Transient absorption study on photoinduced electron transfer between C_{60} and poly(*N*-vinylcarbazole) in polar solvent

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Abstract

Photoinduced electron transfer reactions between C_{60} and poly(*N*-vinylcarbazole) (PVCz) in polar benzonitrile solution have been investigated by observing the transient absorption bands in the visible and near-ir regions. When C_{60} was photoexcited, the electron transfer reaction occurred via both $^3C_{60}^*$ and $^1C_{60}^*$. In the case of the reaction via $^3C_{60}^*$, electron transfer rate constant was 5.1×10^6 M^{-1} s^{-1}, which is larger than that of the reaction between $^3C_{60}^*$ and EtCz by a factor of 7.5, indicating a stabilization of cation radical of carbazole in PVCz. Electron transfer reactions via $^1C_{60}^*$ proceeded at the diffusion-controlled rate, while the quantum yield for electron transfer is not high. When PVCz was photoexcited, direct photo-ejection occurred from PVCz yielding PVCz $\cdot^+$ and solvated electron, in which the latter was captured by C_{60}. Electron transfer from $^3PVCz^*$ to C_{60} was also pointed out as a charge generation mechanism. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photoinduced electron transfer; Fullerene; Poly(*N*-vinylcarbazole)

1. Introduction

Recently, many research groups have paid much attention to fullerenes (C_{60} and C_{70}) as the doping molecule for the photoconductive materials. In many cases, fullerenes act as electron acceptors in the polymer matrix due to their acceptor-ability both in the ground and the excited states. The enhancement of photoconductivity of poly(*N*-vinyl-carbazole) (PVCz) was reported by Wang et al. [1,2]. Similar doping effects of fullerenes have been reported on poly(*p*-phenylene vinylene) [3], poly(2,5-dialkoxy-*p*-phenylene vinylene) [4], and poly(3-alkylthiophene) [5]. The doping of fullerene is also reported to be effective in the enhancement of photoconductivity of non-polymeric materials such as zinc phthalocyanine [6]. As for the C_{60}-doped PVCz films, pico and nanosecond laser flash photolysis studies have been carried out by Kamat et al. [7] and by Itaya et al. [8] independently with observing the transient absorption in the visible and near-ir regions. Kamat et al. reported the prompt formation of charge transfer complex in triplet excited state, while the electron transfer products such as radical anion of C_{60} ($C_{60}\cdot^-$) and radical cation of

PVCz (PVCz $\cdot^+$) were not observed in their experimental condition [7]. Itaya et al. reported the charge separation process within picosecond laser duration and the hole migration process of generated charge which is competitive process of charge recombination [8]. These results indicate that electron transfer of charge transfer complex in C_{60}-PVCz film is responsible for the generation of photoinduced carrier, since most of the C_{60} is expected to form charge transfer complex with PVCz in the ground state due to high concentration of carbazole groups in the film.

As for electron transfer in the solution, different electron transfer processes would be expected because of weak charge transfer interaction in the ground state and the variety of electron transfer media. In a previous communication [9], we reported that the radical ions of C_{60} and PVCz were generated only when both C_{60} and PVCz were excited. However, electron transfer mechanism depending on the excitation wavelength was not clear.

In the present paper, we report the results of the detailed study on photoinduced electron transfer processes in the mixture of C_{60} and PVCz in polar solvent using nanosecond laser flash photolysis method. We confirmed that the generation mechanism of the radical ions of C_{60} and PVCz changes depending on the experimental conditions such as solvent and excitation wavelength. The electron transfer products were generated via three different electron transfer processes: (1) electron transfer via $^3C_{60}^*$; (2) electron

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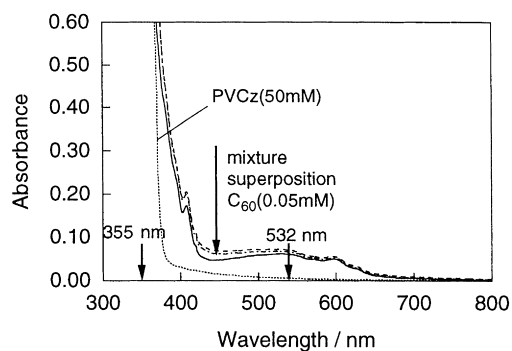
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Fig. 1. Steady-state absorption spectra in benzonitrile; C_{60} (0.05 mM) (solid line), PVCz (50 mM; monomer unit) (dot line), mixture of C_{60} (0.05 mM) and PVCz (50 mM) (dash line), and superposition of the components (dot dash line).

