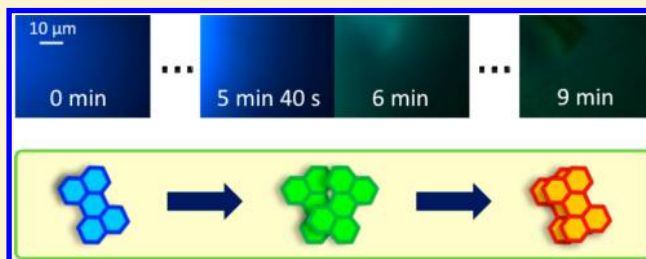


Fluorescence Spectral Changes of Perylene in Polymer Matrices during the Solvent Evaporation Process

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ABSTRACT: This work examined concentration-dependent variations in the fluorescence spectra of solutions of perylene and PMMA in toluene during the process of evaporation, using fluorescence microscopy. At low perylene concentrations, the fluorescence spectra of the resulting perylene/PMMA films exhibited a structural band originating from monomeric perylene. Increasing the concentration resulted in the appearance of new, broader bands due to the formation of two excimer species. An estimation of variations in the fluorescence excitation spectra of these same films with changing concentration and excitation wavelength indicated the formation from monomer to fully overlapped excimer via partially overlapped excimer in terms of the kinetic situation. These species are believed to consist of either ground state aggregates or α -crystals resulting from phase separation within the PMMA films. Dynamic fluorescence changes during solvent evaporation were monitored by fluorescence spectroscopy and CCD photography. Fluorescence emission changed from blue to green with the formation of α -crystals, a pattern which was also observed when increasing perylene concentrations in PMMA films during static trials. The concentration distribution around α -crystals was attributed to the crystal growth process and could be followed by observing the fluorescence color gradient radiating from the crystal. Studying concentration-dependent fluorescence spectral changes during solvent evaporation not only provides insight into the molecular dynamics of the casting process and the compatibility between the dispersed material and the polymer matrix but also provides information concerning molecular assembly and the nucleation and growth of crystals of the fluorescent organic molecules.



INTRODUCTION

In recent years, optoelectronic devices based on organic molecular solids¹ have greatly increased in importance and have attracted significant attention as potential components of advanced sensors,² optical storage media,³ electroluminescence devices and solar cells.⁴ One of the simplest techniques available for the fabrication of these devices is the casting of a solution containing photofunctional organic molecules in a polymeric matrix.⁵ This method has the advantages of minimal material and processing costs and is also important as a green chemistry innovation. When preparing films via casting, the formations adopted by the compounds in the resulting films, such as aggregates or microcrystals, are a crucial aspect of the subsequent performance of the device, since fluorescence bands, charge carrier transport, and exciton diffusion are all influenced by intermolecular interactions of the dyes.⁶ The miscibility between the dye molecules and the polymer is an especially significant factor in controlling the dispersion within the film. For example, the nanoscopic miscibility (in the form of an interpenetrating network) between the donor and acceptor molecules and polymers in so-called “bulk heterojunction” composites allows for efficient charge generation throughout the material.⁷ It is therefore important to both understand and control the dispersion state of dye molecules in the polymer matrix during the casting process.

We have previously reported the fluorescence properties of the pyrene ammonium derivative (PyAm)⁸ and perylene

ammonium derivative (PeryAm)⁹ aggregates formed in a poly(vinyl alcohol) (PVA) matrix by phase separation. At low dye concentrations, only monomer emissions from PyAm and PeryAm in the PVA film are observed, whereas with increasing dye concentrations the fluorescence peak undergoes a red-shift resulting from dimer or excimer-like emission. Observed changes in the fluorescence spectra related to the formation of nanocrystals and/or aggregates in the films increased with increasing dye concentration, due to phase separation. This phenomenon was likely the result of hierarchical changes (such as consecutive reactions) in the fluorescence properties, related to the domain size, and may be attributed to the size effect and to stabilization of surface free energy. We have proposed that concentration-dependent fluorescence spectral changes are due to matrix isolation and/or freezing of crystal nuclei growth by the polymer chains, a method, which we term “polymer matrix isolation”. The fluorescence spectroscopy of films formed from varying concentrations of a dye within a polymer matrix can therefore be applied as a means to find out the state of molecular assembly or crystal nucleation and growth of the dye. This technique essentially consists of the static observation of crystal growth, and although it is useful, complementary dynamic observations are also required to fully understand

Received: January 29, 2013

Revised: February 28, 2013

Published: March 25, 2013

the molecular changes during the actual casting process of the dye/polymer matrix.

