Photocurrent in and miscibility of poly(*N*-vinylcarbazole)/poly(methyl methacrylate) blends

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Summary

Steady-state photocurrent in poly(*N*-vinylcarbazole)(PVCz) (26,48 wt%)/poly (methyl methacrylate)(PMMA) blends is for the first time measured. The PVCz(26,48 wt%)/ PMMA blends showed almost the same carrier-generation efficiencies at electric fields higher than 1×10^5 V · cm^{-1}. The results are explained by high miscibility of the PVCz(26,48 wt%)/ PMMA blends, suggesting the existence of PVCz chains in continous PMMA-rich phase in the phase-separated structure. The miscibility is also evaluated by means of excimer fluorescence of PVCz in these blends and fluorescence microscopy.

Introduction

Poly(*N*-vinylcarbazole)(PVCz), a typical photoconductive polymer, increasingly attracts attention. Electroluminescent polymer blends[1-5] and photorefractive composites[6, 7] contain PVCz as a hole-transport polymer. These blends and composites are studied as materials for display and memory in future. The hole-transport properties of PVCz play an important role in the function of these blends and composites. This function may have a correlation with miscibility of the blends and composites. Miscibility of polymer blends is defined as the degree of homogeneity in the two polymer chains, independent of the ratio of the two components[8].

We evaluated miscibility of PVCz/polyoxyethylene(PEO) and PVCz /polystyrene(PS) blends as model systems by means of excimer fluorescence of PVCz[9, 10]. Excimer

fluorescence gives information on chain aggregation in the scale of ~10 nm. This information is not given by thermal analysis, small angle X-ray scattering, or microscopic methods. Excimers are molecular complexes formed between two identical aromatic rings geometrically parallel to each other, one of which is in a singlet excited state[11]. Frank's group used for the first time excimer fluorescence of poly (2-vinylnapthalene) as a probe for miscibility of polymer blends [12]. 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[13, 14]. There are few studies[15, 16] on miscibility of PVCz blends or composites other than our previous studies[9, 10]. Our previous studies [9, 10] showed that we can evaluate the miscibility of PVCz blends by means of the intensity ratio of fluorescence from the partial-overlap excimer to that from the full-overlap excimer.

Steady-state photocurrent of neat PVCz and copolymers of PVCz as well as transient photocurrent of neat PVCz have been investigated [17-19]. It is not known whether aggregation or dispersion of PVCz chains in the PVCz blends enhances the photoconductivity, since photocurrent in PVCz blends has never been studied to our knowledge. We have stuided in the present work hole-transport properties of PVCz/poly(methyl methacrylate)(PMMA) blends by measuring steady-state photocurrent and characterized miscibility of these blends also by measuring excimer fluorescence of PVCz. We used this time PVCz/PMMA blends, since PVCz/PMMA blends were most suitable so far for electrode fabrications in the photocurrent measurements.

Experimental

We purchased PVCz (weight-average molecular weight (M_w) =1.3 x 10^5, number-average molecular weight (M_n) = 4.7 x 10^4) from Scientific Polymer Products, Inc. and PMMA (M_w = 1.0 x 10^5, M_n = 4.8 x 10^4) from Aldrich, Co. The PVCz and PMMA were used without further purification. Benzene solutions of PVCz(10-100 wt%)/PMMA mixtures were prepared. Total polymer concentration was 3 g/100 mL. The benzene solutions were cast onto indium tinoxide (ITO) glasses or quartz substrates under benzene-saturated atmosphere. The films were dried under vaccum at room temperature for more than 1 days. All the films were turbid or opaque, which shows PVCz/PMMA blends are phase-separated.

Aluminum was vaccum-deposited onto the films cast on ITO glass for photocurrent measurements. We could not fabricate so far such samples with PVCz/PEO blends, PVCz/PS blends, and PVCz(more than 60 t%)/PMMA blends. That is because the films were peeled off from ITO substrates during vaccum drying or aluminum was short-circuited to ITO owing to cracking of films. Steady-state photocurrent measurements of PVCz(26,48 wt%)/PMMA blends and PVCz(100 wt%) were performed

under nitrogen atmosphere at room temperature. The positive electrode (ITO) sides of the samples were illuminated with the light from a He-Cd laser (wavelength 325 nm). The light intensity was ~10^{14}photons · cm^{-2} · S^{-1}. Voltages were applied with a direct-current power supply (TOWA Ltd.) and currents were measured with a microammeter (TOA Electronics Ltd.).

