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Comparison of miscibility in poly(*N*-vinylcarbazole)/polystyrene and polyoxyethylene blends by excimer fluorescence

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Summary

It is for the first time found that poly(*N*-vinylcarbazole)(PVCz)/polystyrene (PS) blends have lower miscibility on molecular level than that of PVCz/polyoxyethylene (PEO) blends. This is obtained from excimer fluorescence properties of PVCz in PVCz (9.1-100%)/PS and PVCz (9.6-100%)/PEO blends. Schematic diagrams of phase-separated structure of the PVCz blends are proposed consistent with emission properties and phase-contrast microscopic images.

Introduction

Recently, polymer blends have been increasingly studied as functional materials, not only as structual materials. Electroluminescent poly(*N*-vinylcarbazole)(PVCz) blends are a kind of such blends[1]-[5]. PVCz in these blends plays an important role as a hole-transport polymer. Function of these blends may have correlation with miscibility of the blends. Miscibility is defined as the degree of homogeneity in the two polymer chains, independent of the ratio of the two components[6].

There are few studies on miscibility of PVCz blends[7]-[9]. We showed in our previous work[9] that excimer fluorescence of PVCz in polymer blends is sensitive to miscibility of PVCz (8.0-100%)/polyoxyethylene (PEO) blends preprared with a solvent-cast method. Thermal analysis[7], small angle X-ray scattering, or microscopic methods do not give information on molecular-level miscibility which could be reported by excimer fluorescence of PVCz. Excimers are molecular complexes formed between two identical aromatic rings geometrically parallel to each other, one of which is in a singlet excited state[10]. Excimer formed by photoexcitaion emits light when it is relaxed from an electronically excited state to a ground state. This emission is observed as excimer fluorescence.

Johnson and Good[8] claimed that excimer fluorescence of PVCz in PVCz (0.01-10%)/polystyrene (PS) or poly(methyl methacrylate) (PMMA) blends is insensitive to miscibility. It is not known whether excimer emission properties of PVCz in PVCz (more than 10%)/PS or PMMA blends are sensitive to miscibility or not. In the present work, we have investigated emission properties of PVCz (9.1-100%)/PS blends and compared them with those of PVCz (9.6-100%)/PEO blends prepared with a spin-cast method.

Experimental

We purchased PVCz prepared with radical polymerization (weight-average molecular weight (M_w) =132,000, number-average molecular weight (M_n) = 46,900), PS (M_w = 120,200, M_n = 115,900), and PEO (M_w = 101,000, M_n = 97,100) from Scientific Polymer Products, Inc.. PVCz was reprecipitated from dichloromethane solution into methanol twice, and PS and PEO was used without further purification. Spectroscopic grade benzene solutions of PVCz and PEO or PVCz and PS mixtures were prepared. Total polymer concentration was 2 g/100 m*L*.

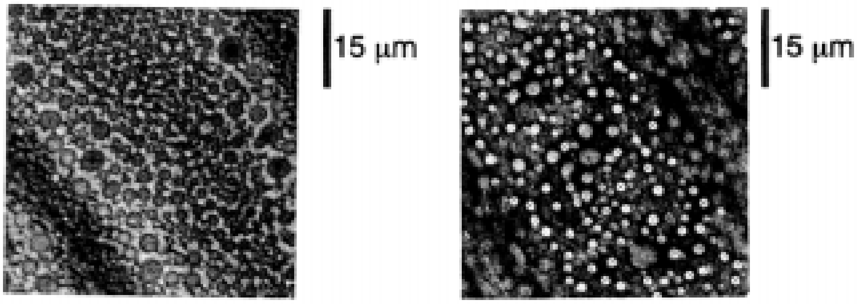
PVCz and PS or PVCz and PEO mixtures were spin cast from the solutions on a quartz substrate for 30 s at 2000 rpm after 30 s at 1000 rpm. Spin cast films were dried under vaccum at room temperature for 2 days. The thickness of the films was 0.33 μm. Solvent-cast films have thermodynamic stability better than spin-cast films. There are two reasons why the present work adopted spin-cast films. First, it is difficult for us to get reproducible fluorescence spectra of solvent-cast films for PVCz/PS blends. As for PVCz/PEO blends, we could obtain similar spectra for the present spin-cast films to those for solvent-cast films in the previous work[9]. Secondly, PVCz blends as electroluminescence devices are usually formed by spin casting[1]-[5]. So, it is useful to investigate miscibility of spin-cast films.

