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CARRIER PHOTOGENERATION INVOLVING TRIPLET - TRIPLET ANNIHILATION IN N-VINYLCARBAZOLE - 1-VINYLNAPHTHALENE COPOLYMER

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The carrier photogeneration mechanism has been investigated in N-vinylcarbazole(VCz) - 1-vinylnaphthalene(VNa) copolymer. The photocurrent as well as the delayed fluorescence of carbazole chromophore due to the triplet - triplet (T-T) annihilation are found to be enhanced by introducing a few mole per cent of VNa units. The photocurrent shows a quadratic dependence upon the illumination light intensity in a high field. In the light of the emission study, the following carrier photogeneration involving T-T annihilation is found to occur in the VCz - VNa copolymer:

$$\mathrm{Cz} \xrightarrow{h\nu} {}^{1}\mathrm{Cz}^{*} \longrightarrow {}^{3}\mathrm{Cz}^{*} \longrightarrow {}^{3}\mathrm{Na}^{*} \xrightarrow{\text{T-T annihilation}} {}^{1}\mathrm{Na}^{**} \longleftrightarrow {}^{1}\mathrm{Cz}^{**} \longrightarrow \text{Carriers.}$$

Here, Cz and Na represent the carbazole and naphthalene chromophores, and the asterisk and double asterisk indicate the lowest and higher excited states, respectively.

The photocurrent in the lowest π-π^* absorption region of poly(N-vinylcarbazole)(PVCz) is attributed to the "extrinsic" carrier photogeneration due to an interaction between the singlet exciton and an electron accepting impurity.1,2) In such carrier photogeneration in PVCz, the participation of the singlet exciton which migrates effectively through a PVCz film is generally considered.1-3) However, with reference to the recent observation4,5) that the triplet exciton of PVCz also migrates along the polymer chain in solid film as well as in rigid solution, we have been investigating the possibility of the participation of the triplet exciton in the carrier photogeneration.

From the present photocurrent and emission measurements of the N-vinylcarbazole(VCz) - 1-vinylnaphthalene(VNa) copolymer, it is found that a new type of carrier photogeneration via triplet state of carbazole (Cz) moiety participates in the photocurrent of this copolymer as shown in the scheme described in the abstract.

The VCz - VNa copolymers having different compositions and PVCz homopolymer were obtained by cationic polymerization with BF_3OEt_2 in methylene chloride at -78°C. The polymers obtained were purified sufficiently by repeated reprecipitation from the tetrahydrofuran - methanol system followed by hot methanol extraction. The solvents, tetrahydrofuran(THF) and 2-methyltetrahydrofuran(MTHF) were distilled from sodium immediately before use. Emission spectra were recorded on a Hitachi MPF-3 emission spectrophotometer equipped with a 150W Xe excitation lamp and an R106F(S-19) photomultiplier (HTV). The delayed emission spectra were obtained by using a cylindrical chopper. The solution samples having the 10^{-3} mol/l concentration of Cz groups in MTHF-THF were sealed in 3 mm quartz capillary tubes after several freeze-pump-thaw cycles. The steady-state photocurrent was measured in vacuo (10^{-7} mmHg) by using a vibrating-reed electrometer (Takeda Riken TR84M). A solvent cast polymer film on a nesa coated quartz plate was provided with an evaporated transparent gold electrode on a free surface to form an Au-Polymer-Nesa sandwich-type cell (area of electrode: 1 cm^2).

As shown in Fig. 1, the energy relation of the excited states in the carbazole(Cz) - naphthalene (Na) system is the unique one that the lowest singlet excited state of Cz ($^1Cz^*$) is located lower than that of Na ($^1Na^*$), but the lowest triplet excited state of Cz ($^3Cz^*$) is higher than that of Na ($^3Na^*$). Hence, the singlet energy transfer from $^1Na^*$ to $^1Cz^*$ and the triplet energy transfer inversely from $^3Cz^*$ to $^3Na^*$ would be expected, if the VNa units are introduced into the VCz polymer by copolymerization.

If mobile Cz triplet exciton were involved in the extrinsic carrier photogeneration, the photocurrent would be expected to decrease in the copolymer due to the energy transfer from $^3Cz^*$ to $^3Na^*$. Contrary to this expectation, however, we observed an enhancement of the photocurrent in this copolymer.

