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Emission spectra and excitation emission matrix of Betaine-30 (B30) dispersed in polymeric solids were determined. Emission wavelength was different for each polymer. The maximum wavelength became long with increasing the polarity of the polymer. A new possibility to determine the polarity of the medium using B30 was suggested.

Keywords: betaine-30; $E_T(30)$; excitation emission matrix; steric hindrance; solvent parameter

INTRODUCTION

Many kinds of polarity probes [1] are available in these days. Some of these compounds are fluorescent and the emission wavelength is highly dependent to the polarity of the medium. The drastic change

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in their maximum emission wavelength (λ_{em}) is observed with changing polarity of the medium. On the other hand, solvatochromic dyes have been used as the indicator of a solvent parameter in various systems, such as solutions, micelles, solids, super-critical fluids, ionic liquids, and so on. A solvatochromic dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate [2–4] (Betaine-30, which was synthesized by Dimroth *et al*. [2], abbreviated as B30, (see Fig. 1(a) (inset), sold as "Reichardt's dye") is one of the most famous solvatochromic dyes to determine a solvent parameter, $E_T(30)$ [2–4], which is used to estimate the polarity of the system. B30 is widely used and well-known to be non-fluorescent in solutions [5], because of the very fast energy transfer from dye molecules to solvent molecules.

In rigid polymeric systems, molar absorption coefficient (ε) of B30 decreases drastically [6] and similar tendency was seen for B30-dispersed polymeric samples used in Ref. [7] and this study. It would be due to the twisted conformation with interrupted π-conjugation system of B30. Therefore, we need a large amount of the dye, if we use B30 in such systems. That is very inconvenient for us. Once, one of the authors determined the emission properties of B30 fluorescence in bulk polymeric films [7], and the lifetime of those emission bands of B30 films were in ns order, we think these bands as "fluorescence". Though fluorescence of B30 in bulk films was determined for poly(vinyl alcohol)(PVA), poly(methyl methacrylate)(PMMA), and

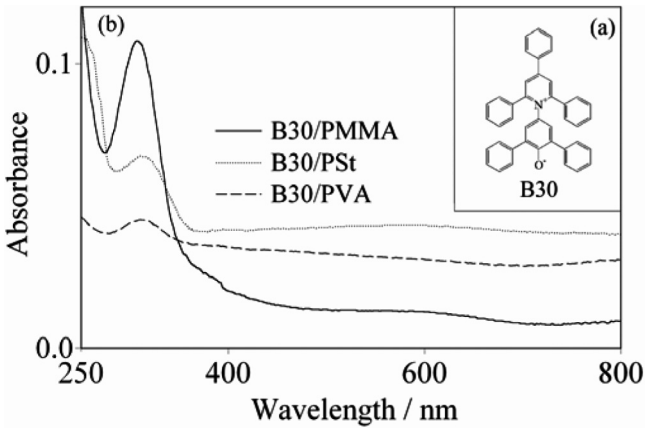


FIGURE 1 (a) Chemical structure of B30 (inset) and (b) absorption spectra of B30 dispersed thin films. The solid, dotted, and broken lines correspond to B30/PMMA (6.8×10^{-3} (mol/kg)), B30/PSt (6.8×10^{-2} (mol/kg)), and B30/PVA PVA (1.7×10^{-2} (mol/kg)), respectively.

polystyrene(PSt) [7], it was difficult to estimate the standard λ_{em} value for each polymer as those bulk polymer films contained much solvent residue. Of course, $E_T(30)$ values for some commercial polymers using B30 absorption were determined previously by Paley *et al*. in '90s [6], and other attempts to use B30 absorption as a polarity indicator in rigid polymeric systems had been done [for example, 8].

In this study, we determined B30 luminescence spectra for B30-dispersed spin-coated films of PVA, PMMA, and PSt after drying over glass transition temperature (T_g), except for PVA, to avoid dehydration) for the attempt to find standard λ_{em}. If we can estimate λ_{em} for rigid systems, B30 would be able to use at lower concentrations in rigid systems.

