

## Fluorescence Study on Miscibility in Poly(*N*-vinylcarbazole)/Poly(oxyethylene) Blends

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**ABSTRACT:** Some miscibility between poly(*N*-vinylcarbazole) (PVCz) and poly(oxyethylene) (PEO) has been found for the first time by means of the two kinds of excimer emission of 8.0–100 wt% PVCz in the PVCz/PEO blends. Interchain energy migration to a full-overlap excimer site in the blends is suggested on the basis of time-resolved fluorescence spectra. The emission ratio between partial-overlap and full-overlap excimers shows PVCz concentration dependence similar to that of film transparency, reflecting chain aggregation in PVCz/PEO blends. Schematic diagrams of microscopic phase-separation structure of the blends for various PVCz contents are also proposed.

**KEY WORDS** Poly(*N*-vinylcarbazole) / Poly(oxyethylene) / Blends / Partial Overlap Excimer / Full Overlap Excimer / Miscibility / Energy Migration /

Poly(*N*-vinylcarbazole) (PVCz) is a typical photoconductive polymer.<sup>1</sup> To elucidate the photoconduction mechanism, it is important to make clear the emission properties, because the carrier generation in photoconduction proceeds through electronically excited states from which emission occurs. For this reason, numerous studies have been performed on fluorescence properties of PVCz in solution and in solid state.<sup>2,3</sup>

Emission properties of PVCz in polymer blends have not been studied from the view point of miscibility except only one case.<sup>4</sup> Miscibility is defined as the degree of homogeneousness in the two polymer chains, independent of the ratio of the two components.<sup>5</sup> Johnson and Good<sup>4</sup> have discussed miscibility of PVCz (0.01–10%) with polystyrene (PS) and poly(methyl methacrylate) (PMMA) on the basis of relative emission intensity of two kinds of excimer in PVCz, namely, full- and partial-overlap excimers.<sup>6,7</sup> An excimer is a molecular complex formed between two identical aromatic rings geometrically parallel to each other, one of which is in a singlet excited state.<sup>8</sup> As for PVCz, carbazolyl groups overlap on whole faces to form a full-overlap excimer, and those overlapping on the part of the benzoic rings form a partial-overlap excimer. However, it is not known whether the intensity ratio of the two kinds of excimer emission of carbazolyl groups reflects miscibility in PVCz blends. This is probably because emission properties of more than 10% PVCz in polymer blends have never been studied from the aspect of miscibility. It has been reported that the ratios of monomer and excimer emission intensities of naphthyl and phenyl groups sensitively reflect the miscibility in poly(2-vinylnaphthalene) blends<sup>9–15</sup> and PS blends.<sup>16,17</sup> Such emission properties should give information about miscibility on the molecular level. This information is not given by thermal analysis, small angle X-ray scattering, or microscopic methods. Miscibility may play an important role in the application of PVCz blends to functional materials such as electroluminescence devices.<sup>18–22</sup>

The present work investigates for the first time emission properties of PVCz (10–100%)/polyoxyethylene blends from aspects of miscibility. Polyoxyethylene (PEO) as a

matrix for PVCz has attracted our interest for two reasons. First, PVCz (50–100%)/PEO blends have been studied with differential thermal analysis (DTA)<sup>23</sup> and PVCz /poly(ethylene glycol) oligomer (0–30%)/tetrahydrofuran mixtures with viscometry and light scattering measurements.<sup>24</sup> Microscopic miscibility of PVCz/PEO blends, if it is clarified by emission of PVCz, will be compared to the results by other methods. Secondly, PVCz is a photoconductive polymer and PEO is a typical ion-conducting polymer. In PVCz/PEO blends, the combination of hole-transport and ion-transport may result in some special properties.

### EXPERIMENTAL

#### *Sample Preparation*

We purchased PVCz prepared with radical polymerization (weight-average molecular weight ( $M_w$ ) = 132000, number-average molecular weight ( $M_n$ ) = 46900) and PEO ( $M_w$  = 101000,  $M_n$  = 97100) from Scientific Polymer Products, Inc. PVCz was reprecipitated from dichloromethane solution into methanol twice, and PEO was used without further purification. Spectroscopic grade benzene solutions of PVCz and PEO mixtures were prepared. Total polymer concentration was 2 g/100 mL.

