Photo-oxidation Effect of Poly(*N*-vinylcarbazole) Film on Photoconductivity and Electronic Spectra[1]

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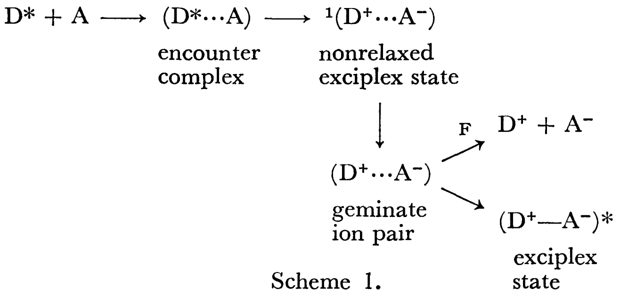
The photo-oxidation effect on poly(*N*-vinylcarbazole) (PVCz) and amorphous 1,3-di(*N*-carbazolyl)propane films was studied by means of ultraviolet absorption, infrared absorption, and fluorescence spectra. The photoconductivity of the photo-oxidized PVCz films was also measured as a function of photoirradiation time. A photo-oxidation product which formed near the surface of films had a carbonyl substituent group, acted as a singlet exciton trap in competition with the excimer-forming sites, and formed an exciplex with an excited carbazolyl chromophore. The very slight amount of the photo-oxidation product enhanced the photoconductivity of PVCz films by a factor of *ca.* 15, suggesting that the product acted as an electron-accepting impurity in the photo-carrier-generation mechanism in the lowest π-π^* absorption region of PVCz films.

There have been many investigations concerning the photo-carrier-generation mechanism in the lowest π-π^* absorption region of poly(*N*-vinylcarbazole) (PVCz) film.[2–7] The following mechanism is considered to be most appropriate at the present stage:[6,7]



Scheme 1.

The singlet excited state(D*) (singlet exciton) of PVCz migrates effectively through the carbazole(Cz) chromophores and encounters some electron-accepting impurity (A) during its lifetime to form an encounter complex ($D^*\cdots A$). The complex goes through a rapid electron transfer and changes to a nonrelaxed exciplex state ${}^1(D^+\cdots A^-)$. The nonrelaxed exciplex state has some excess kinetic energy and undergoes a thermalization of the excess energy to give an electron-hole ion pair ($D^+\cdots A^-$) at a separation r_0. The electron-hole pair will either recombine geminately to give a relaxed fluorescence exciplex state ($(D^+—A^-)^*$), or dissociate into free carriers (D^+, A^-) when it is assisted by an external electric field *F*. Taking account of the ionization potential (6.1 eV) and the electron affinity (1.5 eV) of PVCz in film, the electron affinity of the compound acting as an electron acceptor should be higher than 0.6—0.8 eV. Some unknown impurities contaminated in course of synthesis of the monomer and/or polymer, dissolved oxygen, or a photo-oxidation product of the polymer can be considered as the electron-accepting impurities in a PVCz film. Judging from the migration efficiency of the singlet exciton,[8–10] a concentration of the electron-accepting impurity of about 10^{-3} mol/mol monomer unit seems to be necessary to interpret the high yield of photo-carrier-generation (*ca.* 0.1). Contamination by such a concentration of the impurity is improbable in course of the synthesis. In the case of triplet oxygen in the ground state, of which the electron affinity is *ca.* 0.42 eV,[11] considerable thermal activation should be necessary to give the electron-hole ion pair. Therefore, it is impossible to explain the high yield of the photo-carrier-generation in PVCz films by considering only the unknown contaminating impurity and the oxygen. Then, a photo-oxidation product of PVCz should be considered as an electron-accepting impurity which might be effective for the photo-carrier-generation. Therefore, detailed information on the photo-oxidation of a PVCz film is very important in understanding the origin of the high photoconductive properties of the polymer. It has been briefly reported that photo-oxidation products were obtained by irradiation of PVCz suspended in sulfuric acid–ethanol solution in a stream of air[12] and of a PVCz film in air.[6] However, no detailed study has been reported on the photo-degradation of a PVCz film.

