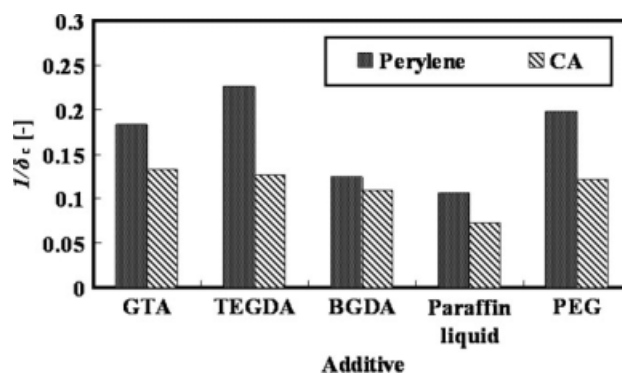


Figure 12 Chemical affinity of the additives to perylene and CA.

**TABLE II**  
***d* and  $\eta$  Values of the Compounds**

Additive	<i>d</i> (nm)	$\eta$ (cPs)
GTA	0.73	17.0
TEGDA	0.71	9.8
BGDA	0.64	3.2
Paraffin liquid	0.96	147.5
PEG	0.71	48.8

diffusion of PEG itself in the CA film. For the perylene/paraffin liquid mixture, we thought that the lowest *D* of perylene was due not only to low chemical effects but also to the physical properties, such as high molecular size and high  $\eta$ , of the paraffin liquid.

### CONCLUSIONS

In this study, the effects of various additives, GTA, TEGDA, BGDA, paraffin liquid, and PEG, on the sorption behavior of perylene into the CA film were compared. The sorption behavior of perylene was visualized dynamically by CLSM methodology, and the *D* values were calculated according to Fick's second law.

Taking these findings together, we confirmed that the *D* value of perylene was influenced by both the chemical affinities for the additives or the CA film and the diffusivity of the additive in the CA film. The highest *D* value of perylene,  $8.9 \times 10^{-15} \text{ m}^2/\text{s}$ , obtained in the TEGDA mixture was due to the high chemical affinity of TEGDA with perylene ( $1/\delta_c$  value was 0.23). In the case of the perylene/GTA, perylene/BGDA, and perylene/PEG mixtures, the difference in the *D* values of perylene ( $1.7 \times 10^{-15}$ ,  $1.3 \times 10^{-15}$ , and  $0.54 \times 10^{-15} \text{ m}^2/\text{s}$ , respectively) could not be explained only by the chemical affinities between the additives and perylene (the  $1/\delta_c$  values were 0.18, 0.12, and 0.20, respectively). On the basis of the physical parameters, we suggest that the lower *D* value of perylene with PEG into the CA film was due to the high  $\eta$  values of PEG. The lowest *D* value of perylene,  $0.34 \times 10^{-15} \text{ m}^2/\text{s}$ , when mixed with paraffin liquid, was caused by both the low chemical affinity and the low diffusivity of paraffin liquid in the CA film.

In further studies, the elaboration of sorption factors, including diverse additives and fluorescent

reagents, will be elucidated with our proposed CLSM system.

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