EXPERIMENTAL

B30 was purchased from Sigma-Aldrich Co. (90%, Aldrich 27,244-2, Lot: 07607DC) and used after washing with acetone to decrease water containing in lumps of B30. All solvents were UV or Fluorescence grade. As typical polymers, PMMA (Sigma-Aldrich Co., 182230, typical M_w is 120,000 g/mol), PVA (Kanto Chemicals Co., $M_w \sim 22{,}000$ g/mol, hydrolyzed at 86.5 ~ 89 mol%), and PSt (Sigma-Aldrich Co., 182427, typical M_w is 280,000 g/mol) were used as received. Each polymer solid was dissolved into a suitable solvent and was stirred overnight to form a viscous transparent solution. Then polymer solution was diluted and mixed with B30. Mikasa Spincoater 1H-D7 spin-coating machine was used for preparing polymer thin films on quartz substrates (rotated at 1500 rpm for 60 s). Polymer films were dried *in vacuo* above *Tg* (130°C for PMMA and PSt, and 70°C for PVA) for 2 h. Concentration of B30 was varied in the range $10^{-2} \sim 10^{-5}$ (mol/kg).

UV-vis absorption spectra were recorded with Hitachi U-3200 Spectrophotometer. Fluorescence spectra and a kind of 2-D expression of emission and excitation spectra (excitation emission matrix:EEM [9,13], once we called it as "emission counter map" [10–12], we found its generic name in Ref. [9] was determined with Hitachi F-4500 Fluorescence Spectrophotometer using a reflection configuration to decrease re-absorption of the emission [13].

RESULTS AND DISCUSSION

Concentrations of B30 in Polymeric Films

Absorption and emission spectra of all B30 dispersed PMMA (B30/PMMA), PVA (B30/PVA), and PSt (B30/PSt) were determined

(see Fig. 1(b)). The charge-transfer (CT) band of B30 has variable ε values according to the polarity of the medium. In the medium with high polarity, ε is much smaller than in the medium with low polarity. Each concentration of B30 in polymer film (appeared in Fig. 1(b)) was 6.8×10^{-3}, 1.7×10^{-2}, 6.8×10^{-2} (mol/kg) for PMMA, PVA, and PSt, respectively. Though the reason of the low absorbance of B30/PSt is incomprehensible at present, the steric hindrance and twisted conformation [1] would be the key to explain absorption and emission phenomena of B30/PSt.

Emission Spectra of B30/PMMA and B30/PVA Films

Absorption and emission spectra of all B30/PMMA were determined. All emission spectra are shown in Figure 2. Concentration of B30 was varied from 6.8×10^{-3} to 6.8×10^{-5} (mol/kg). λ_{em} of B30 was

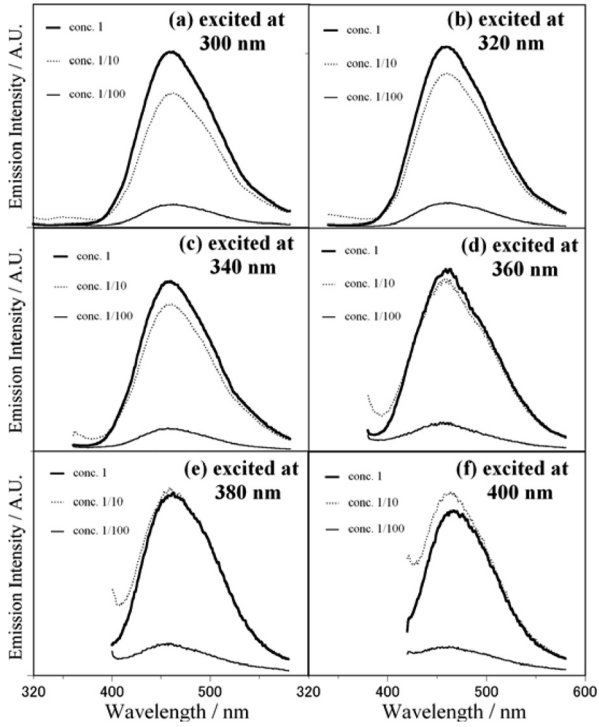


FIGURE 2 Emission spectra of B30/PMMA at various excitation wavelength from 300 to 400 nm. Concentration of B30 was varied from 6.8×10^{-3} to 6.8×10^{-5}.