For measurement of steady-state and time-resolved fluorescence spectra and differential scanning calorimetry (DSC), films which contained PVCz and PEO mixtures were cast from the solutions on a quartz substrate at room temperature. The films were dried under vacuum at about 340 K for 2 days. The thickness of the films was 10  $\mu$ m.

For transmittance measurement, PVCz and PEO mixtures were spin cast from the solutions on a quartz substrate for 30 s at 2000 rpm after 30 s at 1000 rpm. The thickness for all the films was  $0.33 \pm 0.05 \mu$ m. These spin-cast films showed similar dependence of fluorescence intensity ratio on PVCz content to that for the films prepared with the solvent-cast method.

#### *Spectroscopic Measurements*

Steady-state fluorescence spectra were measured at

room temperature in air on Hitachi 850 fluorescence spectrophotometer. The light source was 150 W Xe lamp. The spectra of the films were measured in front-face arrangement. Fluorescence spectra of PVCz was measured with excitation wavelengths of 337 nm ( $S_1 \leftarrow S_0$ ).

Time-resolved fluorescence spectra were measured with a nitrogen gas laser (Laser Photonics, Inc., LN 1000) as light source and streak camera (Hamamatsu, C4334) as detector. The laser was operated at 337 nm with a repetition of 10 Hz. Pulse duration was  $\approx 1$  ns (full width at half maximum). The time-resolved spectra of the films were measured at room temperature.

#### Transmittance and DSC Measurements

Transmittance of the films was measured with JASCO V-570 UV/VIS/NIR spectrophotometer to estimate chain aggregation and phase separation of the films. Transmittance was measured at 515 nm, which is not located in electronic absorption bands of PVCz or PEO. Transmittance of each film was corrected for that of each quartz substrate.

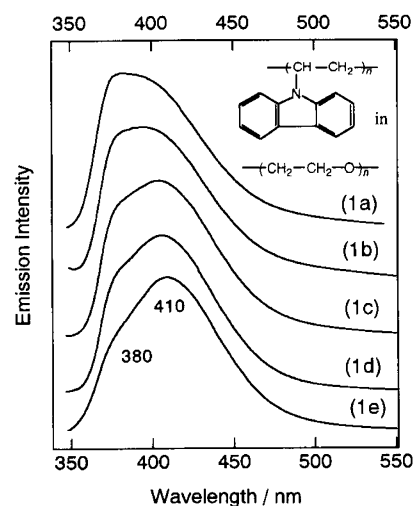
Glass transition temperatures were measured with a differential scanning calorimeter (Mettler DSC 30) with a first heating from room temperature to 553 K, a first cooling to 223 K, and a second heating to 553 K. The heating or cooling rate was  $10 \text{ K min}^{-1}$ .

## RESULTS AND DISCUSSION

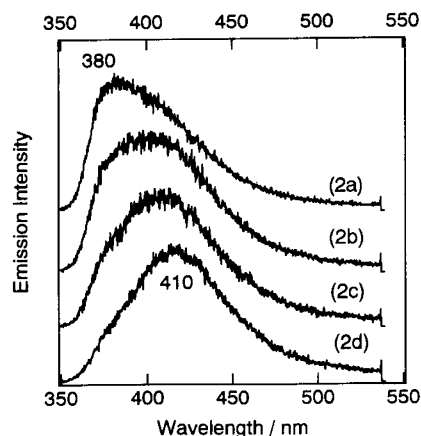
Figure 1 shows fluorescence spectra of various contents PVCz ( $0.42\text{--}5.3$  monomer  $\text{mol kg}^{-1}$ ) in PEO. The broad bands at 380 nm and 410 nm in (1e) correspond to partial- and full-overlap excimer, respectively.<sup>6,7</sup> As the PVCz concentration increases ((1a)—(1e)), the intensity of partial-overlap excimer fluorescence at  $\approx 380$  nm decreases compared to that of full-overlap excimer one at  $\approx 410$  nm.