In the present research, we have investigated the photo-oxidation of an amorphous PVCz film and an amorphous 1,3-di(*N*-carbazolyl)propane (DCzP(a)) film,[13] which is a dimeric model compound of PVCz, by measuring the change in the absorption and fluorescence spectra caused by photoirradiation and have compared the difference in behavior of the photo-oxidation between these two films. We have also investigated how the photo-oxidation affects the photoconductivity of a PVCz film.

Experimental

The PVCz was prepared by free-radical polymerization (initiator; AIBN) and was reprecipitated from benzene solution with methanol. Thin PVCz films used for measuring the absorption and fluorescence spectra were cast on quartz plates from benzene solution and dried *in vacuo*. Films of PVCz 10 μm thick for electrical measurements were cast on nesa-coated conductive quartz plates from benzene solution. A semitransparent gold main electrode was evaporated on the film to prepare a sandwich-type cell. The DCzP(a) films were prepared by the methods described previously.[13]

The absorption and fluorescence spectra were measured with the apparatus described in a previous paper.[14] The electrical measurements (photoconductivity and magnetic field effect on the photoconductivity) were carried out under a vacuum of 10^{-2} Torr at 20 °C by a DC method. Films were irradiated in air at atmospheric pressure though a water filter (21 cm) with the full spectrum of a 500 W high pressure mercury lamp. The radiation density ($\lambda < 350$ nm) was about 1×10^{17} photons/cm^2 s.

Results and Discussion

Electronic Spectra. Figure 1 shows the change in the absorption spectra of PVCz films caused by photoirradiation. With irradiation time, the absorption intensity of Cz chromophores decreased and new absorption (300—340 nm and 350—420 nm) appeared and increased. Three isosbestic points were observed at 348, 341, and 303 nm. These new bands are attributed to a photo-oxidation product, because no change in the absorption was observed for a PVCz film irradiated under a vacuum of 10^{-1} Torr. The further irradiation caused a deviation from these isosbestic points and also a decrease of the absorption intensities of the photo-oxidation product, as is shown in Fig. 2. Similar phenomena (decrease in the absorption intensity of Cz chromophores and appearance of new absorption bands) were also observed for DCzP(a) film, although five isosbestic points were observed. The dependence of the absorption intensity (370 nm) due to the photo-oxidation product on irradiation time is shown in Fig. 2. Assuming that there is no remarkable difference in the molar extinction coefficient of the photo-oxidation product between PVCz and DCzP(a), Fig. 2 shows that the formation rate of the photo-oxidation product observed for a PVCz film is larger than that for a DCzP(a) film by a factor of *ca.* 4. This may be attributed to the presence in the polymer film of sites which are susceptible to photo-oxidation. Judging from the fact that the concentration of the sandwich-like excimer-forming sites in a PVCz film is higher than that in a DCzP(a) film, the sandwich-like excimer-forming sites seem to be susceptible in such a way. This would be supported by the fact that the decrease of the sandwich-like excimer fluorescence (*ca.* 23900 cm^{-1}) caused by photo-oxidation is larger than that of the second excimer fluorescence (*ca.* 26500 cm^{-1}), as is clearly shown in Fig. 4.

