

Photoinduced Electron Transfer Processes of C₆₀-Doped Poly(*N*-vinylcarbazole) Films As Revealed by Picosecond Laser Photolysis

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Photoinduced electron transfer dynamics of poly(*N*-vinylcarbazole) (PVCz) films doped with a small amount of C₆₀ was investigated by using picosecond and nanosecond laser flash photolysis techniques under various experimental conditions. From the time evolution of transient absorption spectra in the 600–1180 nm wavelength region, it was revealed for 0.7 mol % C₆₀-doped PVCz films that the charge-separated state (PVCz⁺–C₆₀[–]) between PVCz and C₆₀ was produced immediately after excitation with a picosecond 532 nm laser pulse. The decay of the initial charge-separated state with a time constant of 1.2 ns comprised the following three channels: the charge-recombination process, the hole-migration reaction to the neighboring carbazolyl chromophores, and the formation of the local triplet state of C₆₀ (³C₆₀*). The reaction yield of the hole migration was estimated to be 30%. The present results were quite different from those reported previously for densely C₆₀-doped PVCz films excited with a picosecond 355 nm laser pulse (*J. Phys. Chem.* **1995**, *99*, 1199). In order to elucidate factors causing the difference, the excitation intensity effect on the dynamics was examined, and it was found that an increase in the excitation laser intensity induced rapid formation of ³C₆₀* by a nonlinear process immediately after excitation of a picosecond laser pulse. Under the condition where the excitation intensity was rather weak and the dense population of the excited state was avoided, the deactivation dynamics of the charge-separated state produced by the excitation at 355 nm was found to be almost the same as that by the 532 nm excitation. The nanosecond to microsecond dynamics of C₆₀-doped PVCz films showed that the effective charge separation did not take place between the triplet state of C₆₀ and PVCz. From these results, it was concluded that the hole-migration process inducing free carriers was effective in the initial charge-separated state of C₆₀-doped PVCz films, and thus, relatively high reaction yield of this process was responsible for the enhancement of the photoconductivity in the films.

Introduction

During a number of investigations of fullerenes and their various interesting properties, it has been presented that photoconductivity of polymer films was enhanced by the doping of fullerenes:^{1–3} poly(*N*-vinylcarbazole) (PVCz) films doped with a small amount of fullerenes (*ca.* 0.71 mol % for PVCz) were reported to show excellent photoconductivities compared to the film without fullerenes.¹ In addition, it has been reported that an addition of a small amount of C₆₀ (*ca.* 1 mol %) to photorefractive polymers based on PVCz resulted in an increase in the quantum yield of the charge-carrier photogeneration and was effective for sensitizing their photorefractive properties.^{4,5} Since the enhancement of the above photoinduced properties is closely related to the photoinduced charge-separation and subsequent charge-shift processes, a number of investigations of photoinduced electron transfer have been accumulated for elucidating the mechanisms in the above properties of conductive conjugated and aromatic vinyl polymer films doped with C₆₀.^{6–8} Furthermore, the photoinduced electron transfer between PVCz and C₆₀ in benzonitrile solution was also investigated.⁹

Recently, the picosecond transient absorption spectroscopy was applied for elucidating the photoprimary processes of densely C₆₀-doped PVCz films (*ca.* 38 mol %).⁸ One of the results was that transient absorption of ionic species (the anion radical of C₆₀ and the cation radical of PVCz) was not detected under the excitation with a picosecond 355 nm laser pulse. This

was interpreted as due to the rapid recombination within the charge-separated (CS) state between C₆₀ and carbazolyl (Cz) chromophore.⁸ This result, however, presented a very difficult problem in the origin of the charge carrier in C₆₀-doped PVCz films, since the rapid deactivation of the CS state does not result in the production of the so-called free carrier of the charge. For the photoinduced electron transfer processes in PVCz films doped with various electron acceptors (less than a few mol %),^{9–14} transient absorption spectra of both an acceptor anion and a PVCz cation (PVCz⁺) were generally observed under the condition where the photoconductivity was enhanced by the addition of electron acceptors. In addition, recent picosecond transient absorption spectroscopy and dichroism measurement of PVCz films doped with various electron acceptors revealed that hole migration in the CS state following the photoinduced electron transfer took place in competition with geminate charge recombination (CR) and that the time constant of the hole migration was *ca.* 2 ns.¹² This time constant of the hole-migration process escaping the geminate CR in the initial CS state was almost independent of electron acceptors, whereas the time constant of the CR process strongly depended on acceptors, which was interpretable in the framework of the energy gap dependence of the electron transfer rate constant.