There are a number of organic molecules which exhibit characteristic spectral changes depending on changes in their electronic state, manner of assembly, size, and ambient environment.¹⁰ This phenomenon can be employed, at least in principle, as a means of probing the status of a molecular assembly, either with only a few molecules or on a bulk scale, by using fluorescence spectroscopy. Perylene is a fluorescent molecule which undergoes characteristic spectral changes and, due to its high absorption coefficient, fluorescence quantum yield and photostability, has been regarded as a model compound for the study of photofunctional organic devices. The molecular association of perylene has been investigated in several different contexts: in solution,¹¹ in crystal form,¹² in a rigid matrix,¹³ in Langmuir–Blodgett (LB) films,¹⁴ and in polymer films.¹⁵ Perylene molecules exhibit various fluorescence bands, associated with its monomer, E-type and Y-type excimer,^{12,16} ground-state dimer and higher aggregates.¹⁷ Two perylene crystal structures have been reported in the literature: a dimeric structure (the α -phase) and a monomeric structure (the β -phase)¹⁸ and perylene has been shown to fluoresce blue-green when in solution, green as aggregates within polymers or organized media (E-type excimer) and as β -crystals,¹⁹ and yellow-orange in excimers and α -crystals²⁰ (Y-type excimer). Size-dependent optical properties have also been exhibited by perylene nanocrystals prepared via either the reprecipitation method^{10b,c} or laser abrasion.^{10d} The fluorescence of perylene, therefore, can be used to study changes in its electronic excited-state properties caused by the aggregation of isolated molecules into densely packed crystals.²¹ Moreover, perylene is useful as a model compound when investigating the phase-dependent electrical and optical properties of organic crystals.²²

In the work reported herein, we assessed the fluorescence spectral changes of perylene in poly(methyl methacrylate) (PMMA)/toluene solutions during the solvent evaporation process, using a fluorescence microscope. As a preliminary step, the fluorescence spectra of perylene in PMMA films at a variety of concentrations were obtained, to provide information concerning the fluorescence of the films at essentially infinite drying time. Analysis of such films under these conditions allows us to investigate the polymer matrix isolation method proposed previously by our group. Subsequent to these static trials, we undertook the measurement of dynamic fluorescence changes of droplets of perylene in PMMA/toluene solution during the solvent evaporation process, via a combination of fluorescence spectroscopy and photography (using a CCD camera) at various time intervals. The concentration-dependent fluorescence spectral changes during the evaporation of solvent from the droplets provides us not only with information regarding the molecular dynamics of the casting process but also with insights into the molecular assembly and crystal formation of the dye molecules.

EXPERIMENTAL SECTION

Perylene was purified by repeated zone refining. Poly(methyl methacrylate) (PMMA) with a number-average molecular weight (M_n) of 350 000 was purchased from Aldrich and was used as-received. Perylene-doped PMMA thin films were prepared by drop-casting toluene solutions, in which the PMMA concentration was fixed at 2 wt %, onto quartz plates. Perylene was added to the PMMA/toluene solutions at concentrations of 0.005, 0.01, 0.1, 0.5, 1.0, 2.0, 4.0, 8.0, and

10 mol % relative to the quantity of PMMA monomer units. The cast films were dried under vacuum for 24 h at 298 K. UV–vis absorption spectra were acquired with a Shimadzu UV-2450 spectrometer and fluorescence spectra were recorded on a Shimadzu RF-5300PC fluorescence spectrophotometer. Fluorescence color, morphology of the films, and crystal shape were captured using an inverted microscope (Olympus IX71) with high pressure mercury lamp excitation and a dichroic mirror (Olympus WU filter cube). The microscope was combined with a CCD camera (Sigma Koki SK-TC202USB-AT) and a USB 4000 (Oscan Optics) spectrometer. This instrumentation was not corrected for wavelength dependence of the detectors. The microscope objective lens was a 40 \times , N.A. 1.45, oil immersion, plan apochromat (1-U2B616 Olympus). All experimental trials were carried out at room temperature.