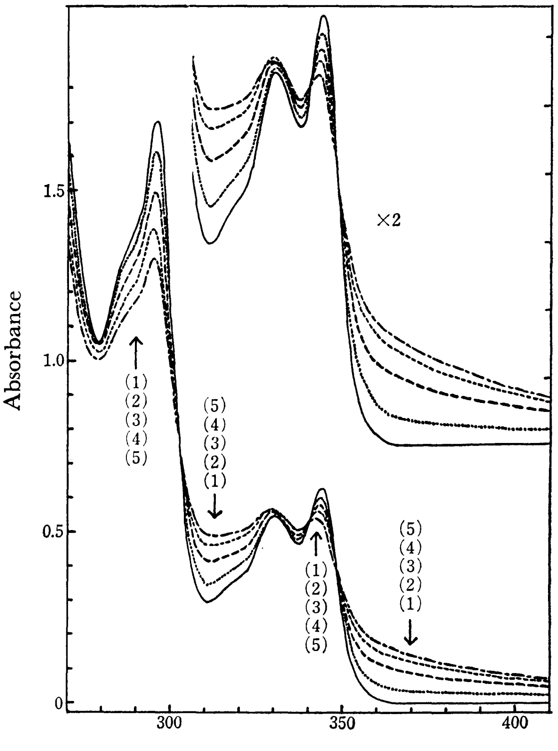


Fig. 1. Change in the absorption spectra of a PVCz film caused by photoirradiation. Irradiation time; (1) 0, (2) 6, (3) 12, (4) 18, and (5) 25 min.

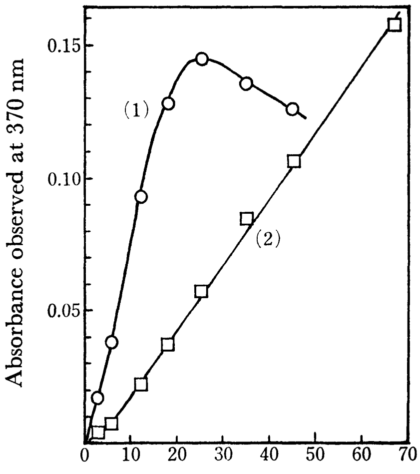


Fig. 2. Dependence of the absorption intensity at 370 nm on photoirradiation time for (1) PVCz and (2) DCzP(a) films.

Infrared spectra of photo-oxidized PVCz films are shown in Fig. 3. The increasing absorption observed at around 1700 cm^{-1} is attributable to carbonyl groups. A similar phenomenon was also observed for a DCzP(a) film. These results show that the photo-oxidation products formed in both PVCz and DCzP(a) films have carbonyl groups, which are electron-accepting substituents. The formation of the carbonyl group in a PVCz film by photo-oxidation is similar to the phenomenon observed for a photo-oxidized polystyrene (PSt) film.[15]

It has been reported that a PSt film becomes brittle by photo-oxidation, although extraction of the photo-oxidized PSt film with chloroform leaves a very small

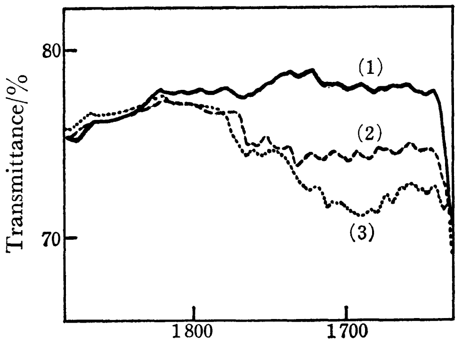


Fig. 3. Change in the infrared absorption spectra of a PVCz film caused by photoirradiation. Irradiation time; (1) 0, (2) 20, and (3) 100 min.

amount of residue.[15] On the other hand, the heavily photo-oxidized PVCz film becomes insoluble in most solvents, such as benzene and 1,2-dichloroethane. This fact suggests that the disruption of the Cz chromophore and a crosslinking reaction seems to take place at the same time in a PVCz film.