Provided that the same reaction scheme as that revealed for the electron acceptor-doped PVCz films is applicable to C₆₀-doped PVCz films and that the lifetime of the CS state between the C₆₀ and Cz chromophore is very short as reported by Kamat et al., the free carrier generation yield would be estimated to be very small and the enhancement of the photoconduction could not be interpreted as due to the photoinduced charge separation.

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In other word, the experimental result of Kamat et al. presented for C₆₀-doped PVCz films⁸ suggests the presence of some peculiar interactions enhancing the photoconduction in PVCz films.

In order to precisely elucidate the primary processes of photoconduction in C₆₀-doped PVCz films, we have investigated both the picosecond dynamics of the above systems by transient absorption spectroscopy covering the wavelength region up to 1180 nm with a picosecond time resolution and the dynamics in the longer time region. By integrating the results of the investigation with those of the inert reference systems such as C₆₀ in benzene solution and in poly(isopropyl methacrylate) (PIPMA) films, the electron transfer dynamics in C₆₀-doped PVCz films will be discussed in the following.

Experimental Section

C₆₀ (99.9%) was obtained from Shinku-yakin Co. *N*-Vinylcarbazole (VCz) was purified by the usual method from commercial product. PVCz was prepared by polymerization of a 1.0 M benzene solution of the purified VCz in the presence of 0.4 mol % azobisisobutyronitrile in an evacuated tube at 60 °C for 9 h and was purified by repeated reprecipitations three times from benzene solution with methanol. Polymer films were cast or spin-coated on quartz or sapphire plates from benzene or toluene solution containing PVCz and a known amount of C₆₀ and dried under vacuum. Solution samples were deaerated with a N₂ gas stream before measurements. Powder samples were prepared in the following way: a benzene solution of PVCz and C₆₀ was solidified on the flask wall by cooling down to -10 °C and degassed so as to evaporate benzene. The powders were contained in a quartz cell and degassed under high vacuum for 10 h. Film samples for measuring transient absorption spectra under transmittance configuration were degassed in a quartz cell, while N₂ gas was flowed on the sample films under multiple-reflection configuration.

A microcomputer-controlled picosecond laser photolysis system with a custom-built repetitive mode-locked Nd³⁺:YAG laser was used for measurements. The optical alignment for the transmittance configuration was almost the same as reported previously.¹² Transient diffuse reflectance absorption spectra were measured also with the same system in which the optical alignment was modified. Transient absorption spectra in the time region from nanosecond to microsecond were measured by using a microcomputer-controlled nanosecond laser photolysis system with an excimer laser (351 nm) as an excitation light source. The optical alignment with multiple-reflection configuration was almost the same as reported previously.^{10,13} The probe light were monitored by an image-intensified multichannel detector with gated function, which was combined with a polychromator (wavelength region 430–850 nm). All the measurements were performed at room temperature.

Results and Discussion

Steady-State Absorption Spectra of C₆₀. Figure 1 shows ground-state absorption spectra of C₆₀ in various media. The spectrum of C₆₀ in poly(isopropyl methacrylate) (PIPMA) films is similar to that in benzene solution. Since C₆₀ has no special interaction with benzene in the ground state, it is safely concluded that ground-state interaction is negligible also in PIPMA films. On the other hand, C₆₀-doped PVCz films show a new and broad absorption band in the 400–700 nm wavelength region. Wang and Kamat et al. assigned the broad absorption band to a charge transfer (CT) complex formed between C₆₀ and carbazolyl (Cz) chromophore.^{1,8} Although aggregates of C₆₀ are known to show broad absorption around

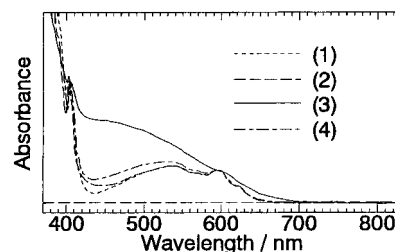


Figure 1. Ground-state absorption spectra of C₆₀ under various conditions: (1) C₆₀ (3.8×10^{-4} M) in benzene solution; (2) 0.7 mol % C₆₀-doped PIPMA films; (3) 0.7 mol % C₆₀-doped PVCz films; (4) C₆₀ (1.4×10^{-3} M)–PVCz (2.7×10^{-1} M) in benzene solution. The spectra are normalized at 602 nm.

