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Direct Observation of Photoinduced Charge Separation Dynamics in Solid Poly(N-vinylcarbazole) Powders by Diffuse Reflectance Laser Photolysis

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Transient absorption spectra of poly(N-vinylcarbazole) powders doped with some electron acceptors are composed of the bands of acceptor anion and carbazole cation, indicating directly charge separation from the excited state. Electronic structure and decay processes of polymer cation are considered and compared with transparent film.

Laser photolysis method has made a great contribution to photophysics and photochemistry. Most of the systems studied were homogeneous, transparent gas phase and solution systems, however, this method has been extended to optically scattering powder systems. Wilkinson et al. developed diffuse reflectance laser photolysis method in 1981,[1)] and molecular and inorganic crystals, semiconductors, polymers, molecules adsorbed on silica gel and cellulose substrate, and so forth are being studied in detail.[2-5)] Intersystem crossing, energy transfer, photothermal, and hydrogen abstraction processes as well as molecular diffusion on the surface were reported. Charge separation process was confirmed for some molecules adsorbed on semiconductor and cellulose powders, while no clear experimental result was obtained for neat solids. As photoinduced charge transfer is one of the most important processes and poly(N-vinylcarbazole) (abbreviated hereafter as PVCz) is a representative organic photoconductors, we applied here diffuse reflectance laser photolysis method to its powders.

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A microcomputer-controlled diffuse reflectance laser photolysis system was used. The 3rd harmonic of Nd^{3+}:YAG laser (JK laser HY750, 355 nm, 5 ns, 5 mJ) and a flash lamp (Hamamatsu 2188, fwhm 1.6 μs) were used as excitation and monitoring pulses, respectively. The details are the same as reported elsewhere.$^{4)}$ The spectral data were averaged over several measurements.

PVCz (Takasago International Corporation) was purified by reprecipitation from benzene-ethanol. p-Dicyanobenzene (DCNB), dimethyl terephthalate (DMTP), and phthalic anhydride (PA) were recrystallized twice from ethanol, three times from ethanol, and twice from benzene, respectively. Neat and doped PVCz powders were prepared by freezing the sample solution to 77 K and drying the latter under vacuum. These dopants were molecularly dispersed. The powders were contained in a suprasil cell with 1 cm thickness, degassed for 5-10 hours, and sealed off for measurement at room temperature.

Fluorescence spectra of doped powders are different from those of neat powders. The sandwich (420 nm) as well as the partial overlap (375 nm) excimers of PVCz powders are quenched by doped acceptors and replaced by structureless, broad emissions in the long wavelength region. DCNB and DMTP do not form a charge-transfer complex with carbazolyl chromophore in the ground state, so that the observed emission is due to an exciplex. On the other hand, the PVCz-PA pair gives a charge-transfer fluorescence of the complex formed in the ground state. These results are similar to those of transparent PVGz films which have been studied already.$^{6,7)}$

Transient absorption spectra at 0-1.2 μs are summarized in Fig.1. The absorption below 400 nm is not reliable because of the weak intensity of the monitoring light. The absorption spectra

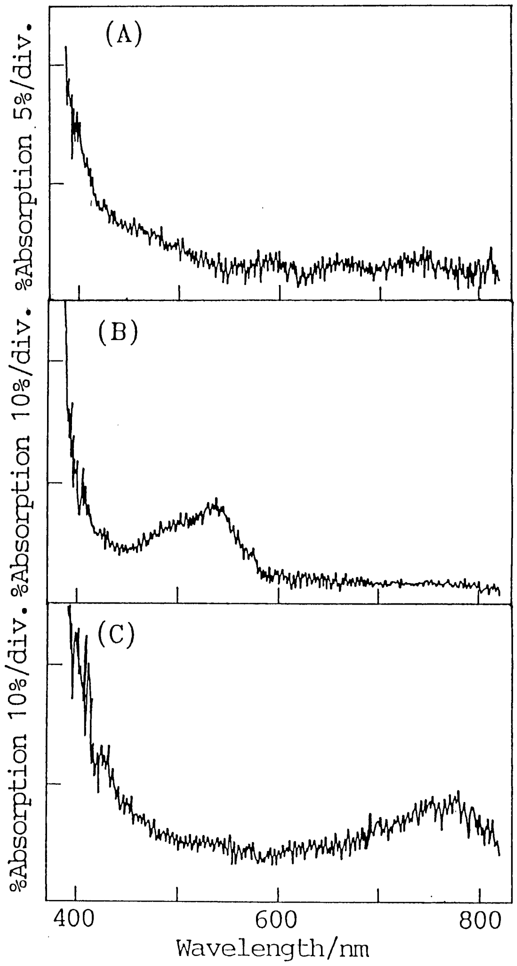

Fig.1. Transient absorption spectra of poly(N-vinyl-carbazole) powders doped with (A) 4.8 mol% DCNB, (B) 4.8 mol% DMTP, and (C) 5.8 mol% PA.