The change in the fluorescence spectra of PVCz films caused by photoirradiation in air is shown in Fig. 4. Little change was observed in the fluorescence spectra of PVCz films by photoirradiation under a vacuum of 10^{-1} Torr. Remarkable changes in the fluorescence spectra were observed for very weakly photo-oxidized PVCz films, compared with the case of absorption spectra. With irradiation time, the excimer fluorescence of PVCz films decreased and a new fluorescence band in the longer-wavelength region ($\nu < 20000$ cm^{-1}) appeared. Further irradiation caused a decrease of the excimer and the new fluorescence intensities. A quite similar phenomenon was observed for DCzP(a) films, as is shown in Fig. 5. The broad and structureless emission band with a peak (or shoulder) at 19000—20000 cm^{-1} of the weakly photo-oxidized PVCz and DCzP(a) films may be assigned to the exciplex fluorescence, which is formed between an excited Cz chromophore and the photo-oxidation product with the carbonyl substituent group. This assignment is supported by the following observation. The fluorescence observed at 515 nm for the weakly photo-oxidized PVCz film was partly quenched by applying an electric field and the decrease in the fluorescence showed a quadratic dependence on the field strength, as is shown in Fig. 6. It has been reported by Yokoyama *et al.* that a similar phenomenon is observed for the exciplex fluorescence of PVCz films doped with dimethyl terephthalate (DMTP).[6,16]

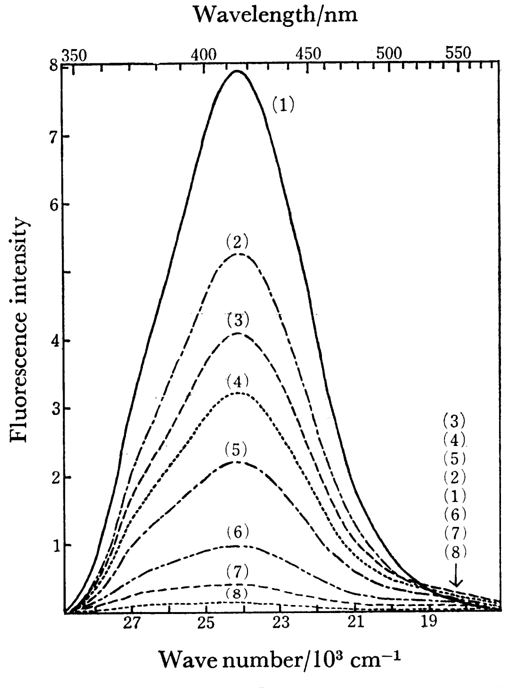


Fig. 4. Change in the fluorescence spectra of PVCz films caused by photoirradiation. Irradiation time; (1) 0, (2) 0.5, (3) 1, (4) 1.5, (5) 2.5, (6) 4.5, (7) 9, and (8) 15 min.

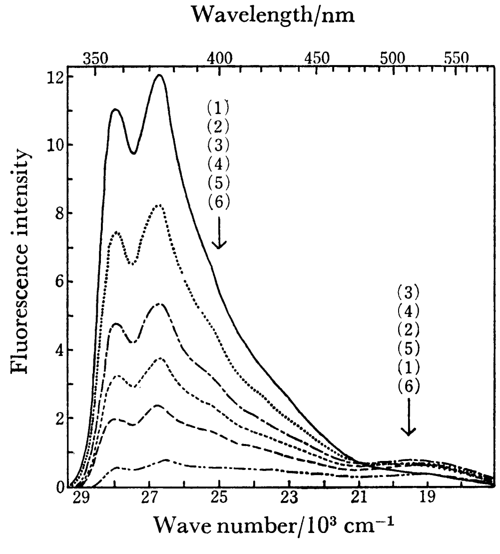


Fig. 5. Change in the fluorescence spectra of DCzP(a) films caused by photoirradiation. Irradiation time; (1) 0, (2) 0.17, (3) 0.5, (4) 1, (5) 1.5, and (6) 10 min.