Steady-state fluorescence spectra of PVCz(10-100 wt%)/PMMA blends were measured at room temperature in air with a Hitachi 850 fluorescence spectrophotometer. These spectra were measured in front-face arrangement. Excitation wavelength was 325 nm.

Fluorescence microscopy was used for examining PVCz chain aggregation in the scale more than μm in phase-separated structures. The microscopic images were measured with an Olympus BX 50 optical microscope.

Results and discussion

Figure 1 shows the carrier-generation efficiencies of PVCz(26,48 wt%)/PMMA blends (**1a**), (**1b**)) and PVCz(100 wt%)((**1c**)). These efficiencies mean the numbers of carriers per photon. These values are given by J_{ph}/eI_{ph}, where J_{ph}(A · cm^{-2}) is the photocurrent density, e(C) is the elementary electric charge, and I_{ph}(photons · cm^{-2} · s^{-1}) is the number of absorbed photons. Absorbances in PVCz(26,48 wt%)/PMMA blends and PVCz(100 wt%) are 0.31, 1.1, and about 3, respectively. This indicates that carriers are generated by the beam in the bulk of the films for PVCz(26,48 wt%)/PMMA blends and at the surface (within 1 μm depth) of the film for PVCz(100 wt%).

The carrier-generation efficiencies for (**1a**) and (**1b**) are from 0.01 to 0.1 times as small as those for (**1c**). The efficiencies in Figure 1 are fitted with powers of electric fields, E. Their dependencies on electric fields in (**1a**),(**1b**) and (**1c**) change at threshold electric fields. In electric fields higher than 1 x 10^5 V · cm^{-1}, PVCz(26,48 wt%)/PMMA blends show the similar amounts of efficiency. In this range of electric fields, PVCz(26,48 wt%)/PMMA blends ((**1a**) and (**1b**)) represent almost same dependencies on electric fields, $E^{3.0}$ and $E^{3.3}$. Such dependendies differ from the dependency in PVCz(100 wt%) ((**1c**)), $E^{2.5}$. In low electric fields, PVCz(26,48 wt%)/PMMA blends ((**1a**) and (**1b**)) and PVCz(100 wt%) ((**1c**)) show similar dependencies on electric fields, $E^{1.4}$, $E^{1.7}$, and $E^{1.5}$.

The most remarkable result in the present paper is that PVCz(26 wt%)/PMMA blend has the similar carrier-generation efficiencies as PVCz(48 wt%)/PMMA blend in electric fields higher than 1 x 10^5 V · cm^{-1}, though PVCz weight fraction in the former is as half as that in the latter. It has been reported that mobilities of hole-transporting diamine in a binder polymer increase drastically with increase in concentrations of the diamine: $\mu = r^2\exp(-2r/r_0)$, where μ is mobility, r is average distance between the