Two premises are essential for elucidating the mechanism of such concentration dependence. First, the full-overlap excimer in PVCz can be formed only between two adjacent carbazolyl groups on the same chain, and the partial-overlap excimer in PVCz is formed mainly also between two adjacent carbazolyl groups on the same chain. This is strongly supported by the facts that poly(2-(9-carbazolyl)ethyl methacrylate) film has shown no excimer emission<sup>25</sup> and that no full-overlap excimer emission was observed in solution for alternating copolymers of *N*-vinylcarbazole.<sup>26</sup> Secondly, PVCz chains aggregate to some extent in the PVCz/PEO blends, since all the samples of PVCz (8.0—79%)/PEO blends look cloudy and a PVCz (35%)/PEO film shows the same glass transition temperature for the PVCz-rich phase (497 K) as that in bulk PVCz (493 K). The results of DTA<sup>23</sup> as well as viscometry and light scattering measurements<sup>24</sup> also indicate such chain aggregation.

On the basis of these two premises, we discuss time-resolved fluorescence spectra of a PVCz (59%)/PEO blend given in Figure 2. The intensity of the fluorescence band at 380 nm in (2a) decreases with time. The band at 410 nm gradually rises with time to become clear in (2d). Our experimental results also showed that the band at 410 nm in pure PVCz rises more rapidly than in



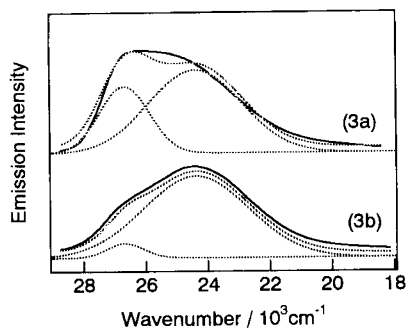
**Figure 1.** Fluorescence spectra of various contents of PVCz in PEO matrix at room temperature. Excitation wavelength is 337 nm. Maximum intensities in (1a)—(1e) are roughly normalized. Weight concentration of PVCz in the blends is (1a) 8.0% (0.42 monomer  $\text{mol kg}^{-1}$ ); (1b) 26%; (1c) 38%; (1d) 79%; (1e) 100% (5.3 monomer  $\text{mol kg}^{-1}$ ).



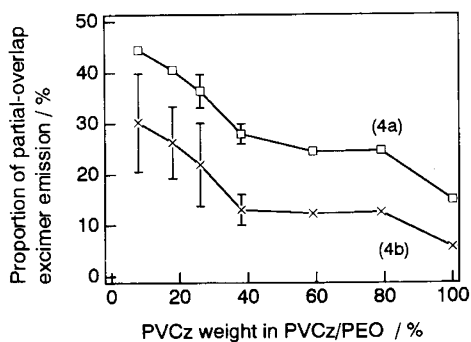
**Figure 2.** Time-resolved fluorescence spectra of PVCz (59 wt%) in a PVCz/PEO blend at room temperature. Excitation wavelength is 337 nm. The gate time after excitation is (2a) 0—5.0; (2b) 5.0—10; (2c) 10—15; (2d) 20—60 ns. Maximum intensities in (2a)—(2d) are roughly normalized.

PVCz (59%)/PEO. The increase in the PVCz content in the blend thus leads to more frequent interchain energy migration to full-overlap excimer sites in the time of  $\sim$  ns. The strong aggregation of PVCz chains causes such interchain energy migration as in a neat PVCz film.<sup>27</sup> The energy of monomer excited states detrapped from the partial-overlap excimer sites probably migrates into the full-overlap excimer sites in the blends; such behavior has been proposed also in a neat PVCz film<sup>28</sup> and in PVCz solution.<sup>29</sup> The interchain energy-migration to the full-overlap excimer sites increases proportion of the full-overlap excimer emission, explaining the concentration dependence in the steady-state fluorescence spectra. Energy migration to the partial-overlap excimer sites is out of the time resolution ( $\sim$  ns) of our present apparatus. This process would be very fast ( $\sim$  ps) in blends as well as in dilute solution<sup>29,30</sup> and solid state.<sup>27</sup>