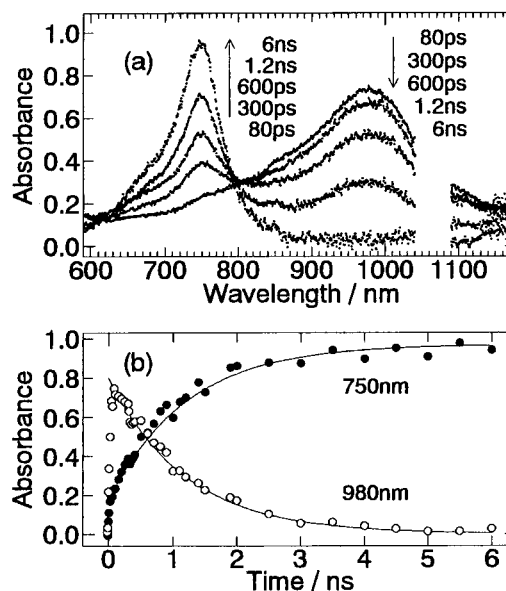


Figure 2. (a) Time-resolved absorption spectra of C₆₀ (1.5×10^{-3} M) in benzene solution, excited with a 532 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 980 nm (¹C₆₀^{*}) and 750 nm (³C₆₀^{*}) of the same sample solution. The solid lines represent the time constant of 1.2 ns.

450 nm¹⁵ and the detailed investigations on the solvent effect on C₆₀ absorption spectrum of the ground state were performed,^{16,17} the spectral change resulting from an addition of PVCz into C₆₀–benzene solution (Figure 1) supports the fact that the broad band is not due to aggregates of C₆₀, but due to the ground-state CT complex between C₆₀ and the Cz chromophore.

Picosecond Dynamics of C₆₀-Doped PVCz Films. In order to obtain direct evidence of the assignment of the broad absorption to the ground-state CT complex in C₆₀-doped PVCz films and to elucidate the dynamic behaviors of the photoinduced electron transfer process in the films, picosecond transient absorption spectroscopy was applied. Prior to the discussion on C₆₀-doped PVCz films, we present transient absorption spectra of C₆₀ in benzene solution and in PIPMA films, excited with a picosecond 532 nm laser pulse, as references. The irradiation at 532 nm corresponds to the excitation of the absorption band of C₆₀ in both media.

In Figure 2a, we show time-resolved absorption spectra of C₆₀ in benzene solution. To avoid a strong 1064 nm fundamental laser pulse going into the sample, this fundamental pulse was removed from the monitoring picosecond white light. Hence, the spectra in the 1040–1090 nm wavelength region could not be detected in the present system. The transient absorption band with a peak around 975 nm in the early stages after excitation is safely assigned to the excited singlet state of

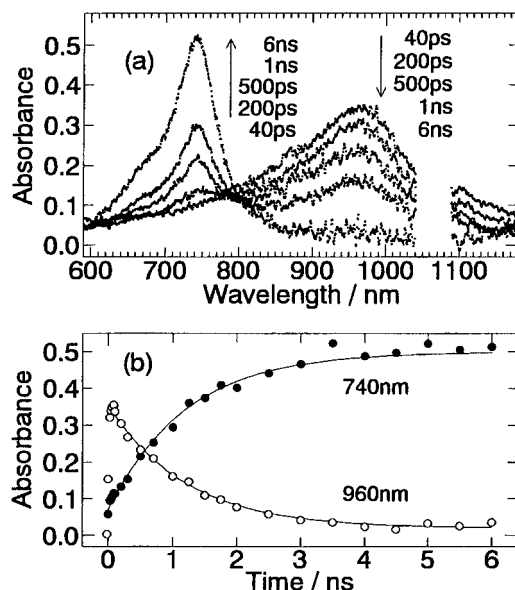


Figure 3. (a) Time-resolved absorption spectra of 0.7 mol % C_{60} -doped PIPMA films, excited with a 532 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 960 nm ($^1C_{60}^*$) and 740 nm ($^3C_{60}^*$) of the same sample film. The solid lines represent the time constant of 1.2 ns.

