

# Emission Modulation of Poly(vinyl acetate)– Tetrabutylphosphonium Tetrafluoroborate Hybrid Film Doped with 4-[Bis(4-methylphenyl)amino]- benzaldehyde

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A hybrid film of poly(vinyl acetate) and tetrabutylphosphonium tetrafluoroborate together with 4-[bis(4-methylphenyl)amino]benzaldehyde as a fluorescent dopant was fabricated. It was found that the film exhibited thermally reversible phase-separation and dissolution transitions and that both homogeneous and phase-separated states could be obtained at room temperature by appropriate thermal treatments. In addition, emission modulation of the film was achieved by using the phase-separation–dissolution transitions. Fluorescence properties including fluorescence life times and quantum yields in homogeneous film seemed to be unchanged by phase separation, suggesting that no significant change in the surrounding environment of the dopant molecules took place by phase-separation–dissolution cycles. Therefore, the emission modulation observed here was suggested to be due to mainly the change in the light-scattering effect caused by phase transitions.

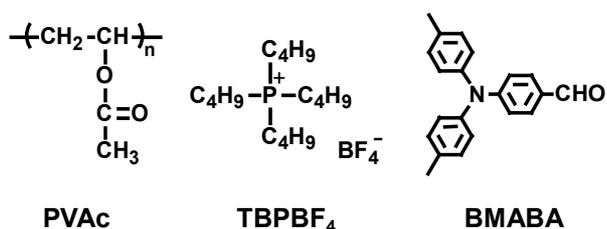
**Keywords :** hybrid film, phase separation, fluorescent dye, quaternary salt, poly(vinyl acetate)

## 1. Introduction

Materials that exhibit reversible change in optical properties upon thermal treatments have attracted attentions from viewpoints of fundamental sciences and of practical applications for e.g. rewritable memories and displays. Several systems such as mixtures of leuco dyes with developers and systems of behenic acid dispersed in vinyl polymers have been used as rewritable displays for kinds of reward cards [1–5]. Creation and application of new rewritable materials systems are the subjects of interest and of importance for coming paperless society.

A variety of studies regarding polymer blends and their phase-separation and dissolution behaviours have been made extensively. In contrast, we have recently started studies on photo-functional hybrid systems that include low molecular-mass component. For instance, hybrid

films composed of azobenzene-based photochromic amorphous molecular materials, namely low molecular-mass photochromic materials that readily form amorphous glasses, and quaternary ammonium and phosphonium salts were found to exhibit phase separation to form dissipative self-assembled microstructures not only by heating but also by photoirradiation [6]. We have also found that hybrid films of azobenzene-based photochromic amorphous molecular materials and poly(vinyl acetate) (PVAc) exhibited thermally reversible phase-separation–dissolution transitions and that the structure of domains produced in the phase-separated film could be deformed by irradiation with polarized laser beam [7]. In addition, we have reported that hybrid films of PVAc and quaternary ammonium and phosphonium salts exhibited thermally reversible phase-separation and dissolution transitions and



that the fluorescence emission intensity of pyrene-doped hybrid film of PVAc and tetrabutylphosphonium tetrafluoroborate (TBPBF<sub>4</sub>) could be modulated by the phase-separation and dissolution transitions [8].

Here we focussed on 4-bis(4-methylphenyl)amino]benzaldehyde (BMABA) as a fluorescent dopant for PVAc–TBPBF<sub>4</sub> system. We have reported that BMABA exhibited solvatofluorochromism, that is, the emission color was depending upon the solvent polarity [9]. It is expected that the fluorescence properties of BMABA in the film provide information about the change in the surrounding environment of the molecule by phase-separation and dissolution transitions. In the present study, emitting properties of BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film have been investigated.

## 2. Experimental

### 2.1. Preparation of BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film

The sample film was prepared onto a glass substrate by spin-coating method (3000 rpm) from a dichloromethane solution of PVAc and TBPBF<sub>4</sub> (1:1 w/w) together with BMABA (1 wt%) by means of a simplified spin coater (MODEL SC 2005, Aiden Co., Ltd.).

### 2.2. Measurements and apparatus

Phase-separation and dissolution behaviors of the sample film were observed by using an optical microscope (Optiphot X2, Nikon) fitted with a TH-600PM hot stage (Linkam).

Fluorescence spectra and absolute fluorescence quantum yields of the films were measured with a fluorescence spectrophotometer (FP-8300, JASCO Co.) at 30 °C. Fluorescence life-times were analyzed by using time-correlated single photon counting method (SPEX Fluorolog-3, HORIBA, Ltd. Excitation wavelength: 360 nm).