diamine molecules, r_0 is a parameter[20]. This holds true for charge-transfer complexes of PVCz/trinitrofluorenone[21]. The remarkable photocurrent-feature in the PVCz(26,48 wt%)/PMMA blends should be correlated to miscibility of these blends, which will be discussed below. Excimer fluorescence of PVCz in these blends is a powerful tool for elucidating the miscibility of PVCz blends.
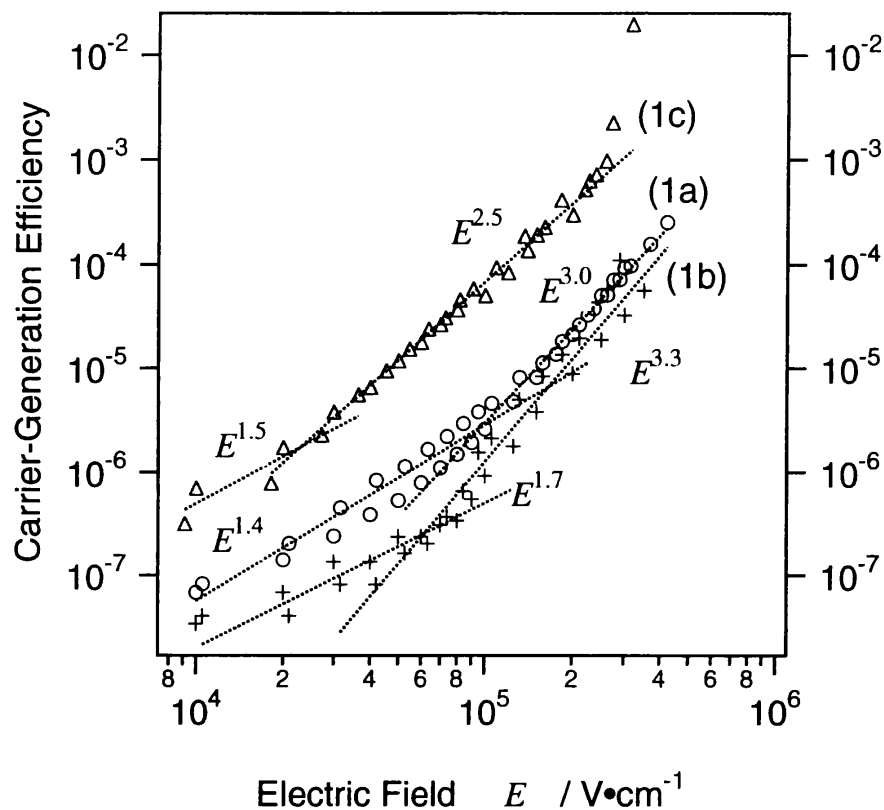

Figure 1. Electric field dependence of carrier-generation efficiency of (1a) PVCz(26 wt%) /PMMA; (1b) PVCz(48 wt%) /PMMA; (1c) PVCz(100 wt%). Results of two samples are shown, respectively. Film thickness is (1a),(1b) (20±2) μm; (1c) (10±1) μm. Dotted lines are fittings with powers of electric fields.

Figure 2 shows fluorescence spectra of PVCz in PVCz(26,48 wt%)/PMMA blends. Two broad bands peaking at 2.65×10^4 cm^{-1} (377 nm) and 2.43×10^4 cm^{-1} (412 nm) correspond to partial- and full- overlap excimers, respectively [13, 14]. Resolving the spectra into two overlapping components gives fraction of each band more explicitly, as is shown in Figure 2. Method of the band-resolving was reported in our previous work[9]. The fittings were performed with two Gaussians. The result became rather poor, when the intensity of partial-overlap excimer emission relative to that of full-

overlap excimer emission in the spectrum is very large as in (**2a**). This is since the spectrum (**2a**) might contain emission band from carbazolyl monomer as the third component[22]. We omitted this third component centered at about 2.86×10^4 cm^{-1} (350 nm) from the band-resolving for the sake of simplicity.
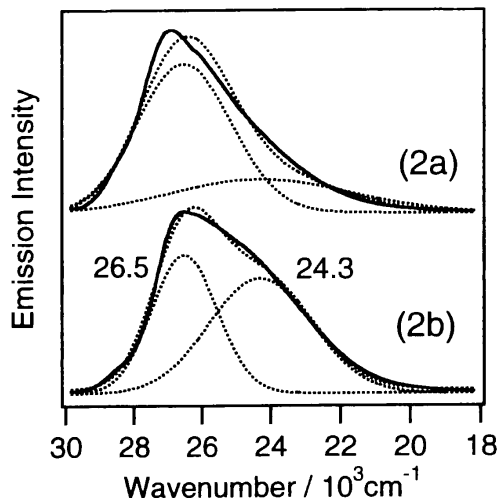