RESULTS AND DISCUSSION

Fluorescence Properties of Perylene in a PMMA Matrix. As an initial step, the fluorescence spectra of cast films formed from perylene in PMMA were measured as a function of perylene concentration, a technique which allows us to apply the polymer matrix isolation effect. Figure 1 shows the

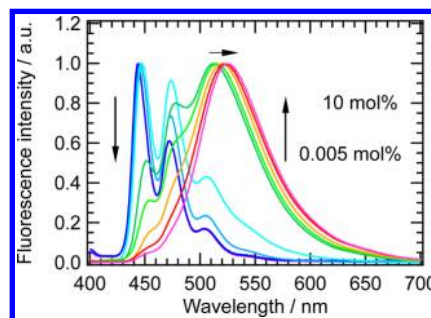


Figure 1. Fluorescence spectra of perylene in PMMA films as a function of concentration (excitation at 365 nm).

fluorescence spectra of perylene/PMMA thin films cast from toluene solutions of varying concentrations, using an excitation wavelength of 365 nm. The fluorescence spectra were normalized by the maximum intensity. At the lower concentrations of 0.005 and 0.01 mol % perylene, structural fluorescence bands were observed at 443, 470, and 505 nm, corresponding to the emission spectrum of monomeric perylene.¹² The fluorescence intensity at both 470 and 505 nm increased at a concentration of 0.5 mol %, although at higher concentrations the monomer fluorescence bands decreased in intensity with increasing perylene concentration, and a broad new fluorescence band appeared around 510 nm at concentrations over 1.0 mol %. The observed decrease of the 443 nm band upon increasing the perylene concentration could be due to reabsorption of the fluorescence or energy transfer to the broad fluorescence band located within the longer wavelength region. The 510 nm peak is red-shifted as the concentration is further increased, eventually extending up to 525 nm at a perylene concentration of 10 mol %. A shoulder in the region of 600–680 nm was also observed at high concentrations. The fluorescence peaks at approximately 510 nm and around 600–680 nm were assigned to the partially overlapped excimer and fully overlapped excimer, as has been reported for LB films and α -crystals, respectively.^{14b} In this paper, the partially overlapped excimer and fully overlapped excimer are abbreviated as excimer 1 and excimer 2,

respectively, using the same nomenclature applied by Akimoto et al., as a matter of convenience.

To obtain information concerning the ground-state molecular structure or intermolecular interactions of perylene, the absorption spectra of perylene/PMMA films were also acquired. Figure 2 presents the absorption spectra of

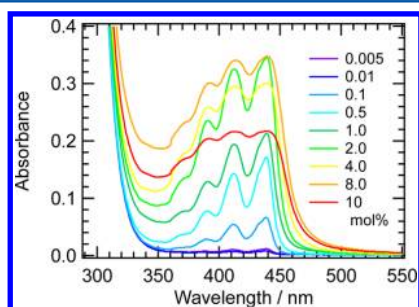


Figure 2. Absorption spectra of perylene in PMMA films as a function of concentration.

peryene/PMMA films obtained over a range of perylene concentrations. At the lower concentrations of 0.005 to 2.0 mol %, absorption peaks were observed at 391, 413, and 439 nm, assigned to vibrational modes of the perylene monomer. The tail of the absorption band is observed extending up to 450 nm with increasing concentrations. The depth of the absorption troughs in the vicinities of 400 and 425 nm are reduced with increasing concentrations over 4.0 mol % and band broadening is also observed with increasing concentration, as a result of association between perylene molecules. The peak-to-trough ratios (P_A) at each concentration were determined by taking the ratio of the peak absorbance at 440 nm to the trough at 425 nm, and are listed in Table 1. Beginning at 0.1 mol %, P_A can be seen to decrease exponentially with increasing concentration until reaching a steady value at 4 mol %. These findings indicate that dimers, aggregates or crystals of perylene in the ground state were formed in the PMMA films.