Figure 2 shows the spectral dependence of the photocurrent in the VCz homopolymer and the VCz - VNa copolymer having 96 mol% VCz content under almost the same condition with respect to the illumination light intensity (about 10^{13} photon/cm^{2}s) and the applied field (13 KV/cm). In the case of PVCz, when a positively biased gold electrode is illuminated, the photocurrent (i_p^+) shows two maxima at 340 and 300 nm, corresponding well to the absorption maxima, while when a negatively biased gold electrode is illuminated (i_p^-), only one distinct peak is observed at 360 nm, corresponding to the absorption edge with red-shift of 20 nm as compared with the case of i_p^+. The magnitude of i_p^- is smaller by one order than i_p^+ in this applied field. Thus, the spectral dependence of the photocurrent in PVCz is in good agreement with the earlier report.[6]

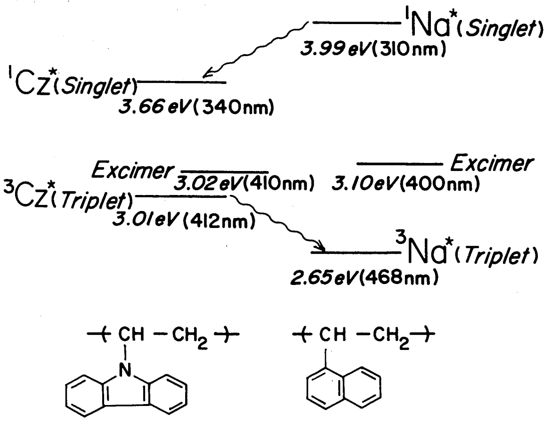

Fig. 1 Energy relation of the lowest excited states of PVCz and PVNa.

In the case of the copolymer, both i_p^+ and i_p^- show larger peak values than in PVCz. It should be noted that i_p^- is considerably enhanced, showing almost the same value as i_p^+. The peak positions of the photocurrent are located at 355 and 310 nm for i_p^+ and at 360 and 310 nm for i_p^-, respectively, being antibatic to the absorption spectrum. Similar spectral dependences were also observed in other copolymers with different compositions (VCz content: 99, 97, and 92 mol%). It is characteristic of the copolymers that i_p^+ and i_p^- exhibit quite similar spectral dependences with respect to the peak positions as well as their magnitudes. Thus, the carrier photogeneration in the copolymers would be considered to be quite different from that of PVCz. First, we examined the behavior of the triplet excitation energy in the copolymer from the delayed emission spectra.

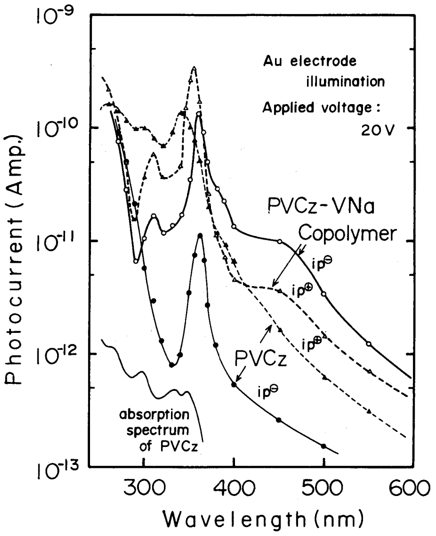

Fig. 2 Spectral dependence of the photocurrent of PVCz and VCz-VNa copolymer (96 mol% VCz); i_p^+ and i_p^- indicate the photocurrent when illuminating positively and negatively biased Au electrodes, respectively; Film thickness: 15μ; Applied voltage: 20 V. All in high vacuum.

Figure 3 shows the delayed emission spectra of the VCz - VNa copolymers having various VCz contents (99, 92, 66, 24 mol%) in rigid solution at 77°K. Here, the Cz chromophore was selectively excited at 340 nm under constant excitation intensity, keeping the concentration at 10^{-3} mol/l(Cz groups). As shown in this figure, the delayed emission spectrum of PVCz consists of the phosphorescence in longer wavelength region (>410 nm) and the delayed fluorescence due to the T-T annihilation in the 360 nm region. In the case of the copolymers, the phosphorescence as well as the delayed fluorescence from Cz is also observed, but the Cz phosphorescence is considerably quenched and instead the sensitized Na phosphorescence appears clearly around 480 - 600 nm due to the triplet energy transfer from ${}^3Cz^*$ to ${}^3Na^*$. Thus, the triplet energy transfer from Cz to Na chromophore occurs effectively in the VCz - VNa copolymers.