C_{60} ($^1C_{60}^*$) on the basis of the agreement of the spectral band shape and its maximum with those reported previously.^{8,18} With an increase in the delay time after excitation, a new absorption with a peak around 750 nm, which is ascribable to the triplet state of C_{60} ($^3C_{60}^*$),^{8,18–20} increases. During this temporal evolution of the spectra, two isosbestic points at *ca.* 615 and 800 nm are detected.

Time profiles of transient absorbance are shown in Figure 2b. The decay profile of $^1C_{60}^*$ monitored at 980 nm is in agreement with the growth profile of $^3C_{60}^*$ monitored at 750 nm. The time constant of the present change of the transient absorbance was found to be 1.2 ns, and this time constant is the same as those (1.2 ns) reported for $^1C_{60}^*$ in toluene solution, polystyrene (PSt) films, and poly(methyl methacrylate) (PMMA) films.^{8,19,21}

The similar time dependence of the transient absorption spectra was observed also for C_{60} -doped PIPMA films excited with a picosecond 532 nm laser pulse, as shown in Figure 3. The temporal evolution of the transient absorption spectra shows the decay of $^1C_{60}^*$ corresponding with the rise of $^3C_{60}^*$. In addition, the time profiles of the transient absorbance show that the lifetime of $^1C_{60}^*$ in PIPMA films is 1.2 ns.

Figure 4a shows time-resolved absorption spectra of 0.7 mol % C_{60} -doped PVCz films excited with a 532 nm picosecond laser pulse. As shown in Figure 1, the irradiation at 532 nm excites mainly the CT absorption band. The transient absorption spectrum observed immediately after excitation is quite different from the $S_n \leftarrow S_1$ spectra observed for C_{60} -benzene solution and for C_{60} -doped PIPMA films and has at least two peaks in the 850–1180 nm wavelength region: a peak around 930 nm and a peak estimated to be between 1050 and 1080 nm. In addition, the absorption maximum in the 600–800 nm wavelength region is located at 770 nm immediately after excitation. The former absorption band with two peaks in the wavelength region above 850 nm is safely ascribed to the anion radical of C_{60} (C_{60}^-), since the present absorption maxima and the spectral band shape are in agreement with those reported for C_{60}^- .^{9,22–24} On the other hand, the absorption band at 770 nm is ascribed to the cation radical of PVCz ($PVCz^+$).²⁵

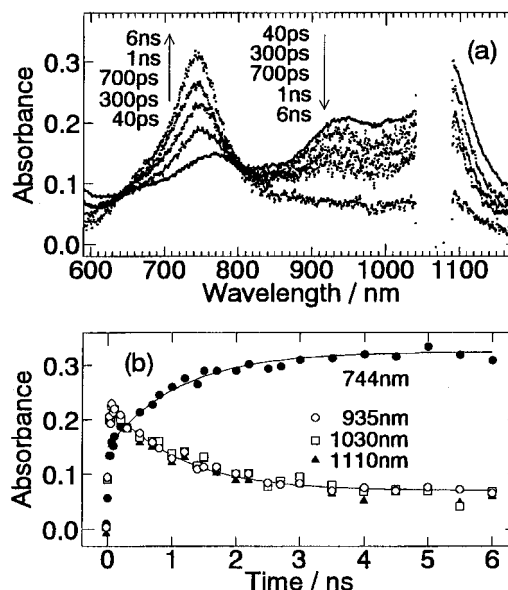


Figure 4. (a) Time-resolved absorption spectra of 0.7 mol % C_{60} -doped PVCz films, excited with a 532 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 935, 1030, and 1110 nm (C_{60}^-) and 744 nm ($^3C_{60}^*$) of the same sample film. The solid lines represent the time constant of 1.2 ns.

The extinction coefficient of C_{60}^- at 930 nm was estimated to be *ca.* 8200 $M^{-1} cm^{-1}$ from both the extinction coefficient of the peak around 1060 nm and the spectral shape of C_{60}^- previously reported,^{23,24} while the extinction coefficient of $PVCz^+$ at 775 nm was estimated to be *ca.* 5400 $M^{-1} cm^{-1}$.²⁶ The peak intensity ratio of the transient absorption at 775 nm of $PVCz^+$ to the absorption at 930 nm of C_{60}^- in the spectrum at 40 ps after excitation is about 0.7, close to the ratio of the extinction coefficients of the two ions. Since the production of the charge-separated state between C_{60} and $PVCz$ was completed almost within the response function of the apparatus, it is supported that the ground-state absorption of C_{60} -doped PVCz films, which shows a different band shape from the absorption of C_{60} in benzene and in PIPMA films (Figure 1), has charge transfer character from the Cz chromophore to C_{60} .