transfer via $^1C_{60}^*$; and (3) solvated electron-capture by C_{60} and/or electron transfer via $^3PVCz^*$. The reaction rate of photoinduced electron transfer via $^3C_{60}^*$ with polymer would be compared with that of ethylcarbazole (EtCz), revealing polymer effect in the electron transfer reaction with C_{60} in solution.

2. Experimental

2.1. Materials

C_{60} (99.9%) was purchased from Texas Fullerene Corp. and used without further purification. PVCz (M_w 3–5 × 10^5 vs. PSt.) and EtCz were purchased from Tokyo Kasei. Other chemicals were the best commercial grade available.

2.2. Measurements

The nanosecond transient absorption spectra were measured by using either SHG (532 nm) or THG (355 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. A pulsed xenon flash lamp was used as a probe light. A Ge-APD module (Hamamatsu Photonics, B2834) attached to a
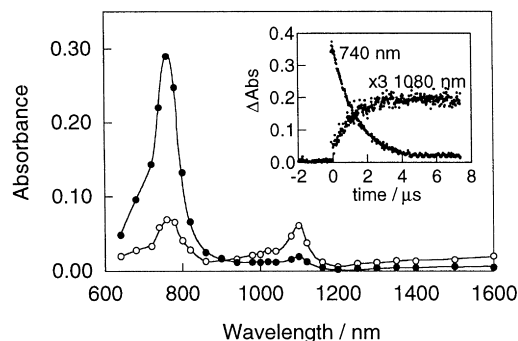

Fig. 2. Transient absorption spectra observed by the 532 nm-laser irradiation of C_{60} (0.1 mM) in the presence of PVCz (53 mM; monomer unit) in deaerated benzonitrile at 250 ns (filled circle) and 2.5 μs (open circle). Inset: absorption-time profiles at 1080 and 740 nm.

monochromator (Ritsu MC-10N) was employed as a detector of transient absorption spectra in the visible and near-ir regions (600–1600 nm) [10]. Transient absorption measurements in sub-millisecond region were carried out using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu Photonics, G5125-10) as a prove light and a detector, respectively.

Time-resolved fluorescence spectra were measured by a single-photon counting method using SHG (380 nm) of a Ti:Sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) and a streakscope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Acton Research, SpectraPro 150) as an excitation source and a detector, respectively.

Steady-state absorption spectra in the visible and near-ir regions were measured on a Jasco V570 DS spectrophotometer.

All the measurements were carried out in 1 cm optical cell after bubbling with Ar-gas for 15 min at ambient temperature.
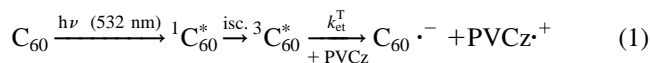
3. Results and discussion

3.1. Steady-state absorption

The absorption spectrum of the mixture of C_{60} and PVCz is almost the same as pure C_{60} (Fig. 1), suggesting that the ground-state interaction is quite weak under the present experimental conditions. Recent report on the PVCz films doped with C_{60} showed the formation of charge transfer complex with broad absorption band [1,2,7,8]. It is interesting to note that such a spectral change was not observed in the solution of the mixture of C_{60} and PVCz (or EtCz), even if the concentrations of PVCz or EtCz are higher than 50 mM. In the present laser flash photolysis study, excitation of samples was carried out using either 355 or 532 nm. By the excitation with the 532 nm-light, C_{60} is solely excited, while EtCz or PVCz are also excited with the 355 nm-light. In order to avoid degradation of the sample, laser experiments were always carried out with fresh samples.