of PVCz cation in solution and film are well known,[8,9] on which the present data are considered. In the case of PVCz-DCNB system, absorption spectrum descends to the long wavelength and almost flat above 550 nm. The shoulder around 430 nm is due to DCNB anion and the counter PVCz cation should be located in 600-800 nm.[8,9] An absorption peak was observed at 535 nm for the PVCz-DMTP system. This is just the same as reported in solution and can be assigned to DMTP anion.[8] Since this anion has no absorption above 600 nm, a flat band in the long wavelength is again ascribed to the PVCz cation. Transient absorption spectrum of the PVCz-PA system show a shoulder around 420 nm and a peak at 780 nm. The former is assigned to the PA anion and the latter is similar to the absorption of PVCz cation in solution and film. It is worth noting that the spectral shape of PVCz cation in the powders depends on the doped electron acceptor.

Relative orientation and mutual distance of carbazolyl chromophores determine electronic nature of the PVCz cation.[8] In the exciplex system, various dimer cations are involved since no favorite geometry is taken in the ground state. This should be an origin of the flat band for the PVCz cation of PVCz-DCNB and -DMTP systems. On the other hand, a rather fixed structure is formed for the PVCz-PA complex, and the hole produced by photoinduced charge separation is trapped in that structure. The present spectral shape of polymer cation in PVCz-DCNB and PVCz-DMTP systems is different from that of transparent PVCz thin films.[9] This indicates that the polymer cation in the powders takes a different structure from that in the film.

Decay curves of donor cation and acceptor anion of the PVCz-DMTP system are shown in Fig.2. Both decays are completed within 1μs and faster than those of the transparent film. The anion band shows a monotonous decay, while a two-component decay process was observed for the cation. One explanation is that the hole transfers from the initial charge separated state to a more stable site. The other is to

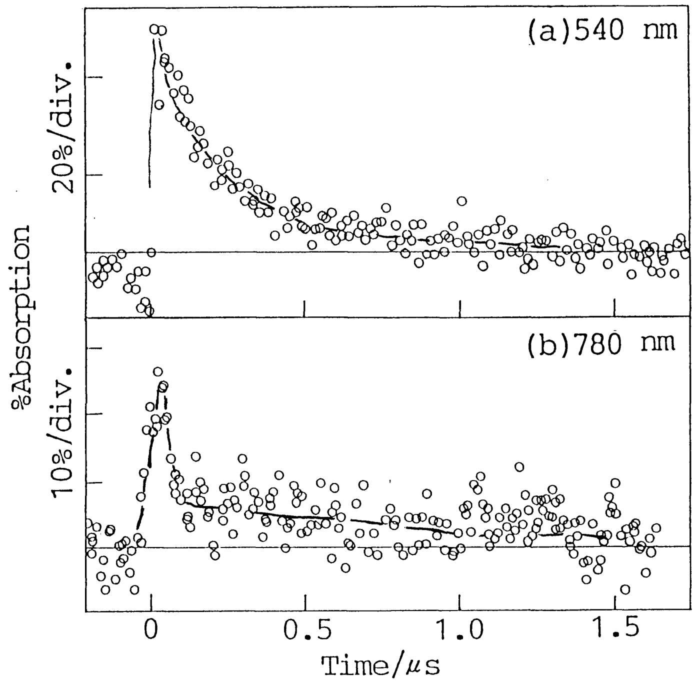

Fig.2. Decay curves of produced ionic species in poly(N-vinylcarbazole) powders doped with 4.8 mol% DMTP.

consider a hole transfer from PVCz to an impurity (for example, photooxidized site). In contrast, geminate and homogeneous recombination processes determine the decay behavior of the PVCz film.[9] Polymer association and conformation is dependent on morphology (powder or film), so that the present study on absorption spectra and dynamics is indispensable for elucidating the molecular nature of photoinduced charge transfer processes.

In the studies on photoinduced change transfer dynamics, fluorescence measurements have provided quantitative evaluation of thermodynamic and kinetic parameters. By transient absorption spectroscopic measurement, which is rather complementary to the fluorescence technique, electronic as well as geometrical structures of ionic species are made clear and the nature of intermolecular interaction is elucidated. The present work reports the first transient absorption spectral measurement of change transfer dynamics in organic solid powders. A more detailed study is being performed in this group.

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