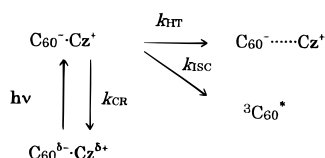
With an increase in the delay time after excitation, the charge-separated (CS) state ($C_{60}^- - PVCz^+$) decreases with an increase in the new absorption with a peak around 745 nm. This new absorption is safely ascribed to $^3C_{60}^*$, as discussed in previous sections. In addition, the residual absorption remains in the wavelength region above 850 nm even at several nanoseconds after excitation.

In order to obtain the precise kinetics of both the decay of the CS and the appearance of $^3C_{60}^*$, the time profiles of the absorbance are plotted in Figure 4b. The transient absorbance monitored at 935, 1030, and 1110 nm decreases up to a few nanoseconds after excitation and attains a constant value in the longer time region. As discussed above, the time profiles of the absorbance at these wavelengths are ascribed to the decay of the CS state. The time constant of the decay was found to be 1.2 ns. On the other hand, the time profile of the absorbance monitored at 744 nm shows an increase in the few nanoseconds time region. The kinetics at 744 nm is mainly ascribable to the production of $^3C_{60}^*$, and the time constant was found to be 1.2 ns. Since the time constant of the rise of $^3C_{60}^*$ is in agreement with that of the decay of the CS state and since the two isosbestic points around 645 and 795 nm are observed for the temporal evolution of the spectra in Figure 4a, it can be concluded that the deactivation of the CS state ($C_{60}^- - PVCz^+$) includes the channel of the formation of the local triplet state

of C₆₀ (³C₆₀*). The residual absorption signals in the wavelength region above 900 nm indicate that the long-lived CS state is also produced following the deactivation of the initial CS state. The amount of the long-lived CS state is *ca.* 30% of that of the initial CS state. In addition to these two reaction pathways in the initial CS state, the charge-recombination (CR) process to the ground state may be involved in the deactivation of the initial CS state produced by the excitation at 532 nm. The sum of the rate constants of these three reactions is concluded to be (1.2 ns)⁻¹.

As aforementioned, applying the picosecond transient absorption spectroscopy and dichroism measurements for the direct elucidation of the primary processes of the electron transfer dynamics of PVCz films doped with electron acceptors, we revealed that the hole transfer from the initial CS state produced by the excitation of the ground-state CT complex to neighboring Cz chromophores took place in competition with the charge recombination to produce the long-lived ionic species.¹² In addition, the rate constant of the hole migration was found to be $(5 \pm 1) \times 10^8 \text{ s}^{-1}$ for PVCz films doped with electron acceptors such as 1,2,4,5-tetracyanobenzene, *p*-chloranil, and 2,4,7-trinitrofluorenone. Integrating the present results with the previous investigation, the following Scheme 1 may be proposed for the present system:

SCHEME 1



where k_{CR} , k_{ISC} , and k_{HT} are rate constants of the charge recombination, the intersystem crossing, and the hole transfer, respectively. Provided that the reaction profiles such as charge recombination, intersystem crossing resulting in the formation of ³C₆₀*, and the hole transfer are first-order, the time profile of the transient absorbance $A(t)$ due to the CS state can be represented by eq 1.

$$A(t) = B + C \exp[-(k_{\text{CR}} + k_{\text{ISC}} + k_{\text{HT}})t] \quad (1)$$