The fluorescence excitation spectra of two different perylene/PMMA films (concentrations of (a) 0.005 (most dilute) and (b) 10 (most concentrated) mol %) are shown in Figure 3. The fluorescence peaks can be observed at 450 and 470 nm, 510 and 530 nm, and 570 and 600 nm and are assigned to the monomer, excimer 1, and excimer 2, respectively. The vibrational bands appearing at approximately 390, 413, and 438 nm in response to excitation at 450 or 470 nm appear largely independent of the film concentration, indicating that the fluorescence band around 450 to 470 nm can be assigned to monomer emission. The excitation spectra observed in response to excitation at 510 and 530 nm, which correspond to excimer 1, are similar to the spectra of the monomer band, which implies that the excimer 1 species is formed only in the excited state or that partial overlap interactions are quite weak in the ground state. Excimer 1 is expected to have either a one-center or partial overlapping

conformation. Conversely, the spectral shape observed for the concentrated film in response to excitation at 570 and 600 nm changes dramatically, with a broad structureless band extending up to 450 nm. Therefore the excimer 2 species is not only formed in the excited state but may also result from dimers or aggregates in the ground state, as in the perylene α -crystal.

On the basis of the above fluorescence, absorption, and fluorescence excitation spectral data, we can draw some conclusions regarding the molecular forms and states of perylene in a PMMA matrix. At lower concentrations (below 0.01 mol %), perylene exists in these thin films in the form of a monomer. The fluorescence intensity resulting from excimer 1 then increases with increasing concentration over the range from 0.1 to 0.5 mol %. Energy migration and trapping at partially overlapped perylene sites is expected to occur in PMMA films, as reported by Akimoto et al.^{14b} The green emissive species consists not only of excimer 1 but also the β -crystal, which emits at 510 nm with a very sharp band, as the result of a weakly trapped excited state due to dimers and small aggregates in which there is partial overlap between the perylenes (just as in the β -crystal).²³ It is difficult to distinguish clearly between excimer 1 and micro β -crystals solely on the basis of spectra obtained using only a conventional fluorescence spectrophotometer (need to space-resolved spectroscopy), although micro β -crystals have occasionally been observed in PMMA thin films by fluorescence microscopy, a point which will be discussed in the following section. The shoulder at longer wavelengths around 600 nm can be assigned to excimer 2, which corresponds to the α -crystal. Since the increasing localized concentrations of perylene in the films during solvent evaporation will result in crystallization, these findings suggest that perylene forms nanocrystals as a result of phase separation, depending on its concentration in the PMMA films.

Fluorescence Spectral Change during the Solvent Evaporation Process. We subsequently attempted to monitor dynamic fluorescence changes in these films over time, using a combination of fluorescence spectroscopy and CCD camera photography. As a preliminary step, the polymer matrix effect on the molecular dispersion of perylene following solvent evaporation was studied by examining the fluorescence spectral changes of toluene solutions of perylene as they dried after being dropped onto glass. Figure 4 shows the fluorescence spectra of droplets of 1.74×10^{-5} mol·dm⁻³ perylene in toluene (without PMMA) over time, as the solvent evaporates. The fluorescence spectra were normalized at maximum intensity. Fluorescence peaks are observed at 443, 474, and 505 nm, originating from the perylene monomer structure. At approximately 4 min, corresponding to almost complete evaporation of the solvent, the fluorescence intensity decreases dramatically and the fluorescence peak shifts to approximately 530 nm. The fluorescence spectra after 4 min are identical to the excimer fluorescence as described above, suggesting that solvent evaporation results in the formation of molecular assemblies due to increasing local concentrations of perylene

Table 1. Peak (440 nm, A^{Peak}) to Valley (425 nm, A^{Trough}) Absorbance Ratios Obtained for Perylene/PMMA Films^a

mol %	0.005	0.01	0.1	0.5	1.0	2.0	4.0	8.0	10
A^{Trough}	0.012	0.008	0.067	0.172	0.213	0.345	0.301	0.348	0.217
A^{Peak}	0.007	0.005	0.030	0.084	0.139	0.253	0.271	0.316	0.207
P_A	1.714	1.600	2.233	2.048	1.532	1.364	1.111	1.101	1.048

^a P_A is defined as $A^{\text{Trough}}/A^{\text{Peak}}$.