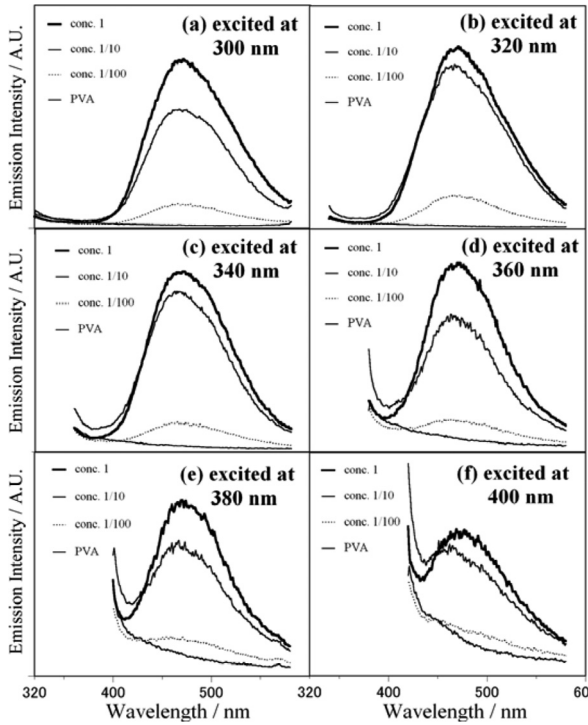


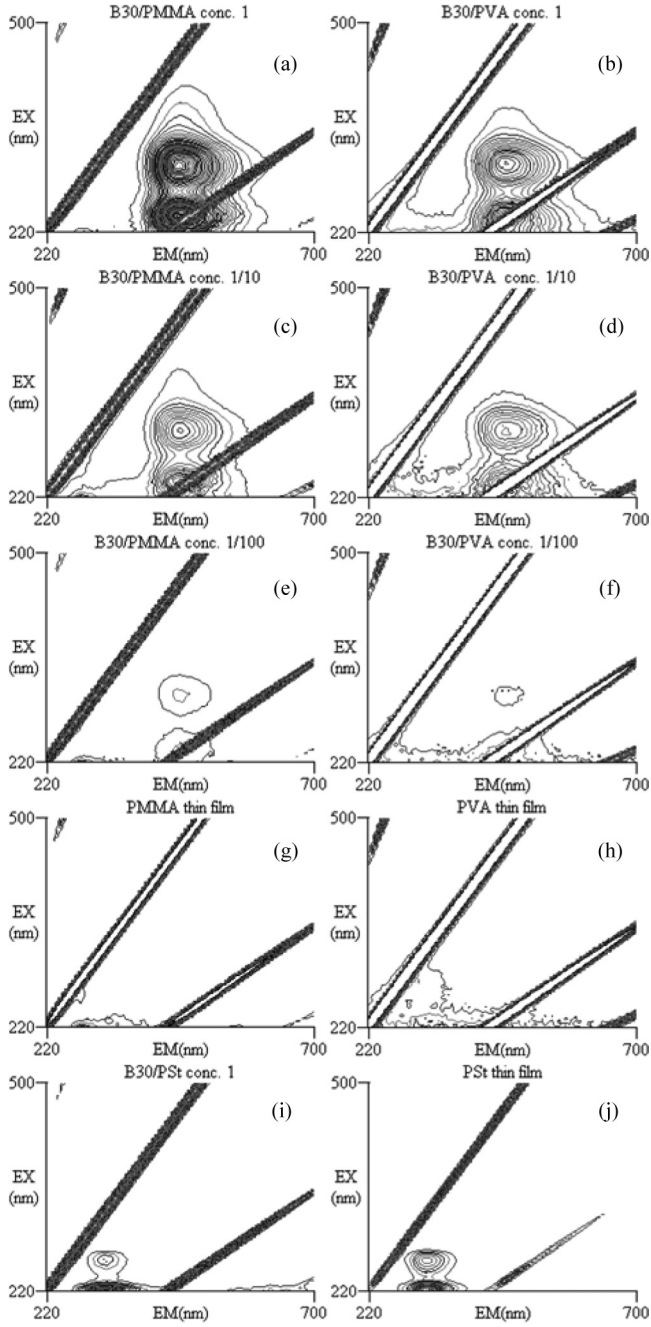
FIGURE 3 Emission spectra of B30/PVA at various excitation wavelength from 300 to 400 nm. Concentration of B30 was varied from 1.7×10^{-2} to 1.7×10^{-4}.

457 ~ 463 nm with the excitation at 300 ~ 400 nm. From these results, the standard λ_{em} was estimated to ~460 nm (excited at 300 ~ 400 nm).