Here, $(k_{\text{CR}} + k_{\text{ISC}} + k_{\text{HT}})$ is (1.2 ns)⁻¹. In the wavelength where the absorption of ³C₆₀* is negligible, B and C are $[k_{\text{HT}}/(k_{\text{CR}} + k_{\text{ISC}} + k_{\text{HT}})] \times A(t=0)$ and $[(k_{\text{CR}} + k_{\text{ISC}})/(k_{\text{CR}} + k_{\text{ISC}} + k_{\text{HT}})] \times A(t=0)$, respectively. From the application of the above equation into the analysis of the time profiles of the transient absorbance in the wavelength region above 1000 nm where ³C₆₀* has no remarkable absorption, the k_{HT} value for the present C₆₀-PVCz system was estimated to be *ca.* $2.5 \times 10^8 \text{ s}^{-1}$. This value is almost on the same order as those for other acceptors as mentioned above. In addition, the rate constant of the intersystem crossing could be estimated by using the extinction coefficients of C₆₀⁻ (*ca.* 8200 M⁻¹ cm⁻¹ at 930 nm) and ³C₆₀* (16100 M⁻¹ cm⁻¹ at 750 nm),²⁸ on the assumption that these extinction coefficients previously reported are unaffected in PVCz films. From the comparison of the absorption of the CS state immediately after excitation with the absorption at 6 ns after excitation, the formation yield of ³C₆₀* from the CS state was estimated to be *ca.* 0.66. Thus, the rate constant of the intersystem crossing, k_{ISC} , was *ca.* $5.5 \times 10^8 \text{ s}^{-1}$. It should be noticed that the rate constant of k_{ISC} is less reliable, since we postulated that the extinction coefficients were the same as those reported in different environments. The estimation, however, indicates that the charge-recombination rate constant on the order of 10^8 s^{-1} is involved in the present decay of the initial CS state.

The deactivation process of the CS state is rationally interpreted also from the energy levels of the states appearing in the photoprimary process. The energy level of the CS state in the C₆₀-PVCz system was estimated to be 2.3–2.1 eV by the Born equation on the basis of the reduction potential of C₆₀ and the oxidation potential of PVCz.²⁹ The dielectric constant of 3.38 was used for PVCz films, and the interionic distance of the CS state was set to be 8.5 Å. Although it is difficult to precisely determine the energy level of the CS state because of the approximated nature of the Born equation, it may be concluded that the CS state is close to the level of ¹C₆₀* (2.0 eV).³⁴ The experimental result that the photoinduced charge separation between ¹C₆₀* and PVCz did not take place in a less polar solution of benzene ($\epsilon = 2.28$) indicates also that the energy level of the CS state in benzene solution is higher than that of ¹C₆₀*, and a slight increase in the dielectric constant of PVCz films enabled the observation of the CS state. In addition, the small energy difference between the CS state (PVCz⁺:C₆₀⁻) and the excited singlet state of C₆₀ in PVCz films (¹C₆₀*+PVCz) is likely to make it possible to establish the rapid equilibrium between them. Thus, actually, the deactivation of the CS state resulted in the production of the locally excited triplet state of C₆₀ (1.56 eV)^{30,34} via ¹C₆₀*.

As aforementioned, the primary processes of the photoinduced electron transfer dynamics in the present C₆₀-doped PVCz films are similar to those in PVCz films doped with various acceptors. Hence, in C₆₀-doped PVCz films, the long-lived ionic species generated by the hole-migration process in the initial CS state are most likely to disappear due to the same process as that in PVCz-acceptor films in the time region from several microseconds to several milliseconds: a hole diffusion-controlled geminate recombination process.³⁵

As mentioned in the Introduction, picosecond dynamics in PVCz films doped with a large amount of C₆₀ ([C₆₀]:[Cz] = 1:1.6, *i.e.* 38 mol %) was investigated by Kamat et al.⁸ The films were excited with a picosecond 355 nm laser pulse. They detected neither isosbestic points nor absorption spectra due to transient ionic species, but only transient absorption spectra with two peaks around 730 and 910 nm. The former band appeared immediately after excitation, and its intensity remained unchanged during the period of 8 ns after excitation. The latter absorption of ¹C₆₀* monitored at 910 nm decreased with a time constant of 825 ps, while the growth in the transient absorption at 740 nm due to intersystem crossing of ¹C₆₀* was not observed. They ascribed the prompt appearance of the absorption band around 730 nm to the formation of a triplet excited CT complex due to rapid intersystem crossing of a singlet excited CT complex within the laser pulse duration of 20 ps. These results are quite different from our present results, although one notices that the experimental condition (the excitation wavelength and the dopant concentration) is not the same.