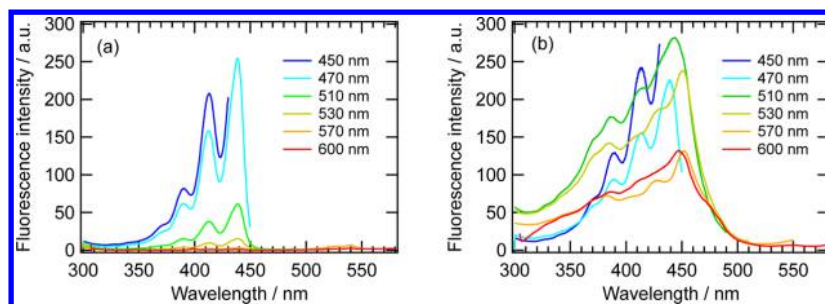


Figure 3. Fluorescence excitation spectra monitored at various wavelengths of perylene/PMMA films of concentration (a) 0.005 and (b) 10 mol %.

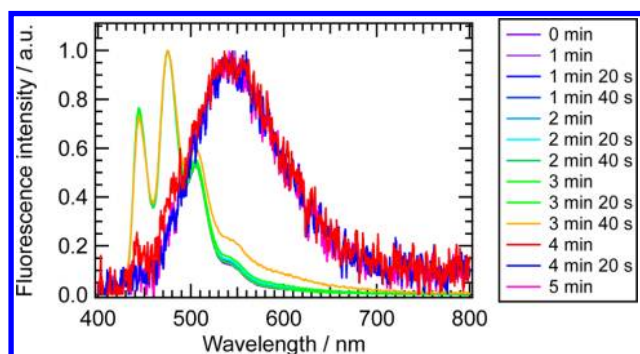


Figure 4. Fluorescence spectral changes of a $1.74 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ perylene in toluene droplet during solvent evaporation.

molecules, even when starting with a dilute solution. To confirm whether the addition of polymer produces a matrix isolation effect, we also observed the fluorescence spectral changes of an evaporating droplet of perylene in 2 wt % PMMA/toluene solution. The perylene concentration in the droplet was 0.01 mol %, corresponding to a concentration of $1.74 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. Fluorescence peaks are observed at 443, 474, and 505 nm, again originating from the perylene monomer. The fluorescence spectra, however, are almost unchanged before and after the solvent evaporation, as shown in Figure 5, up to a time of 10 min, at which point the cast film

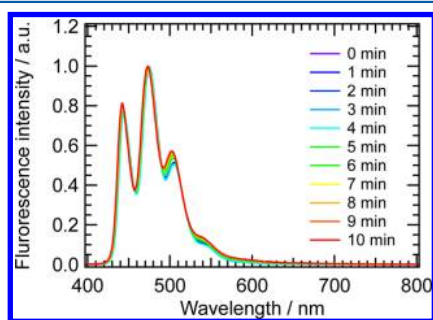


Figure 5. Fluorescence spectral changes of 0.01 mol % perylene in PMMA/toluene solution during solvent evaporation.

of perylene in PMMA was almost dry. The perylene evidently cannot assemble within the PMMA polymer matrix, which acts to inhibit such assembly. These findings indicate that the polymer matrix can ensure that perylene molecules remain dispersed in the monomeric state even after the solvent evaporation of a 0.01 mol % solution. We next examined the concentration dependence of fluorescence spectral changes during solvent evaporation. Figure 6 presents both the fluorescence spectra and fluorescence microscope images of a

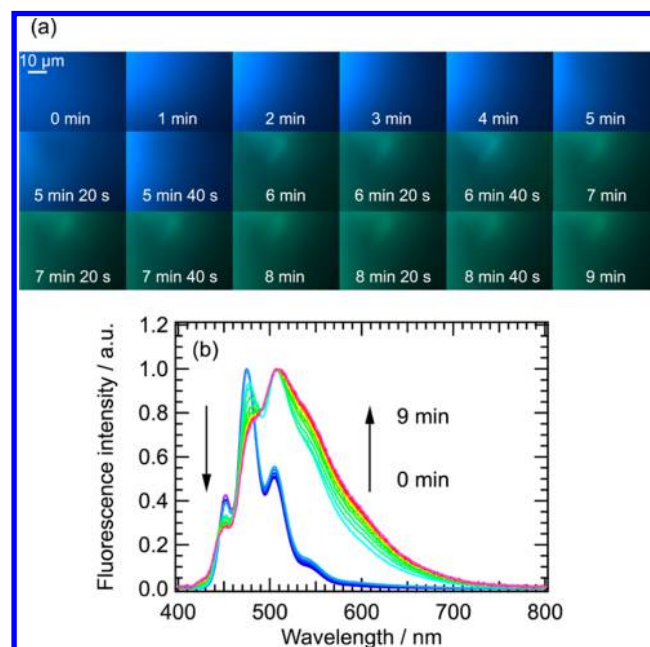


Figure 6. (a) Fluorescence microscope images and (b) fluorescence spectra of a 6 mol % perylene in 2 wt % PMMA/toluene solution during solvent evaporation.