Phase-contrast transmission optical microscopy was used for examining the morphology of the phase-separeated films. The microscopic images were measured with an Olympus BX 50 optical microscope.

Steady-state fluorescence spectra were measured at room temperature in air with a Hitachi 850 fluorescence spectrophotometer. The spectra of the films were measured in front-face arrangement. Excitation wavelength was 290 nm ($S_2 \leftarrow S_0$), since excitation at 337 nm ($S_1 \leftarrow S_0$) caused scattering.

In some measurements we used PVCz/PS spin-cast films annealed at 373 K, glass transition temperature of PS [11], under vaccum for 2 hours. Such annealing had little influence on emission properties of the blends. We did not anneal PVCz/PEO films, since we thought that PVCz/PEO films has some stability at room temperature. Glass transition temperature of PEO is 220 K[11].

Results and discussion



(1a) (1b)

Figure 1. Phase-contrast microscopic images of phase-separated structure for (**1a**) PVCz (50%)/PS; (**1b**) PVCz (48%)/PEO. Dark areas are PVCz-rich phase. Light areas are PS-rich phase for (**1a**) and PEO-rich phase for (**1b**). Diagonal streaks are made by substrate rotation during spin-casting.

We observed phase-separated structure for PVCz (9.1-100%)/PS blends and PVCz (9.6-100%)/PEO blends in images by phase-contrast transmission optical microscopy. Continuous phase begins to turn with the increase in PVCz content from PS-rich phase into PVCz-rich phase at PVCz (50%)/PS for PVCz/PS blends, and from PEO-rich phase into PVCz-rich phase at PVCz (29%)/PEO for PVCz/PEO blends. Figure 1 shows microscopic images for PVCz (50%)/PS ((**1a**)) and PVCz (48%)/PEO ((**1b**)). Phase-contrast is made by refractive index difference between two components in blends. Dark areas in (**1a**) and (**1b**) correspond to the phases rich in PVCz chains with large refractive index, 1.68[11]. Light areas in (**1a**) and (**1b**) are PS-rich and PEO-rich phases with refractive indices, 1.59 and 1.46, respectively[11].

It should be noted that the boundary of each circle in (**1a**) is clearer than that in (**1b**), though a refractive index difference in (**1a**) is 0.09, smaller than that in (**1b**), 0.22. This suggests that PVCz/PS blends have lower miscibility than PVCz/PEO blends. PVCz chains in PVCz (50%)/PS blend aggregate strongly as will be proved below by a fluorescence study, resulting in clear interfaces between the PVCz-rich phase and PS-rich phase. This intensifies phase contrast. PVCz chains in PVCz (48%)/PEO blend partially contain PEO chains, providing ambigious interfaces between PVCz-rich phase and PEO-rich phase. This weakens phase contrast.

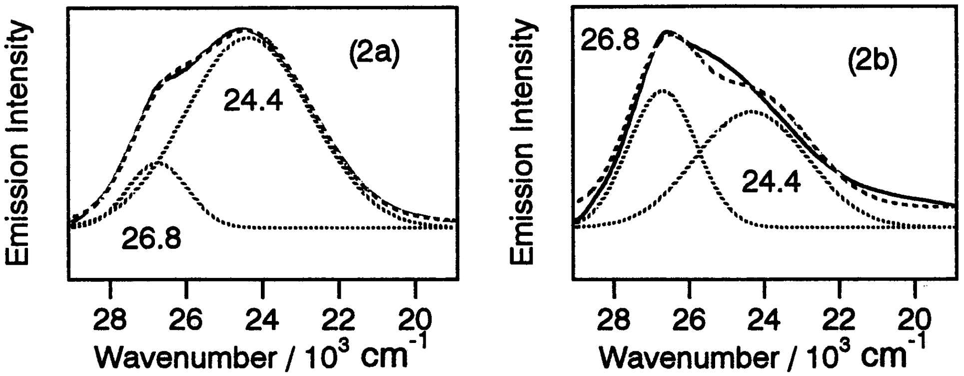


Figure 2. Fluorescence spectra of PVCz in (**2a**) PVCz (20%)/PS; (**2b**) PVCz (19%)/ PEO. Excitation wavelength is 290 nm. Solid lines are experimental spectra and maximum intensities of them are roughly normalized for (**2a**) and (**2b**), respectively. Three dotted lines are fitting curves, and two of which are components as a result of band resolving for (**2a**) and (**2b**), respectively. Constant baselines used in band resolving are not shown.