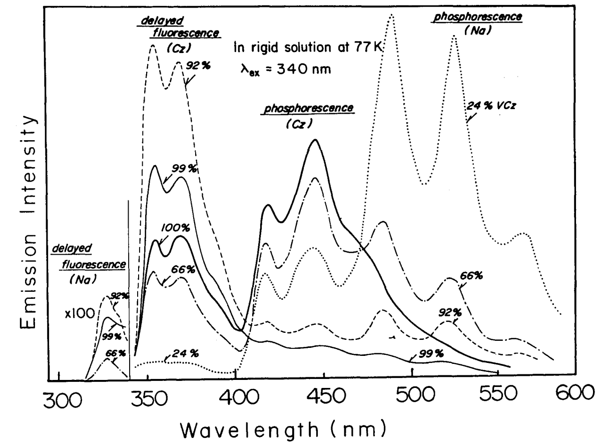

Fig. 3 Delayed emission spectra in rigid solution (77°K) of PVCz (▬), and VCz-VNa copolymers of different compositions: 99 mol% VCz content (—), 92 mol% (---), 66 mol% (—·—), and 24 mol% (···). λ_{ex} = 340 nm. Concentration: 10^{-3} mol(Cz group)/l. These spectra were measured under almost the same condition, and the delayed fluorescence of Na was measured by using a lock-in amplifier.

As can be seen from this figure, the following two interesting results were obtained; (i) The Cz delayed fluorescence is enhanced by introducing a few mole per cent of VNa units, and this amount corresponds just to the copolymer composition to give a maximum enhancement of the photocurrent, and (ii) In spite of the selective excitation of Cz chromophore alone a delayed emission is observed, although very weak, with a maximum at 327 nm, which is higher in energy than the excitation light (340 nm). The peak position of this emission coincides with that of the Na monomer fluorescence observed in rigid solution of poly(1-vinylnaphthalene)[7] at 77°K, and this emission intensity shows the quadratic dependence upon the excitation intensity. From the measurements of the lifetime and the excitation spectrum, which will be described in the forthcoming full paper[8] in detail, we assigned this emission to the delayed fluorescence of the Na chromophore resulting from the T-T annihilation in the VNa sequence of the copolymer due to two Na triplets produced by the effective triplet energy transfer from ${}^3Cz^*$. It is thus concluded that the following photophysical process occurs in the copolymer when the Cz chromophore is excited selectively;

$$\begin{tikzcd}
Cz \arrow[r, "h\nu"] & {}^1Cz^* \arrow[r, "ISC"] & {}^3Cz^* \arrow[r] \arrow[d] & {}^3Na^* \arrow[r, "\text{T-T annihilation}"] \arrow[d] & {}^1Na^{**} \arrow[r] \arrow[d] & {}^1Cz^{**} \arrow[d] \\
 & & \begin{array}{c}\text{Phosphorescence}\\ \text{(Cz)}\end{array} & \begin{array}{c}\text{Phosphorescence}\\ \text{(Na)}\end{array} & {}^1Na^* \arrow[d] & {}^1Cz^* \arrow[d] \\
 & & & & \begin{array}{c}\text{Delayed}\\ \text{fluorescence}\\ \text{(Na)}\end{array} & \begin{array}{c}\text{Delayed}\\ \text{fluorescence}\\ \text{(Cz)}\end{array}
\end{tikzcd} \tag{1}$$

Such photophysical process will be described diagramatically in Fig. 4. The enhancement of the Cz delayed fluorescence in the copolymer can be reasonably understood by this photophysical process.

As shown in Fig. 4, there is a possibility of obtaining a higher excited singlet state of Cz (${}^1Cz^{**}$) by the energy transfer from ${}^1Na^{**}$ produced immediately after the T-T annihilation of two Na triplets in the VNa sequence of the copolymer. It should be noted here that the energy of the ${}^1Cz^{**}$ state thus produced is higher than 4.7 eV which is considered to be the "conductive state" of PVCz. Hence, the carrier photogeneration from this state is expected to be possible by an autoionization process just as is known in organic molecular crystals such as anthracene[9] and tetracene.[10] If so, we should observe the quadratic dependence of the photocurrent upon the illumination light intensity, since the above-mentioned carrier generation process involves a biphotonic process of the T-T annihilation.

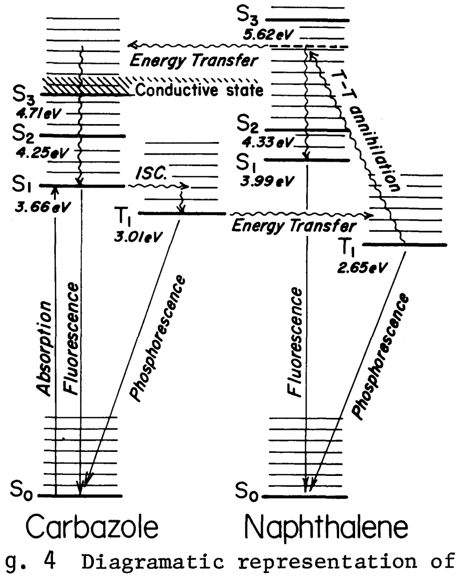

Fig. 4 Diagramatic representation of the photophysical process in the VCz-VNa copolymer in selective excitation of Cz chromophore.