Emission properties of PVCz reflect the difference in



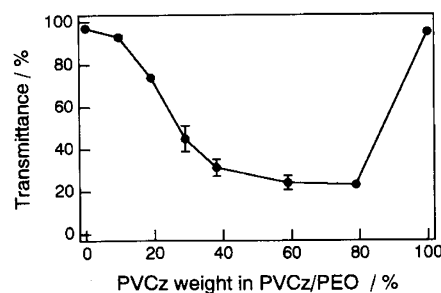
**Figure 3.** Schematic band resolution of the fluorescence spectra of PVCz in PEO. Weight concentrations of PVCz in mixtures are (3a) 8.0%; (3b) 100%. Abscissa in Figure 3 is transformed to wavenumber. The fluorescence spectra are fitted with the sum of constant baseline and two Gaussians,  $k_0 + k_1 \exp(-(v - 2.67 \times 10^4)^2/a_1) + k_2 \exp(-(v - 2.44 \times 10^4)^2/a_2)$ . The solid lines are experimental spectra and the three dotted lines are fitting curves and two Gaussians, for (3a) and (3b), respectively. The values of the band center in the two Gaussians are determined by the fitting of the spectra for PVCz (100%).



**Figure 4.** Proportion of the partial-overlap excimer emission in the total excimer emission based on band resolution. The values calculated from pregaussian factors,  $k_1/(k_1 + k_2)$ , are shown in (4a). The values calculated from areas of the two Gaussians,  $k_1\sqrt{a_1}/(k_1\sqrt{a_1} + k_2\sqrt{a_2})$ , are shown in (4b).

the tacticity.<sup>7,27,29-31</sup> The present PVCz prepared by radical polymerization has syndiotactic sequence more than isotactic sequence.<sup>32</sup> Other studies on PVCz and model compounds strongly indicate that syndiotactic and isotactic sequence in PVCz provide partial- and full-overlap excimer sites, respectively.<sup>33-35</sup>

The fluorescence spectra of PVCz (8.0–79%)/PEO blends give information on chain aggregation and microscopic phase separation. To examine this point quantitatively, the fluorescence spectra were resolved into two overlapping components with peaks at 380 nm and 410 nm. These components correspond to the bands of partial- and full-overlap excimers. The band resolution is as follows. The abscissa of the fluorescence spectra of PVCz (8.0–100%)/PEO blends was transformed from wavelength into wavenumber. These spectra were fitted by the sum of two Gaussian functions and constant baseline, assuming that the emission bands of partial- and full-overlap excimers have inhomogeneous band width, reflecting distributions of the energy levels of the excimer-forming sites. The assumption of Gaussian band shape in the emission of PVCz was adopted by Burkhardt and Dawood.<sup>36</sup> Figure 3 shows the two Gaussians and the fitting curve for PVCz (8.0%)/PEO and PVCz (100%) films. The Gaussian function centered at 380 nm in (3a) grows compared to that in (3b).



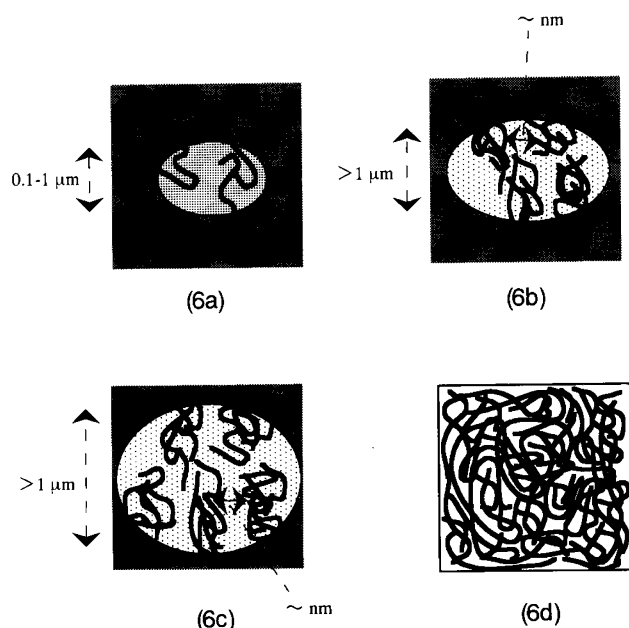
**Figure 5.** Transmittance at 515 nm of PVCz/PEO blends. High transmittance means low turbidity.