All B30 dispersed PVA films (B30/PVA) were determined. Concentration of B30 was varied from 1.7×10^{-2} to 1.7×10^{-4} (mol/kg). λ_{em} of B30 was 460 ~ 470 nm with the excitation at 300 ~ 400 nm. All emission spectra are shown in Figure 3. From Figures 3(d)–3(f), excitation at longer wavelength region, 360 ~ 400 nm appeared not to be suitable to obtain standard value, as λ_{em} was comparatively different at different concentration than λ_{em} with 300 ~ 340 nm excitation. From these results, the standard λ_{em} appeared to ~467 nm (excited at 300 ~ 340 nm).

EEMs of B30/PMMA and B30/PVA

EEMs were also determined for all B30/PMMA and B30/PVA thin films. They are shown in Figure 4. Diagonal straight lines in



EEMs are scattering. In the EEMs of all B30/PMMA and B30/PVA films, strong emission bands were seen and the intensity of the emission bands was decreased with decreasing B30-concentration. The difference of λ_{em} was about $6 \sim 7$ nm. Figure 4(a) and 4(b) are the EEMs of highest concentration. EEMs for pure polymers (PMMA, PVA, and PSt) are also displayed in Figure 4(g), 4(h), and 4(j), respectively.

λ_{em} of the emission bands appeared for B30/PMMA and B30/PVA were shorter than the wavelength of $S_0 \rightarrow S_1$ excitation band (CT band) for B30. This would imply the absence of the $S_0 \rightarrow S_1$ band of B30 in those polymeric thin films, because of the steric hindrance derived from the complicated structure of B30 molecule and nearby polymer chains.

Emission Bands of B30/PSt Films

Emission spectra and EEMs for all B30/PSt films with B30 concentration from 6.8×10^{-2} to 6.8×10^{-5} (mol/kg) were determined. Though their EEMs showed strong luminescence in very short wavelength region, these emission bands with high intensity in the EEMs for B30/PSt was same to that of PSt. Even at the concentration of 3.4×10^{-2} mol/kg, the peak position of the emission bands was same to that PSt, just after preparation. It seemed to be difficult to distinguish B30 emission from PSt emission in UV-excited region. One possible reason for the disappearance of B30-emission would be the large number of phenyl rings in those films, which have strong absorption band in the same wavelength region. Another possibility might be some fluorescence quenching process. As the fast energy transfer from B30 molecules to solvent molecules in solutions are famous [5], large free-volumes in the polymeric solids could be responsible for the relaxation processes in those films. In addition, emission spectra and EEMs of all B30/PSt and PSt films found to change after months (data not shown). Weak emission bands similar to those of B30 in PMMA and PVA appeared for B30/PSt (not for PSt). Similar complex phenomena were seen for other pyridine or pyridinium derivatives in halogenated hydrocarbon [16]. Compared with the cases of fluorescence quenching

FIGURE 4 EEMs of B30/PMMA, B30/PVA, B30/PSt and polymer films without B30. (a), (c), and (e): EEMs of B30/PMMA (with B30 concentration at 6.8×10^{-3}, 6.8×10^{-4}, and 6.8×10^{-5}, respectively); (b), (d), and (f): EEMs of B30/PVA (with B30 concentration at 1.7×10^{-2}, 1.7×10^{-3}, and 1.7×10^{-4}, respectively); (i): EEM of B30/PSt with B30-concentration at 6.8×10^{-2}); (g), (h), and (j): EEMs for PMMA, PVA, and PSt, respectively.

by halogenated compounds [for example, 14,15], the quenching behavior of B30/St would be related to CH_2Cl_2 (solvent) residues in those films. As these behaviors are complicated, therefore we need more detailed determination for B30/PSt.

CONCLUSIONS

Though many things remain pending, especially for B30/PSt, these results of B30-dispersed polymeric systems suggest that it would be possible to establish standard λ_{em} values for polymer films using B30, not with its absorbance, but with its luminescence. The excitation in the UV-region means the excitation to higher excited states (usual S_2 or higher excited state of B30), as the usual lowest excitation is in visible region (it corresponds to the CT band of B30 [2–4]). Though the relaxation processes would be complex, it might be revealed with detailed studies by means of fluorescence measurement and EEMs, gradually. We consider the excited state of B30 which causes emission as the (pseudo) lowest excited state in these polymeric rigid systems, and not to be an exception to Kasha's rule [17]. The quenching behavior observed for B30/PSt would be related to some external heavy-atom effect [14,15] derived from solvent (CH_2Cl_2 in this case). It could be helpful for the elucidation of the very unique feature of the excited states of pyridiniums.

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