Figure 2. Fluorescence spectra of PVCz in (**2a**) PVCz(26 wt%)/PMMA; (**2b**) PVCz (48 wt%)/PMMA. Excitation wavelength is 325 nm. Solid lines are experimental spectra and their maximum intensities are roughly normalized for (**2a**) and (**2b**). Three dotted lines are fitting curves, two of which are components as a result of band-resolving for (**2a**) and (**2b**), respectively.
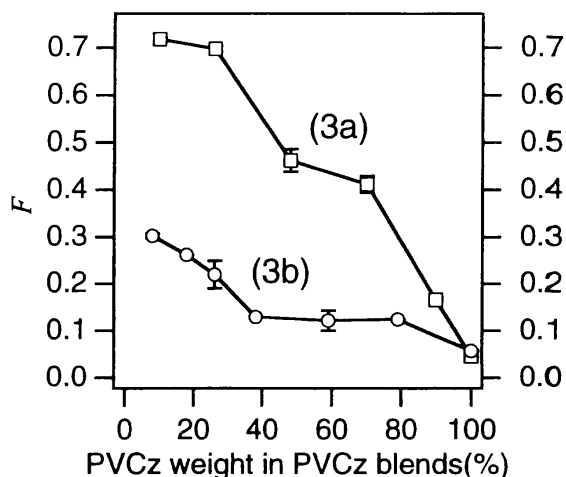
Figure 3. Fractions, F, of partial-overlap excimer emission in the total excimer emission based on the band-resolving for (**3a**) PVCz/PMMA blends; (**3b**) PVCz/ PEO blends[9]. These F values were calculated as $S_1/(S_1 + S_2)$, where S_1 and S_2 represent areas of emission bands centered at 2.65×10^4 cm^{-1} and that at 2.43×10^4 cm^{-1}, respectively.

Figure 3 shows results of band-resolving for PVCz(10-100 wt%)/PMMA blends ((**3a**)) and for PVCz(8.0-100 wt%)/PEO blends[9] as comparison ((**3b**)). The F values in Figure 3 are calulculated as the fraction of partial-overlap excimer emission on the basis of band-resolving. Large F values mean that PVCz chains aggregate weakly or rather dispersed in the phase-separated structure[9, 10]. This is because the excited energy detrapped from the partail-overlap excimer sites mainly migrates intermolecularly to neighboring PVCz chains in aggregates, resulting in further intrachain migration to full-overlap excimer sites [9, 10]. All the F values of PVCz/PMMA ((**3a**)) and PEO ((**3b**)) blends are larger than the F value for PVCz(100 wt%). This indicates that there are several amounts of PMMA chains or PEO chains existing among PVCz chains in PVCz-rich phase in the phase-separated structures. All the F values

for PVCz/PMMA blends ((**3a**)) are larger than those for PVCz/PEO blends of corresponding PVCz fractions ((**3b**)). This indicates that PVCz/PMMA blends are more miscible than PVCz/PEO blends: PMMA chains tend to be in and between PVCz aggregates more than PEO chains do in the local structure of ~10 nm in scale, and PVCz chains can be dissolved in PMMA-rich phase.

Figure 4 shows fluorescence microscopic images for PVCz(26,48 wt%)/PMMA. These images manifest two points for both of PVCz(26 wt%)/PMMA and PVCz(48 wt%)/PMMA blends. Firstly, PMMA-rich phase forms continuous phase and PVCz-rich phase forms dispersion phase. Secondly, some of white areas in (**4a**) and (**4b**) are not pure-white, containing dark spots. This indicates that the dispersed PVCz-rich phase contains PMMA chains, leading to existence of multiple PMMA-rich phase which contains PVCz chains inside. Excimer fluorescence properties of PVCz(26,48 wt%)/PMMA blends indicate that PVCz chains also exist in PMMA-rich phase on molecular level. Information from the microscopic images supports the information from the excimer fluorescence, which suggests high miscibility of PVCz and PMMA, though sizes of phase-separated structure observed by two methods are quite different.
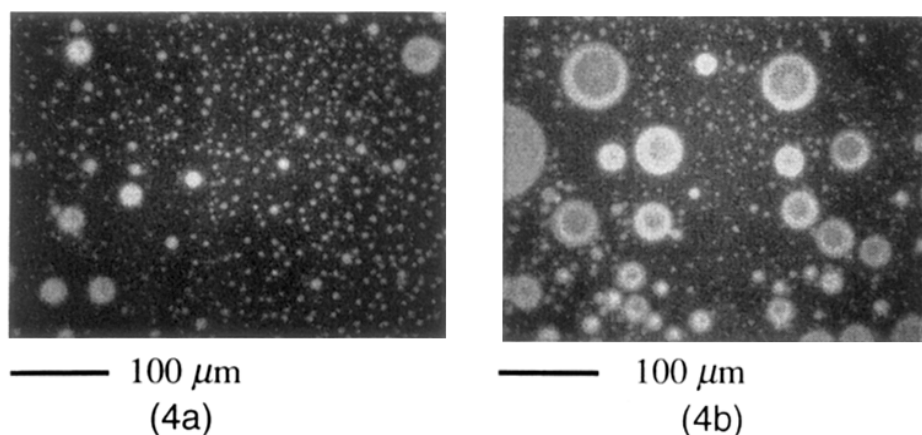
—— 100 μm