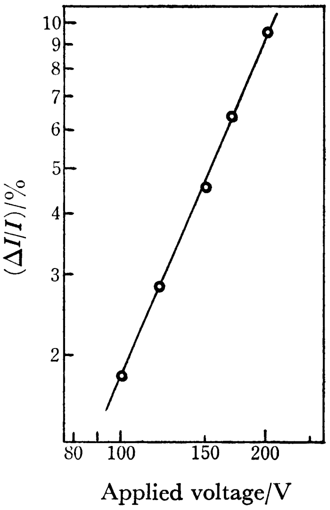


Fig. 6. Electric field-strength dependence of the fluorescence decrease observed at 510 nm for the weakly photo-oxidized PVCz film (≈0.5 μm thick). Irradiation time; 25 s. Excitation wavelength; 335 nm.

In order to represent the decrease of fluorescence, a quenching factor, Q, which has frequently been used in investigations of energy migration in polymer films,[8-10,17] is defined for convenience by the following equation:

$$Q_t = (I_0 - I_t)/I_t$$

where I_0 and I_t are fluorescence peak intensities before and after photo-irradiation, respectively. The dependence of the quenching factor of photo-oxidized PVCz and DCzP(a) films on the irradiation time is shown in Fig. 7. The value of Q obtained for thin films was larger than that obtained for thick films. This result suggests that the process of the photo-oxidation proceeds near the surface of films. Therefore, the photo-oxidation product is not formed in the bulk of film uniformly.

However, an approximately linear relationship existed between the quenching factor, Q, and the irradiation time, t, in an early stage of photoirradiation. This phenomenon seems to suggest that the photo-oxidation product acts as an exciton trap in competition with the excimer-forming sites. The value of Q obtained for DCzP(a) films was larger than that obtained for PVCz films. Considering that the concentration of the photo-oxidation product formed in PVCz films is higher than that formed in DCzP(a) films, as mentioned above, this fact suggests that the number of Cz chromophores covered by a singlet excition during its lifetime in a DCzP(a) film is larger than that in a PVCz film. This fact is consistent with the result obtained by investigation of the excitation energy migration, in which the fluorescence quenching by a guest molecule such as DMTP in PVCz and DCzP(a) films was investigated.[18]

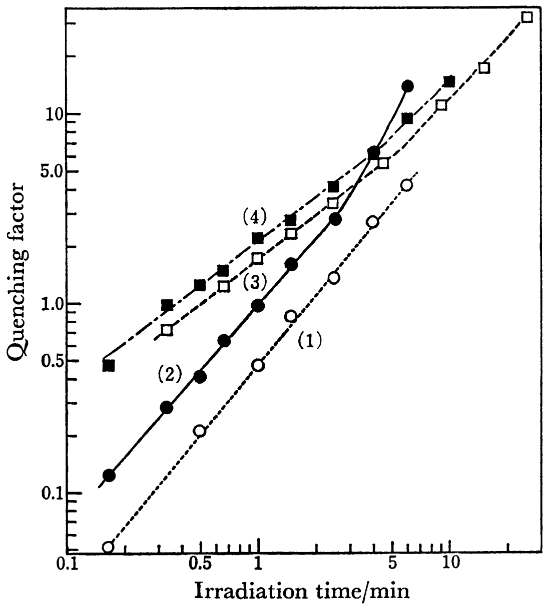


Fig. 7. Quenching factor *vs.* irradiation time. (1) PVCz film (≈0.7 μm thick), (2) PVCz film (≈0.2 μm thick), (3) DCzP(a) film (≈0.3 μm thick), and (4) DCzP(a) film (≈0.2 μm thick). Excitation wavelength; 330 nm.

The host fluorescence was depressed to half its original intensity ($Q=1$) at a guest concentration equal to the concentration of excimer-forming sites, in the case of PVCz films.[8–10] The concentration of excimer-forming sites in the PVCz film used in the present investigation was *ca.* 3×10^{-3} mol/mol basic unit.[10] Therefore, the concentration of the photo-oxidation product in a thin PVCz film (≈0.2 μm), where the product might be formed comparatively uniformly, became *ca.* 3×10^{-3} mol/mol basic unit by the irradiation for one minute, as is shown in Fig. 7. Considering the number of absorbed photons, the yield of the formation of the photo-oxidation product was estimated to be *ca.* 10^{-4}.

