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ELECTRONIC SPECTRA OF 1,3-BIS(N-CARBAZOLYL)PROPANE IN THE AMORPHOUS STATE

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An amorphous-state film of 1,3-bis(N-carbazolyl)propane(DCzP) was prepared by a solvent-evaporation technique of the solution, and the absorption and fluorescence spectra were measured in air at room temperature. The spectra were compared with those of glassy-state DCzP, polycrystalline DCzP, polycrystalline N-isopropylcarbazole, and amorphous poly(N-vinylcarbazole) films. The fluorescence spectrum is composed of three components; monomer-like, second excimer, and sandwich-like excimer fluorescences.

1,3-Bis(N-carbazolyl)propane(DCzP) is known as a model compound of two neighboring side groups of poly(N-vinylcarbazole)(PVCz), which has received considerable interest in recent years in connection with the high photoconductive vinyl polymers. Because of the interest in the mechanism of the intramolecular excimer formation of DCzP, considerable data on the spectroscopic properties in the solution have been accumulated.[1-4) However, very little is known about the spectroscopic properties of the solid state.

We have found that DCzP forms an amorphous state by a fast evaporation of the solvent and also forms a stable glassy-state by a supercooling. In order to reveal an origin of the high photoconductive properties of PVCz, it is very important to compare the spectroscopic behavior of the amorphous state DCzP with that of the amorphous PVCz film.

In this report, we present some findings on the electronic spectra of the amorphous and polycrystalline DCzP films and compare the spectra with those of the polycrystalline N-isopropylcarbazole(i-PrCz) and the amorphous PVCz films.

It has been known that the deposition of polycyclic aromatic compounds onto a substrate kept at a low temperature yields amorphous films. There exist some literatures on measuring the electronic spectra of the amorphous deposited films and comparing them with the spectra of the corresponding crystalline films.5-8) However, to the knowledge of the present authors, a comparison of the spectra of an amorphous film of a dimeric model compound with the spectra of an amorphous film of a corresponding vinyl polymer has not hitherto been performed.

The compounds studied(DCzP and i-PrCz) were prepared from rigorously purified carbazole according to literatures.9,10) The PVCz was prepared by radical polymerization(initiator; AIBN) and was reprecipitated from the benzene solution with methanol. All of the solvents used were purified by the usual methods. The amorphous DCzP and polycrystalline i-PrCz films were cast on quartz plates from benzene solution followed by fast evaporation of the solvent at 10^{-1} Torr at room temperature. The

DCzP glassy-state film was prepared by melting and cooling the powder of DCzP placed between two clean quartz plates. The PVCz film was prepared by casting a benzene solution of PVCz. The absorption and fluorescence spectra were measured with the apparatus described in a previous paper.[11)]

By means of a polarizing microscope, a dark image is observed for the DCzP film prepared by fast evaporation of solvent at room temperature using crossed nicols. With time, bright crystallites are found in the dark background and both the number and the size increase. It is also observed, by means of the polarizing microscope, that the DCzP film prepared by fast evaporation of solvent changed to the polycrystalline state by annealing on a hot plate.

Although several X-ray diffraction lines were found for the annealed DCzP film, no line could be observed for the DCzP film prepared by fast evaporation of solvent. These facts show that the DCzP film prepared by fast evaporation of solvent is initially amorphous and crystallizes gradually with a change in the temperature and also with time.

Figures 1 and 2 show the absorption spectra of the amorphous DCzP, polycrystalline DCzP, amorphous PVCz, polycrystalline i-PrCz films, and the DCzP molecule in 1,2-dichloroethane solution. The absorption spectrum of the amorphous DCzP film is very similar to that of the amorphous PVCz film, although the absorption bands are shifted to lower frequency by 120—300 cm^{-1}, as compared with those of the amorphous PVCz film, and also similar to the DCzP molecular spectrum in the solution. However, it is very different from that of the polycrystalline DCzP film. That is, the ratios of the intensities of the ^1L_a, ^1B_b, and ^1B_a bands to that of ^1L_b band in the polycrystalline DCzP film is much smaller than that in the amorphous film. The crystallization of the amorphous film yields the vibronic structure of ^1L_a band, which is observed for the polycrystalline i-PrCz film.