Figure 4 shows the results of band resolution. Each pregaussian factor,  $k_1$  and  $k_2$ , indicates the largest population in the excimers with the energy distribution. The area of each Gaussian,  $k_1\sqrt{\pi a_1}$  and  $k_2\sqrt{\pi a_2}$ , indicates the sum of populations of excimers in the range of the energy distribution. Proportion of the partial-overlap excimer emission calculated from the pregaussian factors is given in (4a), and that calculated from areas of the Gaussians is given in (4b). As for blends of 8.0–38% PVCz with PEO, (4a) and (4b) show that the proportions decrease from 45 to 28%, and from 30 to 13% with the increase in PVCz content, respectively. As for blends of 38–79% PVCz with PEO, (4a) and (4b) show that the proportions change only slightly: these values do not shift from  $\approx 25\%$  and  $\approx 12\%$ , respectively.

Such concentration dependence was observed in the transmittance reflecting the turbidity of the films. Figure 5 shows the transmittance of PVCz (8.0–100%)/PEO blends. As for blends of 8.0–38% PVCz with PEO, these values decrease from 94 to 31% with increase in PVCz content. As for blends of 38–79% PVCz with PEO, transmittance values change only slightly from 31 to 23%.

The proportions of partial-overlap excimer emission and transmittance have good correspondence in the PVCz concentration dependence. Low transmittance means high turbidity, reflecting directly the extent of phase separation caused by chain aggregation. Thus the proportions of partial-overlap excimer emission serve as excellent probe for the extent of the chain aggregation. It should be noted that the proportions of partial-overlap excimer emission reflect the extent of chain aggregation on a scale of  $\sim$  nm, while the transmittance reflect the domain of much larger scale. The emission properties and transmittance have good correspondence, though the two values reflect information with different sizes.

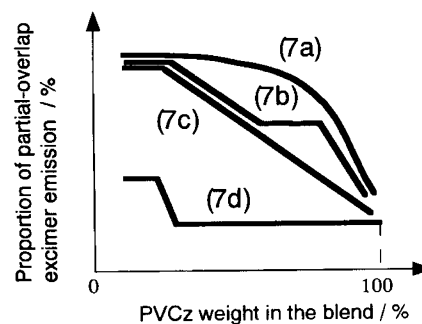
The concentration dependence of the proportions of the partial-overlap excimer emission and reason for this correspondence are based on the microscopic phase-separation structure of the blends. Figure 6 gives schematic diagrams of the chain aggregation in the blends. In the course of increase in PVCz content from 0 to 8.0%, the aggregation of PVCz chains induces microscopic phase separation. The local concentration of PVCz chains in the PEO-lean phase is still low for PVCz (8.0%)/PEO blends ((6a)), but increases with PVCz content up to 38% ((6b)). The increase in the local concentration of PVCz chains in the PEO-lean phase promotes energy migration between PVCz chains, leading to decrease in the proportion of partial-overlap



**Figure 6.** Schematic diagrams of microscopic phase-separation structure in PVCz/PEO blends. PVCz content is (6a) 8.0; (6b) 38; (6c) 79; (6d) 100%. Entangled lines indicate PVCz chains, area outside the ellipse corresponds to PEO or PEO-rich phase, and area inside the ellipse to PEO-lean phase. The density of dotted points in the ellipse indicates the density of PEO chains for each of the diagrams.

excimer emission in (4b) from about 30 to 12%. Even when PVCz content rises from 38 ((6b)) to 79% ((6c)), the proportion of partial-overlap excimer emission in (4b) shows little change. This indicates that the density of the PEO chains among PVCz chains inside the PEO-lean phase in (6b) is kept constant in (6c). Growing PVCz chains do not purge PEO chains inside, but induce increase in PEO-lean phase with PVCz content. When PVCz content rises from 79 ((6c)) to 100% ((6d)), PEO chains among PVCz chains in (6c) begin to be purged. This enhances the energy migration between PVCz chains to decrease the proportion of partial-overlap excimer emission in (4b).