Microscopic images, however, are insufficient for detection of miscibility on molecular level. Figure 2 shows fluorescence spectra of PVCz (20%)/PS ((**2a**)), PVCz (19%)/PEO ((**2b**)). A broad band peaking at 2.44 x 10^4 cm^{-1} (410 nm) and a shoulder band at 2.68 x 10^4 cm^{-1} (373 nm) corresponds to full- and partial-overlap excimer, respectively [12, 13]. Carbazolyl groups of PVCz 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. We showed in the previous work[9] that such excimer formation sensitively reflects PVCz-chain aggregation in PVCz(8.0-100%)/PEO blends on the basis of steady-state and time-resolved fluorescence spectra. We adopted the premise based on other studies [13]-[15]: 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. Resolving the spectra into the two overlapping components gives fraction of each band more explicitly as shown in Figure 2. Method of the band resolving is reported in detail elsewhere[9].

Figure 3 shows results of band resolving for PVCz (9.1-100%)/PS ((**3a**)) and PVCz (9.6-100%)/PEO ((**3b**)). Fraction of partial-overlap excimer emission is calculated based on areas of two bands. As was shown in our previous work[9], strong aggregation of PVCz chains enhances interchain energy-migration between PVCz chains. Energy detrapped from the partial-overlap excimer sites mainly migrates intermolecularly to neighboring PVCz chains in aggregates, resulting in further intrachain migration to full-overlap excimer sites. Such processes decrease partial-overlap excimer emission in intensity and increase full-overlap excimer emission in intensity. It can also be said that shrinking or folding of PVCz chains in blends enhances intrachain energy-migration to decrease partial-overlap excimer emission in intensity, since polyurethane with carbazolyl chromophores in a poor solvent shows more efficient intrachain energy-migration than that in a good solvent [16]. Average distance of the interchain or intrachain energy migration in neat PVCz film is 10-20 nm[17, 18]. This indicates that fraction of partial-overlap excimer emission in blends reflects PVCz-chain aggregation and shrinking in blends in the scale of nm. The fractions of partial-overlap excimer emission of solvent-cast films of PVCz/PEO blends [9] and those of spin-cast films shown in (**3b**) depend on PVCz contents in a similar manner, though absolute values differ from each other.

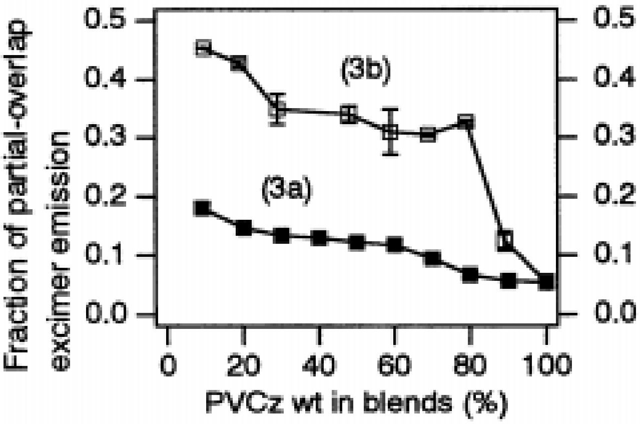


Figure 3. Fraction of partial-overlap excimer emission in the total excimer emission based on the band resolving for (**3a**) PVCz/PS blends; (**3b**) PVCz/PEO blends. These values are calculated as $S_1/(S_1 + S_2)$, where S_1 and S_2 represent areas of emission bands centered at $2.68 \times 10^4 \mathrm{cm}^{-1}$ and that at $2.44 \times 10^4 \mathrm{cm}^{-1}$, respectively.

Figure 3 shows that fractions of partial-overlap excimer emission of PVCz (9.1-100%)/PS blends ((**3a**)) are smaller than those of PVCz (9.6-100%)/PEO blends ((**3b**)) for all the PVCz contents. This fact means that PVCz chains in PVCz (9.1-100%)/PS blends aggregates more strongly than those in PVCz (9.6-100%)/PEO blends. Such a difference indicates that PVCz/PS blends has lower miscibility than PVCz/PEO blends. Explanation in detail is as follows.