The fluorescence spectra of the films in air at room temperature are shown in Figs. 3 and 4. The spectrum of DCzP molecule in aerated benzene solution is also shown for comparison. The relative intensities of the vibrational bands change with film-thickness because of reabsorption. In order to avoid influence of the reabsorption, the thin films(0.1—0.04 μ thick) are used except for the DCzP glassy-state film. Although the spectrum of the DCzP glassy-state film is influenced by the reabsorption, the spectrum is very similar to that of the amorphous DCzP film. As is shown in Fig. 3, the fluorescence spectrum of the amorphous DCzP film is remarkably different from those of the amorphous PVCz film and the polycrystalline DCzP film. It is known that the PVCz film shows one broad fluorescence, which is mainly composed of sandwich-like excimer component, although weak second excimer fluorescence(ca. 26700 cm^{-1}) is also observed.[12)] On the other hand, the amorphous DCzP film shows structured fluorescence and a tailing in the long wavelength side of the band.* The intensity of the second peak(26800 cm^{-1}) in the structured band is anomalously large, compared with

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* The weak and broad fluorescence band at ca. 20000 cm^{-1} may be emitted from an exciplex fromed between the carbazolyl ring and a photoproduct judging from the facts that the intensity increases with an increase in the photoirradiation-time and that the same phenomenon is also observed for the PVCz film.[13)] The details of the results will appear elsewhere.

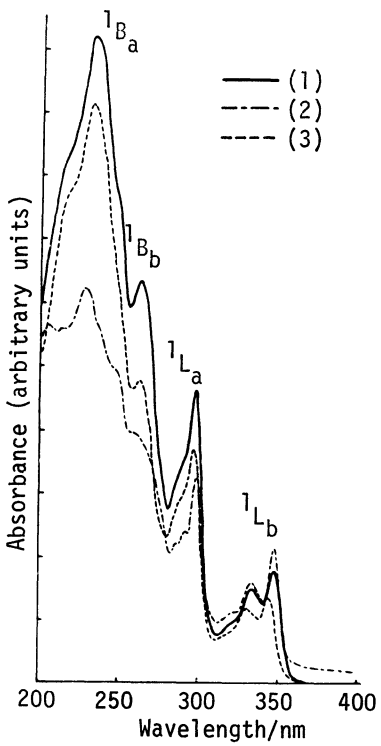

Fig. 1. Absorption spectra at 20°C.
(1) Amorphous DCzP film.
(2) Polycrystalline DCzP film.
(3) Amorphous PVCz film.

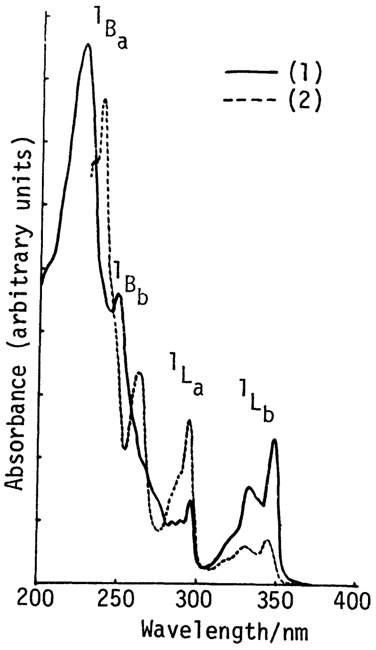

Fig. 2. Absorption spectra at 20°C.
(1) Polycrystalline i-PrCz film.
(2) DCzP molecule in 1,2-dichloroethane solution.