Figure 6 ((6a)—(6c)) shows that PVCz chains in the PEO lean-phase form aggregates, and aggregates locally contain PEO chains in each aggregate or among aggregates. The distance between PVCz chains would be of the order of nm, making possible interchain energy migration to full-overlap excimer sites. Average distance for this type of energy migration is supposed to be about 10 nm.<sup>31</sup> It is difficult to evaluate the sizes of the domains of the PEO-lean phase, size of the ellipses in Figure 6. The sizes of PEO-lean domain for 8.0% PVCz blend ((6a)) may be 0.1—1 μm based on cloudiness. The interchain energy migration in the PEO-lean phase is enhanced in the range of 10 nm with increase of PVCz content. The domain sizes for 38 and 79% PVCz blends ((6b) and (6c)) would be larger than 1 μm based on optical microscopy. For blends with PVCz content of 38—79%, the proportion of the partial-overlap excimer emission is kept constant owing to constant concentration of PVCz chains in the PEO-lean phase. The constancy of transmittance for the films in the same PVCz content region in spite of the change in amount of the PEO-lean phase may be attributed to the constant re-



**Figure 7.** Several emission properties of PVCz in blends. (7a) Miscible PVCz blends; (7b) (7c) (7d) immiscible PVCz blends. The PVCz (8.0—100%)/PEO blends correspond to (7b). See the text.

fractive index difference between the PEO-rich and the PEO-lean phase and large domain size compared to the wavelength of the monitoring light.

Figure 7 shows probable emission properties of PVCz in blends. The PVCz blends miscible at room temperature may show the concentration dependence shown in (7a). When PVCz content is low, single PVCz chains isolated by matrix polymer chains suppress interchain energy migration. The proportion of the partial-overlap excimer emission is kept constant, though the PVCz content increases. This corresponds to the almost flat line in (7a). The distance between PVCz chains decreases to ~ nm with increase in PVCz content. Interchain energy migration begins to occur. This causes decrease in the proportion of the partial-overlap excimer emission. This corresponds to the curve in (7a).

PVCz blends immiscible at room temperature may show concentration dependence in (7b), (7c), and (7d). When PVCz blends show the lowest miscibility in the four types in Figure 7, concentration dependence would correspond to (7d). These blends form pure PVCz aggregates and pure matrix-polymer aggregates. The interchain energy migration is suppressed for the quite low PVCz content due to the small size of the PVCz aggregates. As PVCz content increases, the size of the pure PVCz aggregates exceeds the average distance of energy migration. These aggregates may show the same emission spectrum as that of neat PVCz. The extent of energy migration may not depend on PVCz content at mid and high PVCz content.

When PVCz blends form a small size of PVCz aggregates, interchain energy migration is enhanced with increase in PVCz content. This corresponds to (7b) and (7c). In both of (7b) and (7c), interchain energy migration is still suppressed for low PVCz content as in (7d). This corresponds to the flat line on the left side of (7b) and (7c). PVCz (8.0—100%)/PEO blends in the present work showed the concentration dependence of (7b), but not of (7c); *i.e.*, PVCz chains in the PEO-lean phase contain PEO chains at a constant fraction on the molecular level even in the phase-separated PVCz (38—79%)/PEO blends. This is evidence that PVCz and PEO have some miscibility, though the blends are immiscible. We found for the first time that PVCz and PEO show some miscibility by emission of PVCz. This could not be detected by other methods.<sup>23,24</sup> The present work shows that the relative intensity of the two kinds of excimer emission of PVCz is a good probe for the degree of

miscibility between PVCz and PEO on the molecular level.

Johnson and Good claim that the ratio of emission intensity of partial-overlap excimer to that of full-overlap excimer is a poor probe for miscibility, since the ratio is insensitive to the PVCz content, 0.01–10% in PS or PMMA.<sup>4</sup> This insensitivity should be due to the low content of PVCz in blends. The 0.01–10% PVCz chains in PS or PMMA may form a small number and size of aggregates. A large number of PS or PMMA chains surround and dilute these aggregates. This suppresses the energy migration between PVCz chains. Even if the PVCz content increases from 0.01% to 10%, the distance between these aggregates is too large to enhance interchain energy-migration. As for PVCz (8.0–100%)/PEO blends, the relative intensity of two excimer emissions in PVCz in polymer blends serves as a good probe for the degree of miscibility. The relative intensity of emission can be measured easily with a conventional fluorescence spectrophotometer.

### CONCLUSIONS

Two excimer emissions in PVCz serve as a good probe for the degree of miscibility in PVCz (8.0–100%)/PEO blends. The blends with PVCz-rich phase in the 40–80 wt% PVCz content contain constant local concentrations of PEO chains, though these blends are immiscible and double-phase in character.

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