Photoconductivity. Dependence of the photocurrent of the photo-oxidized PVCz films on irradiation time is shown in Fig. 8. The photocurrent observed in the π-π* absorption region increased steeply, by a factor of about 15, with photo-oxidation. It decreased when the film was exposed to radiation until a change in the absorption spectra by photo-oxidation could be observed. Voltage, spectral, light-intensity, and temperature dependence of the photocurrent of the photo-oxidized PVCz film were almost the same as those of the unirradiated PVCz film.[19]

It has been reported that an external magnetic field increased the photocurrent in a PVCz film and that this magnetic filed effect was enhanced by doping with a weak acceptor such as DMTP.[7] Figure 9 shows the dependence of the positive magnetic field effect of the photo-oxidized PVCz films on irradiation time. The effect was enhanced by a factor of about 3 by weak photo-oxidation.

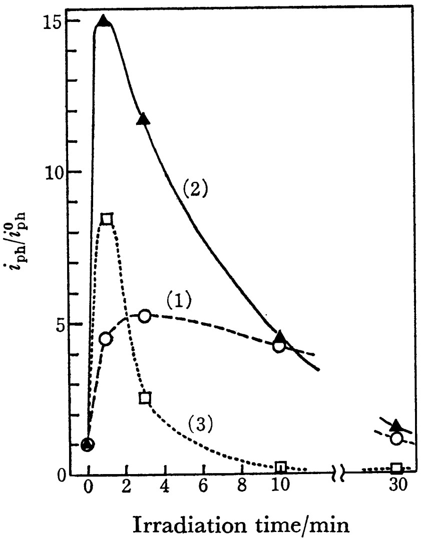


Fig. 8. Irradiation time dependence of the relative photocurrent(i^+_{ph}) of a photo-oxidized PVCz film under 35000 V/cm.
(1) 400, (2) 360, and (3) 330 nm.

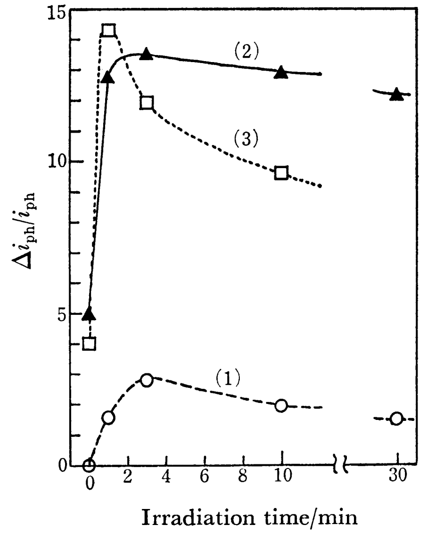


Fig. 9. Dependence of the positive magnetic field effect of a photo-oxidized PVCz film on irradiation time. Magnetic field; 1000 G. Applied voltage; 35000 V/cm.
(1) 400, (2) 360, and (3) 330 nm.

It is clear from the above-mentioned results that the yield of photo-carrier-generation of the weakly photo-oxidized PVCz films is much higher than the yield of the unirradiated PVCz films. That is, even if the concentration of the photo-oxidation product is too low to be detected by the absorption spectra, the product acts effectively as an electron-accepting impurity(A) in the Scheme 1 to enhance effectively the yield of photo-carrier-generation of a PVCz film. A high yield of photo-carrier-generation is obtained by a xerographic method,[5,20] where the surface of samples is exposed to a corona-charge under an ambient condition, and by measuring the photoconductivity of polymer films dried for a prolonged time under an ambient condition at a high temperature.[21] Such yields might be attributable to the mechanism of photo-carrier-generation described in Scheme 1, in which the electron-accepting impurity(A) seems to be a photo-oxidation product formed near the surface of PVCz films.

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