Figure 5 shows the light intensity dependence of the i_p^+ photocurrent (at 360 nm) in the copolymer. The quadratic dependence can apparently be observed in high fields. The i_p^- photocurrent also exhibits similar dependence. The photocurrent in PVCz is always linearly dependent on the light intensity even in a high field.⁶⁾ Thus, it is ascertained that a biphotonic process is involved in the carrier photogeneration of the copolymer in the lowest π-π^* absorption region.

In Fig. 6 are shown the v-i characteristics of the photocurrent peak at 360 nm. The i_p^+ and i_p^- exhibit almost the same behavior, i.e., both increase with the high power (about 3.0) of the applied field in higher fields. In the case of PVCz, such a super linear dependence is reported only for i_p^+ in higher fields, but i_p^- does invariably show a linear dependence on the applied field.

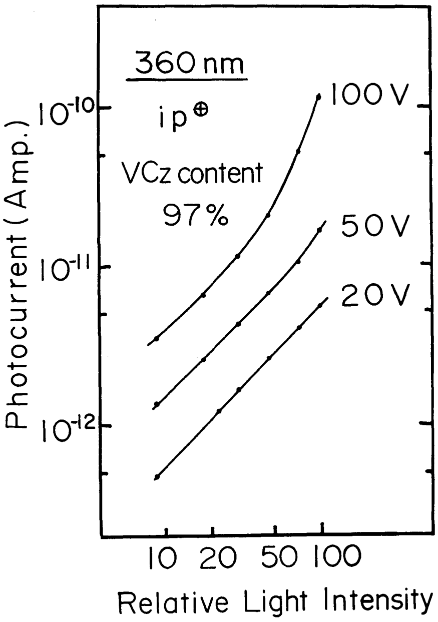

Fig. 5 Light intensity dependence of the i_p^+ photocurrent in the copolymer (97 mol% VCz). Illumination at 360 nm; Applied voltage: 20, 50, and 100V; Film thickness: 15µ. i_p^- shows the same behavior.

Thus, the photoconductive behavior of the copolymers is unique in that (i) the i_p^- photocurrent is significantly enhanced, (ii) the quite similar behavior is observed between i_p^+ and i_p^- in the spectral dependence as well as in the voltage dependence, and (iii) the photocurrent depends quadratically upon the light intensity.

It is concluded that the following carrier photogeneration involving the T-T annihilation via triplet state of the Cz moiety occurs effectively in the copolymer:

$$\mathrm{Cz} \xrightarrow{h\nu} {}^1\mathrm{Cz}^* \longrightarrow {}^3\mathrm{Cz}^* \longrightarrow {}^3\mathrm{Na}^* \xrightarrow{\text{T-T annihilation}} {}^1\mathrm{Na}^{**} \longrightarrow {}^1\mathrm{Cz}^{**} \longrightarrow \text{Carriers.} \qquad (2)$$

Contrary to the extrinsic carrier photogeneration in which the negative charge located on an acceptor molecule is not mobile, it can be easily understood in the above photogeneration process involving the autoionization that both hole and electron would be operative as effective carriers.

We found a new type of "intrinsic" carrier photogeneration in the VCz - VNa copolymer, and we believe that even in PVCz such carrier photogeneration process may occur, in principle, by autoionization from a higher singlet excited state through the T-T annihilation of two Cz triplets. The further discussion will be given in the forthcoming full paper with more detailed experimental results.

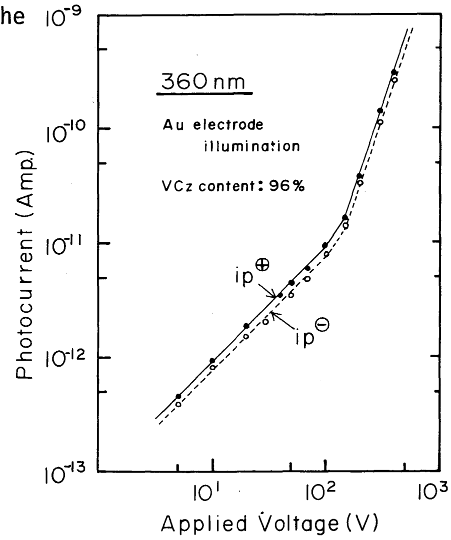

Fig. 6 Applied voltage dependence of the photocurrent in the copolymer (96 mol% VCz). Illumination onto positively (i_p^+) and negatively (i_p^-) biased Au electrodes with 360 nm UV light. Film thickness: 15µ.

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