In order to elucidate the difference between these two results, we examined the excitation intensity effect on the dynamic behaviors. Figure 5 shows transient absorption spectra of 0.7 mol % C₆₀-doped PVCz films excited with a 532 nm picosecond laser pulse with 4 times higher fluence than that used in Figure 4. This figure shows that ³C₆₀* is produced immediately after excitation, as observed by Kamat et al.⁸ Although it is rather difficult to derive a clear conclusion of the mechanism of the nonlinear rapid triplet formation process of the present system, it was reported that the intense picosecond laser excitation easily induced a nonlinear rapid triplet production of the solute under the condition where the solute excited state was densely produced and the solvent (or medium) was nonlinearly excited.³⁶ Actually, the application of the 355 nm laser pulse into densely

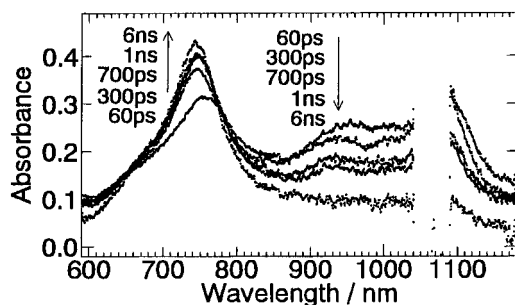


Figure 5. Time-resolved absorption spectra of 0.7 mol % C_{60} -doped PVCz films, excited with a 532 nm picosecond laser pulse. Excitation laser fluence is 4 times larger in this figure than in Figure 4.

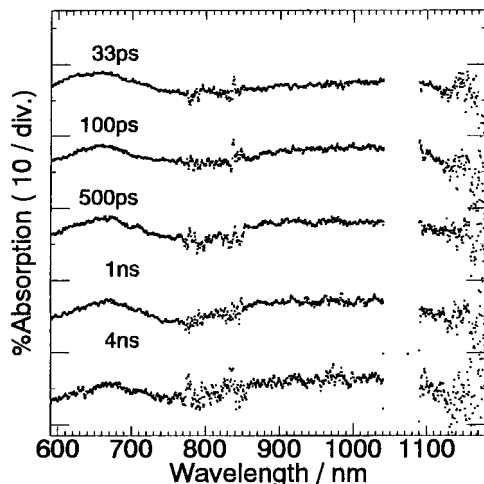


Figure 6. Time-resolved absorption spectra of PVCz powders, excited with a 355 nm picosecond laser pulse. The spectra were measured by a diffuse-reflectance laser photolysis method.

C_{60} -doped PVCz films might induce a dense population of the C_{60} excited state, medium (PVCz) excited state, and so on. In addition, an intense laser excitation may lead to cracking of the solid matrix and the dense population of excited states undergoing local heating as well as nonlinear events. At any rate, some nonlinear formation processes of $^3C_{60}^*$ might be involved in the previous work.⁸

For avoiding such effects and obtaining information on the dynamic behaviors upon excitation of PVCz, we have employed diffuse-reflectance time-resolved absorption spectroscopy for 1 mol % C_{60} -doped PVCz powders under excitation with a 355 nm picosecond laser pulse. For the reference, time-resolved absorption spectra of neat PVCz powders without C_{60} are shown in Figure 6. The broad absorption with a peak around 650 nm observed immediately after excitation shifts to 670 nm with time and evolves into a sharper spectral shape. This spectral evolution as a function of the delay time was attributed to the sandwich-excimer formation from the monomer excited state or partial overlap excimer state.³⁷ Since the absorption spectra and their time evolution are similar to those reported previously,³⁷ an apparent nonlinear process is not induced under the present experimental conditions.

Time-resolved absorption spectra of 1 mol % C_{60} -doped PVCz powders are exhibited in Figure 7. Although the concentration of C_{60} is low, the degree of CT complex formation in the ground state is incomplete. Hence, the sample contains two types of C_{60} : C_{60} that forms CT complexes with Cz chromophores and noncomplexed C_{60} molecules. This is supported by the fact that the ground-state absorption of C_{60} around 600 and 405 nm is observed in addition to the CT

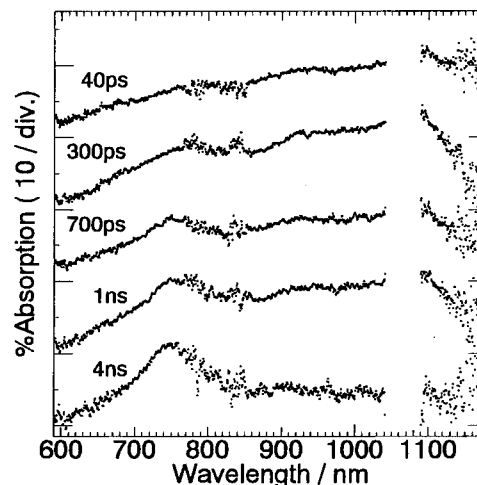


Figure 7. Time-resolved absorption spectra of 1.0 mol % C_{60} -doped PVCz powders, excited with a 355 nm picosecond laser pulse. The spectra were measured by a diffuse-reflectance laser photolysis method.