droplet of 6 mol % perylene in PMMA/toluene solution (2 wt %) during solvent evaporation. The fluorescence spectra in this figure have been normalized to the height of the maximum peak. The fluorescence spectrum acquired immediately after applying the droplet exhibits peaks at 443, 474, and 505 nm, corresponding to monomer emission. The intensity at 443 nm is lower than expected, most likely as a result of the effects of reabsorption and the sharp cut filter employed with the fluorescence microscope (Olympus WU filter cube). The fluorescence spectra are essentially unchanged up to 5 min 40 s, following which, between 5 min 40 s and 6 min, the fluorescence peak shifts to 510 nm with a concurrent decrease in intensity. After 6 min, the fluorescence intensity at 510 nm and above is seen to increase with time. Figure 6a presents fluorescence microscope images of a droplet of perylene in PMMA/toluene during solvent evaporation. The images from just after the application up to 5 min show only a relatively uniform blue color, with the appearance of a pale white structure in the left upper corner at approximately 5 min 20 s. The fluorescence image color changes from blue to green after 6 min, which is in agreement with the changes seen in the fluorescence spectra at this same point in time, and this color remains constant up until the completion of evaporation at 9 min. By varying the focus of the microscope, we were able to

determine that the white structure was a rectangular crystal with orange emission, which, based on its shape and emission, can be considered an α -crystal of perylene.¹⁹ The formation of such crystals is likely due to phase separation in the polymer matrix. At this perylene concentration, the evaporation of toluene over time results in a constant decrease of the mean intermolecular distance, which in turn results in the observed fluorescence spectral changes. Ohta et al. mentioned that perylene micro α -crystals may be formed in PMMA films, based on an analysis of the temperature dependence of the electric field effect on fluorescence spectra.^{15b} Combining the results of Ohta et al. with the data obtained through our fluorescence microscope images, we can conclude that micro α -crystals will most probably form as a consequence of phase separation in the PMMA matrix at a perylene concentration of approximately 3 to 4 mol %, indicating that the compatibility between perylene and PMMA is relatively poor.

In some cases, perylene β -crystals may be formed under the same conditions as α -crystals. Since solvent evaporation is a heterogeneous, nonequilibrium process, it is difficult to create conditions which will result in the selective formation of solely α - or β -crystals. In our work, the formation of both α - and β -type microcrystals in the PMMA films was confirmed by fluorescence microscope images at 400 \times magnification, although it is likely that the β -crystals are rarely formed in those films exhibiting green fluorescence with rhombic crystal. Tachikawa et al. reported the anomalous fluorescence of perylene in polystyrene,^{15a} in which a band was observed at 527 nm which differed from the expected fluorescence peaks of the β -crystal at 535 and 565 nm and was assigned to an excimer-like perylene species. To clarify whether partially overlapped excimers or β -crystals were responsible for the green fluorescent emission of PMMA, we obtained the fluorescence spectra of both micro α - and β -crystals formed in PMMA by fluorescence microscopy, as shown in Figure 7. The α -crystal

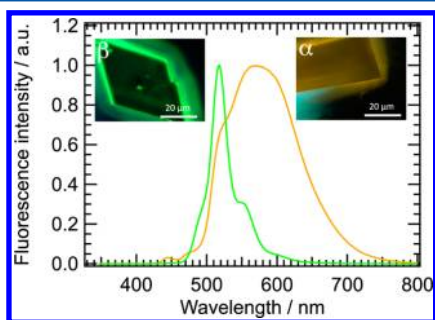


Figure 7. Fluorescence spectra and (inset) fluorescence microscope images of perylene (yellow line) α - and (green line) β -microcrystals.

shows broad yellow emission with a peak around 580 nm, which is identical to the emission of the fully overlapped excimer. The β -crystal exhibits a green emission peak at 515 nm with a narrowed band as compared to the fluorescence spectra of the green emissive species in PMMA films. This spectral narrowing can be attributed to the elongation of the coherence length in the excited states of the well-organized perylene molecules. These findings indicate that the green emission from perylene in PMMA films primarily originates from the partially overlapped excimer rather than the β -crystal. In general, then, the fluorescence spectra of perylene in PMMA/toluene solutions underwent dramatic changes as a result of increased local concentration during the solvent evaporation, with

concurrent sequential fluorescence color changes from blue to green which were observable by fluorescence microscope.