## 3. Results and discussion

### 3.1. Phase-separation and dissolution behaviors of

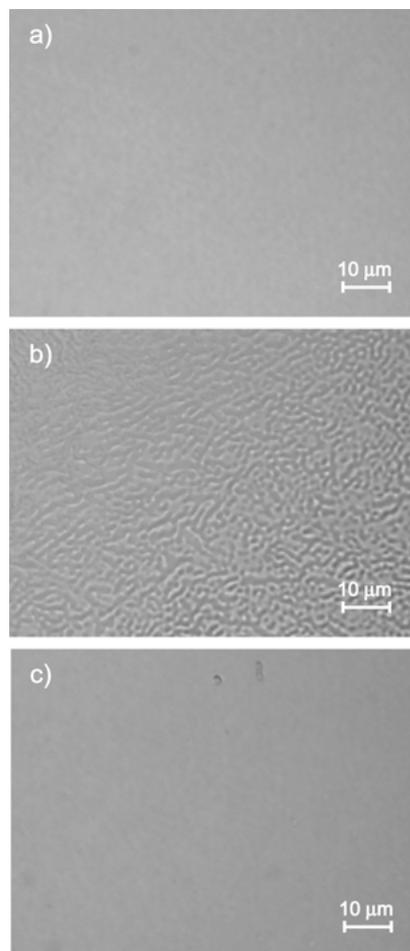


Fig. 1. Optical microphotographs of BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film. a) As-prepared film at room temperature, b) 90 °C, c) 110 °C.

### BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film

The BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film obtained by spin-coating method was found to be homogeneous (Fig. 1a). When the film was heated, phase separation was found to take place around 90 °C (Fig. 1b). On further heating, the film again become homogeneous above 110 °C (Fig. 1c). When the resulting homogeneous film was cooled rapidly, the film kept in the homogeneous state at room temperature. On the other hand, the phase-separated state was obtained by cooling the phase-separated film obtained above 90 °C. The phase-separation and dissolution temperatures of the film were almost similar to those for PVAc–TBPBF<sub>4</sub> film without the dopant. Therefore, doping with BMABA did not affect to the phase behaviors of the present hybrid films.

### 3.2. Modulation of fluorescence emission

Both homogeneous and phase-separated films of the BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film

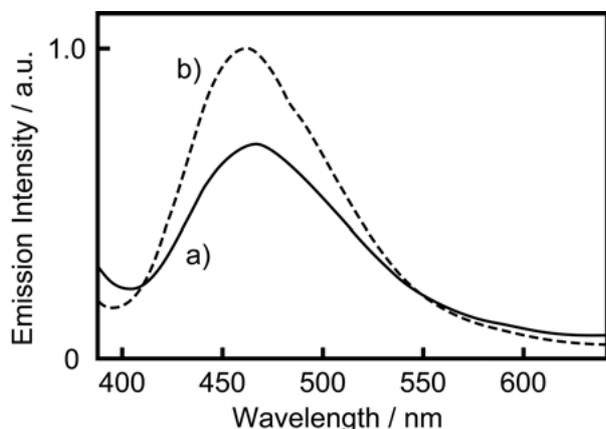


Fig. 2. Fluorescence spectra of BMABA-doped PVAc-TBPBF<sub>4</sub> hybrid film at 30 °C. a) Homogeneous state. b) Phase-separated state.

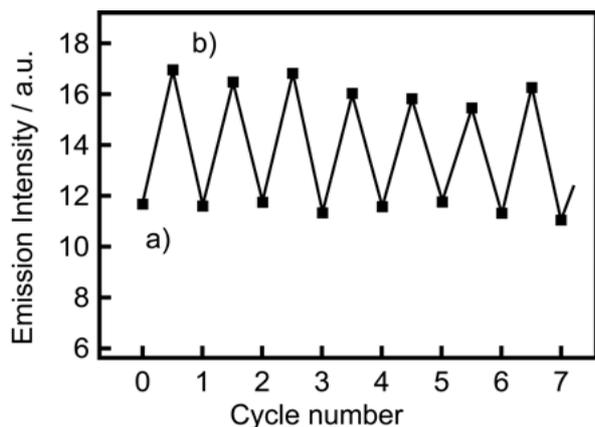


Fig. 3. Change in relative emission intensity of BMABA-doped PVAc-TBPBF<sub>4</sub> hybrid film at 30 °C upon repetition of phase-separation-dissolution cycles. a) Homogeneous state. b) Phase-separated state.