absorption for 0.7 mol % C_{60} -doped PVCz films in Figure 1. That is, the irradiation at 355 nm excites PVCz, C_{60} , and the CT complex. The energy of the excited singlet state of PVCz ($^1PVCz^*$) transfers to C_{60} via the migration process of the Cz excited singlet state to form $^1C_{60}^*$.³⁸ In addition, the electron transfer from $^1PVCz^*$ to C_{60} occurs, resulting in the CS state. However, not all of $^1PVCz^*$ are quenched by C_{60} because of the low concentration of C_{60} . Hence, the absorption spectra immediately after excitation are considered to consist mainly of C_{60}^- absorption with two peaks around 930 and 1040–1090 nm, $PVCz^+$ absorption with a peak around 790 nm, $^1PVCz^*$ absorption, and $^1C_{60}^*$ absorption,³⁹ although the spectra are broad and cannot be resolved to these components clearly. With increasing delay time, these absorption decrease, and finally, the spectrum at 4 ns consists of the absorption of $^3C_{60}^*$ with a peak at 750 nm and the weak absorption of C_{60}^- . This spectrum is similar to that of C_{60} -doped PVCz films at 6 ns in Figure 4a. Subtracting the contribution of the broad absorption spectrum of $^1PVCz^*$ shown in Figure 6 from these spectra, we are likely to interpret the time evolution of the transient absorption spectra using Scheme 1 proposed for C_{60} -doped PVCz films excited at 532 nm. The present results for 1 mol % C_{60} -slightly-doped PVCz powders under excitation at 355 nm are different from those reported for 38 mol % C_{60} -densely-doped PVCz films.⁸

Nano- and Microsecond Dynamics of the C_{60} Excited State in PVCz Films. The above results indicate that when C_{60} -doped PVCz films and powders are excited with 532 and 355 nm picosecond lasers, respectively, $^3C_{60}^*$ is formed. As aforementioned, the energy level of the CS is beyond the energy level of $^3C_{60}^*$. In Figure 8 are exhibited time-resolved absorption spectra of 2 mol % C_{60} -doped PVCz films measured under multiple-reflection conditions, excited with a 351 nm excimer laser. This multiple-reflection method was adopted for obtaining rather high transient absorbance under weak excitation conditions.^{10,13} The absorption spectrum around 740 nm assigned to $^3C_{60}^*$ decreases with time, and the apparent absorption spectrum of $PVCz^+$ was not observed until the delay time up to 10 μ s, indicating that the photoinduced electron transfer in C_{60} -doped PVCz films did not occur in the triplet state. The present result is consistent with the energy levels described in the previous section.

Conclusion

As mentioned in the Introduction, the sensitization of the photoconductivity was reported for PVCz films doped with a

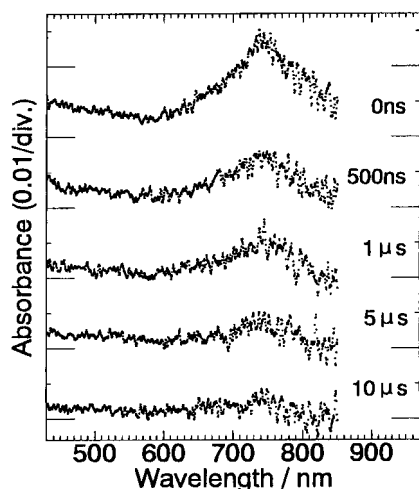


Figure 8. Time-resolved absorption spectra of 2 mol % C₆₀-doped PVCz films, excited with a 351 nm excimer laser. The spectra were measured by a laser photolysis method with multiple-reflection configuration. The gated width was 100 ns.

small amount of C₆₀. From the present results, it was concluded that the hole migration in the initial charge-separated state in the singlet manifold was the effective pathway of the free carrier formation in C₆₀-doped PVCz films and that relatively high reaction yield of this process (30%) was responsible for the enhancement of the photoconductivity in the PVCz films.

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- (39) Under excitation with a 355 nm picosecond laser pulse, fluorescence of C₆₀ was observed weakly.