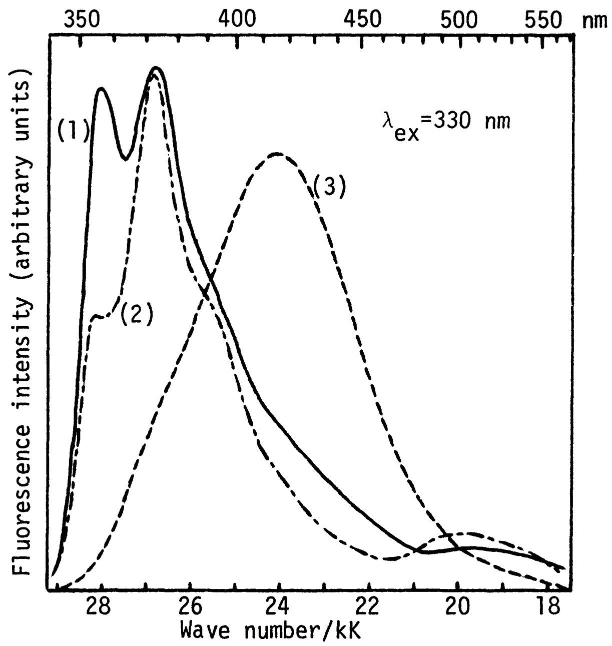

Fig. 3. Fluorescence spectra at 20°C.
(1) Amorphous DCzP film.
(2) Polycrystalline DCzP film.
(3) Amorphous PVCz film.

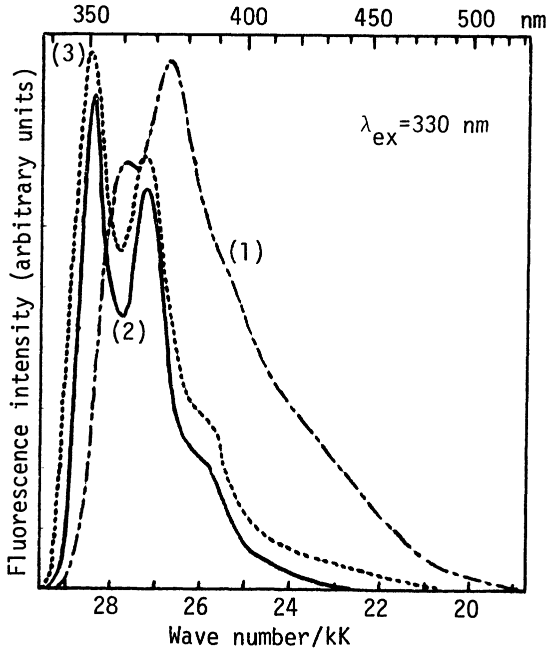

Fig. 4. Fluorescence spectra at 20°C.
(1) DCzP glassy-state film.
(2) Polycrystalline i-PrCz film.
(3) DCzP molecule in aerated benzene solution.

those observed for the polycrystalline i-PrCz film and DCzP molecule in the solution. A position of the second peak is nearly equal to that of the second excimer fluorescence in the PVCz film. The fluorescence-decay curves of the amorphous DCzP film and the DCzP glassy-state film are multi-components(23±3 ns and an initial fast decay) in the longer-wavelength region(λ_{obs}>400 nm). The long-lived component is nearly equal to the lifetime of the sandwich-like excimer fluorescence in the PVCz film(22±2 ns).12,14) Excitation spectra of the amorphous DCzP film, obtained by monitoring at several wavelength(355–500 nm), duplicate the absorption spectrum of the film exactly. Therefore, the fluorescence spectra of the amorphous DCzP film and the DCzP glassy-state seem to be composed of three components; monomer-like, second excimer, and sandwich-like excimer fluorescences. Klöpffer has briefly reported that DCzP glassy-state film shows second excimer fluorescence.14) As is shown in Fig. 3, the polycrystalline DCzP film shows no sandwich-like excimer fluorescence. This is also supported by the fact that the long-lived component(ca. 23 ns) in the longer-wavelength region is not observed. These are the same as the case of the polycrystalline i-PrCz film.15) However, the spectrum of the polycrystalline DCzP film is different from that of the polycrystalline i-PrCz film. The intensity of the second peak observed for the DCzP film is much larger than that of the first peak, as compared with the spectrum of i-PrCz film. The position of the second peak is the same as that observed for the amorphous DCzP film. Therefore, the polycrystalline DCzP film may show both monomer-like fluorescence and second excimer fluorescence. The further investigation is now in progress.

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