We propose schematic diagrams of phase-separated structure of the blends in Figure 4 on the basis of Figure 1 and Figure 3. White circles in Figure 4 represent local density of PVCz chains in PVCz-rich phase. The strong aggregation of PVCz-chains increases the local density. The local density increases with increase in PVCz content from 9.1% to 80% ((**4a**), (**4b**), (**4c**)) in PVCz/PS blends. This causes the decrease in fraction of partial-overlap excimer emission in the order of 0.18, 0.12, and 0.067, respectively. Fraction of partial-overlap excimer emission in (**4c**), 0.067, is close to that of PVCz neat film, 0.055. This fact means that PVCz-rich phase in (**4c**) consists of almost only PVCz chains, containing few PS chains.

As for PVCz/PEO blends, density of PVCz chains in PVCz-rich phase increases with the increase in PVCz content from 9.6% ((**4x**)) to 29% in PVCz/PEO blends. This diminishes the fraction of partial-overlap excimer emission from 0.45 to 0.35. Density of PVCz chains in PVCz-rich phase is almost constant even with increase in PVCz content from 48% ((**4y**)) to 79% ((**4z**)); fraction of partial-overlap excimer emission in (**4y**) and (**4z**) is 0.34 and 0.33, nearly equal to each other. This fact reflects some degree of miscibility even in immiscible PVCz/PEO blends. Some degree of miscibility has also been observed for solvent-cast films of PVCz/PEO blends in our previous work [9].

The PVCz-chain density in PVCz-rich phase for PVCz (9.1%)/PS blend ((**4a**)) is much larger than that for PVCz (79%)/PEO blend ((**4z**)). This strongly indicates that PVCz/PS blends has lower miscibility than PVCz/PEO blends on molecular level.

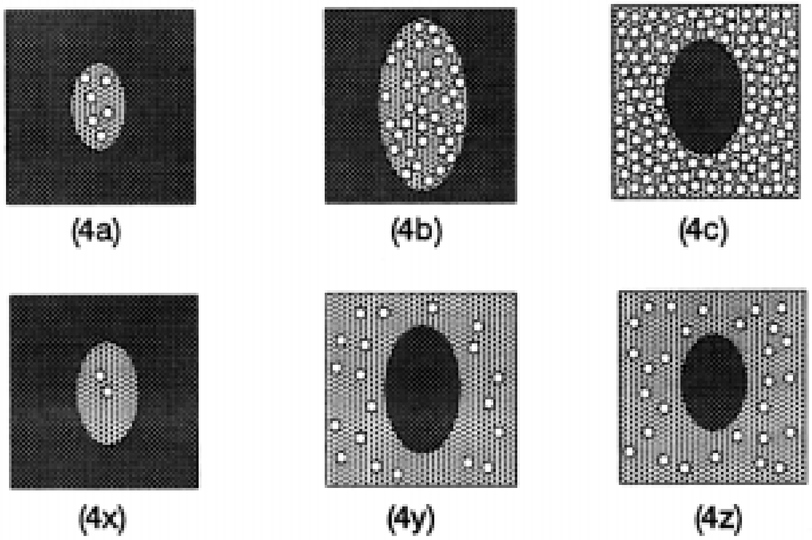


Figure 4. Schematic diagrams of microscopic phase-separated structure in (**4a**) PVCz (9.1%)/PS; (**4b**) PVCz (50%)/PS; (**4c**) PVCz (80%)/PS; (**4x**) PVCz (9.6%) /PEO; (**4y**) PVCz (48%)/PEO; (**4z**) PVCz (79%)/PEO. Continuous phases are shown as areas outside of ellipse based on microscopic images. Areas outside ellipse represent PS-rich phase for (**4a**) and (**4b**), and PEO-rich phase for (**4x**). Areas inside ellipse represent PS-rich phase for (**4c**), and PEO-rich phase for (**4y**) and (**4z**). Areas which contain white circles inside or outside of ellipse represent PVCz-rich phase, respectively. White circles correspond to density of PVCz chains in PVCz-rich phase. Density of PVCz chains in PVCz-rich phase is in the order of (**4x**) < (**4y**) ≈ (**4z**) < (**4a**) < (**4b**) < (**4c**) ≈ PVCz neat film.

Conclusion

It was found from excimer fluorescence of PVCz that PVCz/PS blends have lower miscibility than PVCz/PEO blends.

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