were found to emit fluorescence upon UV irradiation. Fig. 2 shows fluorescence spectra of the film. The fluorescence spectrum for the homogeneous state showed a broad emission band with  $\lambda_{\text{max}}$  of ca. 470 nm. When the film was changed to be in phase-separated state by heating to ca. 100 °C followed by cooling to room temperature, the intensity of the fluorescence was found to increase. When the film was changes to be in homogeneous state again by heating to ca. 120 °C followed by rapid cooling to room temperature, the spectrum almost recovered to the original. Thus, the modulation of the fluorescence intensity could be achieved by thermal treatments. Such modulation of the fluorescence intensity of the hybrid film could be

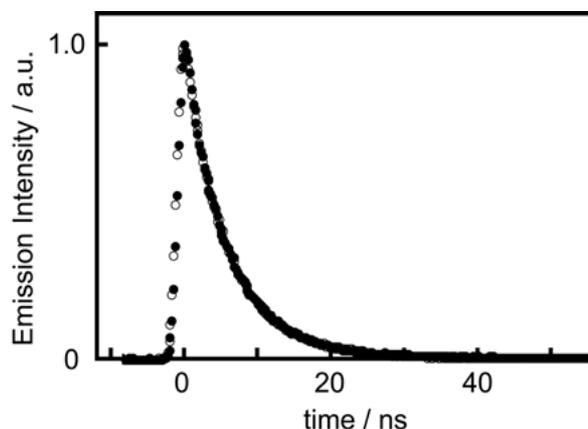


Fig. 4. Fluorescence decays for the BMABA-doped PVAc-TBPBF<sub>4</sub> hybrid film. ○ : Homogeneous state. ● : Phase-separated state. Excitation wavelength: 360 nm, Monitored wavelength: 490 nm.

Table 1. Fluorescence life time for BMABA-doped PVAc-TBPBF<sub>4</sub> hybrid film

Monitored wavelength	homogeneous state	phase-separated state
430 nm	1.8 ns (0.47)	1.8 ns (0.55)
	4.8 ns (0.53)	4.9 ns (0.45)
490 nm	4.9 ns (0.70)	5.2 ns (0.80)
	8.4 ns (0.30)	8.9 ns (0.20)

induced repeatedly without significant fatigue as shown in Fig. 3.

### 3.3. Fluorescence life times and quantum yields

It is conceivable that the modulation of the fluorescence intensity was caused by change in the light-scattering effect by phase transitions. However, there was a possibility that the surrounding environments of BMABA molecules changed by phase transitions, resulting in the emission modulation. In order to gain further information, fluorescence life times and quantum yields were investigated.

Fluorescence life times for the homogeneous and the phase-separated films were analyzed by conventional time-correlated single photon counting method. Fig. 4 shows the fluorescence decays for the hybrid film at homogeneous and phase-separated states, indicating that the resulting decay profiles were quite similar to each other. These fluorescence decays could be analyzed with two components as summarized in Table 1,

indicating that the fluorescence decays for the homogeneous and phase-separated states were almost similar to each other. The absolute fluorescence quantum yields were determined to be 0.27 and 0.29 for homogeneous and phase-separated states, respectively, indicating that the values were almost identical to each other within experimental error. In addition, no considerable change in emission maxima was observed in the fluorescence spectra between homogeneous and phase-separated states as shown in Fig. 2, although the emission maxima of BMABA in solutions were depending upon the polarity of the solvent [9]. All these results suggested that the surrounding environment of BMABA in the hybrid film seemed to be unchanged by phase-separation–dissolution cycles. Thus, the modulation of the fluorescence intensity of the film by phase-separation–dissolution cycles was suggested to be due to mainly difference in the light-scattering effect between the homogeneous and phase separated states.

#### 4. Conclusion

Fluorescence intensity modulation of the BMABA-doped PVAc–TBPBF<sub>4</sub> hybrid film was achieved by thermal treatments. Studies of fluorescence properties including fluorescence life

time and quantum yields suggested that no significant change in the surrounding environments of BMABA molecules in the hybrid film took place by phase-separation–dissolution cycles. Thus the modulation of the fluorescence intensity of the film by phase-separation–dissolution cycles was suggested to be due to mainly difference in the light-scattering effect between the homogeneous and phase separated states.

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