(4a)

—— 100 μm

(4b)

Figure 4. Fluorescence microscopic images of phase-separated structure for (**4a**) PVCz(26,wt%)/PMMA; (**4b**) PVCz(48 wt%)/PMMA. White areas are PVCz-rich phase. Black areas are PMMA-rich phase.

Carriers generated by light in the blends can move between the dispersed PVCz-aggregates through continuous PMMA-rich phase, since this PMMA-rich phase contains PVCz-chains. The carriers must move through continuous PMMA-rich phase as well as through PVCz-rich phase to reach aluminum elctrodes. The PVCz chains in PMMA-rich phase of PVCz(26 wt%)/PMMA and PVCz(48 wt%)/PMMA blends are presumably dispersed similarly. That is why PVCz(26 wt%)/PMMA and PVCz(48

wt%)/ PMMA blends show similar carrier-generation efficiencies. Such a mechanism would be specific to polymer blends with binary phases. In contrast to the present case, the diamine molecules in a binder polymer form small crystals or solid solutions, leading to single local concentration of diamine molecules. This results in the strong dependence of hole mobilities on the concentration of diamine molecules[20].

The images of (**4a**) and (**4b**) are measured from the top of the films. The maximum size of the dispersed PVCz-aggregates in (**4a**) and (**4b**) is from 50 to 100 μm, which is larger than the film thickness, 20 μm. The PVCz-rich phase may contact with both of ITO and aluminum electrodes in the sandwitch configuration. If all the carriers moved through the PVCz-rich phase which contacts with the two electrodes, carrier-generation efficiencies of PVCz(48 wt%)/PMMA blend should have been larger than those PVCz(26 wt%)/PMMA blend, since PVCz-rich phase which contacts with the two electrodes has larger area in PVCz(48 wt%)/PMMA blend than in PVCz(26 wt%)/PMMA blend, as is shown in (**4a**) and (**4b**). Carrier-transport not only through PVCz-rich phase but also through PMMA-rich phase is of necessity, judging from our experimental results. We confirmed that PMMA (100 wt%) film does not show any photocurrent.

Fluorescence spectroscopy observes mainly the situation of PVCz-rich phase. The *F* value, reflecting degree of dispersion of PVCz chains in PVCz-rich phase[9], is larger for PVCz(26 wt%)/PMMA blend than for PVCz(48 wt%)/PMMA blend, as is shown by (**3a**). This indicates that the local concentraion of PVCz chains in PVCz-rich phase in the former is smaller than that in the latter. On the other hand, the same carrier-generation efficiencies of these blends in electric fields higher than 1×10^{5} V $\cdot$ cm^{-1} are largely affected by PVCz chains in PMMA-rich phase, whose local concentration might not be so different in both of the blends.

Conclusion

PVCz(26 wt%)/PMMA blend showed carrier-generation efficiencies under photoirradiation similar to those of PVCz(48 wt%)/PMMA blend. This can be explained by existence of PVCz chains in continuous PMMA-rich phase in the phase-separated structure.

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