Polymer Matrix Isolation and the Concentration Gradient around a Crystal Due to Growth. One goal of the present study was to clarify the dynamics of the formation and growth process of perylene crystals in response to polymer matrix isolation or freezing. In some instances, clear evidence of the formation of α -crystals was observed using the polymer matrix isolation method. Figure 8 shows the fluorescence

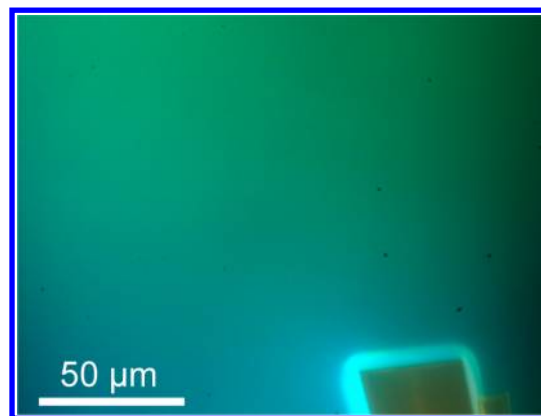


Figure 8. Fluorescence microscope image of a 4.0 mol % perylene in PMMA film following solvent evaporation.

microscope image of a 4 mol % perylene in PMMA film following solvent evaporation, in which a perylene α -crystal with yellow emission can be seen in the lower right corner. A bright sky-blue emission is observed around the perimeter of the crystal, which gradually transitions to green moving out from the crystal. As noted above, the fluorescence of perylene depends on its concentration, and these blue and green emissions are assigned to the monomer and partially overlapped excimer of perylene, respectively. The decreased perylene concentration in the vicinity of the α -crystal occurs because the rate of molecular adsorption to the crystal surface is faster than that of molecular desorption from the crystal, such that this area corresponds to the catchment area in the crystal growth process. This suggests that the formation of these partial-overlap dimers (or small aggregates) is somewhat reversible. The emission gradient moving out from the crystal shows that there is a corresponding concentration gradient around the crystal. We have therefore succeeded in demonstrating matrix isolation of the crystal growth process in a polymer matrix solution by fluorescence imaging.

CONCLUSION

We tracked the fluorescence spectral changes of perylene in PMMA films during the solvent evaporation process of single droplets using fluorescence microscopy. The fluorescence spectra of perylene in PMMA films were increasingly red-shifted with increasing concentration, which suggested a transition from monomer to fully overlapped excimer via partially overlapped excimer in terms of the kinetic situation. Investigating the concentration and wavelength dependence of the fluorescence excitation spectra of these films revealed the formation of ground state aggregates or α -crystals as the result of phase separation in the PMMA films, and also indicated that perylene and PMMA are relatively immiscible. We also monitored dynamic fluorescence changes over time using

fluorescence spectroscopy and CCD photography. The fluorescence emission was observed to transition from blue to green concurrent with solvent evaporation, a change associated with the formation of α -crystals. These spectral changes were in good agreement with spectra obtained from dried perylene/PMMA films made at increasing concentrations. The perylene concentration distribution in the vicinity of an α -crystal, attributed to the crystal growth process, can be observed visually from the associated gradient in fluorescence color. On the basis of these results, it seems reasonable to propose that polymer matrix isolation or freezing effects may be used to study molecular assembly processes by following fluorescence changes. These findings indicate that concentration-dependent fluorescence spectral changes during solvent evaporation can elucidate not only the molecular dynamics of the casting process and the degree of compatibility between the dispersed material and polymer matrix but can also provide information concerning the molecular assembly and nucleation and growth of crystals of the fluorescent organic molecules.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Zone-refined perylene was supplied by Prof. R. Katoh of Nihon University. This work was partly supported by a Grant-in-Aid for Young Scientists (B) (No. 21750021) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government, by the Iketani Science and Technology Foundation, and by the JGC-S Scholarship Foundation.

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