3.2. Electron-transfer reaction via $^3C_{60}^*$

Fig. 2 shows transient absorption spectra observed by the excitation of C_{60} with the 532 nm-light in the presence of PVCz in benzonitrile. The absorption band appeared at 740 nm immediately after the laser pulse was assigned to $^3C_{60}^*$ [11–14]. With the decay of $^3C_{60}^*$, the sharp absorption band appeared at 1080 nm, which was ascribed to $C_{60}^{\cdot-}$ [15–18]. This finding indicates the generation of $C_{60}^{\cdot-}$ by electron transfer via $^3C_{60}^*$ (Eq. (1)).

$$C_{60} \xrightarrow{h\nu \ (532 \ nm)} {}^1C_{60}^* \xrightarrow{isc.} {}^3C_{60}^* \xrightarrow[+ \ PVCz]{k_{et}^T} C_{60}^{\cdot-} + PVCz^{\cdot+} \qquad (1)$$

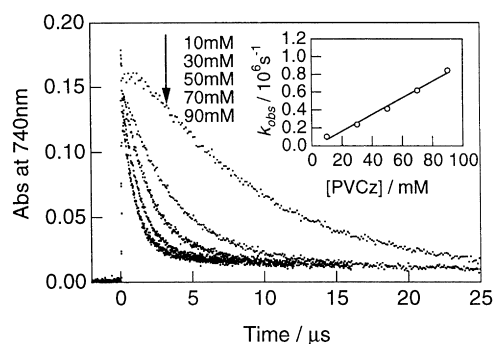Furthermore, an absorption band around 1600 nm which

Fig. 3. Absorption-time profiles at 740 nm observed by the 532 nm-laser irradiation of C_{60} (0.1 mM) in the presence of PVCz (10, 30, 50, 70, 90 mM). Inset: relation between concentration of PVCz and observed decay rate constants (k_{obs}) at 740 nm.

appeared with the decay of $^3C_{60}^*$ can be attributed to the charge resonance band of PVCz$\cdot^+$ [19]. The radical cation of PVCz is reported to show an absorption band at 780 nm [19,20], which is quite close to the absorption band of $^3C_{60}^*$.

The decay rate of the absorption of $^3C_{60}^*$ at 740 nm was accelerated with a concentration of PVCz as shown in Fig. 3. The absorption-time profiles at 740 nm did not decrease to zero-absorbance within the estimated time region, because of spectral overlap with the absorption band of PVCz$\cdot^+$ at 780 nm. Therefore, decay rate of $^3C_{60}^*$ was estimated by curve-fitting by assuming the generation of PVCz$\cdot^+$ as well as the decay of $^3C_{60}^*$. From the relation between the decay rate of $^3C_{60}^*$ and the concentration of PVCz in monomer unit (inset of Fig. 3), the bimolecular quenching rate constants of $^3C_{60}^*$ (k_q^T) by PVCz was evaluated to be 9.3×10^6 M^{-1} s^{-1}. The quantum yield of electron transfer via $^3C_{60}^*$ (Φ_{et}^T) was estimated to be 0.55 from $[C_{60}\cdot^-]_{max}/[^3C_{60}^*]_{max}$ using reported extinction coefficient of $C_{60}\cdot^-$ and $^3C_{60}^*$ [21,22]. The rate constants of electron transfer (k_{et}^T) can be evaluated to be 5.1×10^6 M^{-1} s^{-1} from the relation $k_{et}^T = k_q^T \times \Phi_{et}^T$ [23,24]. The estimated k_{et}^T value is quite smaller than the diffusion-controlled rate constant of

benzonitrile ($k_{diff} = 5.3 \times 10^9$ M^{-1} s^{-1} at 298 K) [25]. In our previous communication, we failed to observe the electron transfer reaction when benzonitrile solution of C_{60} and PVCz was excited with the 532 nm-laser light which excited C_{60} only [9], because of the quite slow reaction rate on the order of 10^6 M^{-1} s^{-1}.

When the 532 nm-laser light was irradiated to benzonitrile solution containing C_{60} and EtCz, which corresponds to the repeating unit of PVCz, generation of $C_{60}\cdot^-$ with the decrease of $^3C_{60}^*$ was also confirmed, indicating the electron transfer reaction via $^3C_{60}^*$ as in the case of PVCz. In this case, transient absorption band due to charge resonance band around 1600 nm was not observed. The k_q^T, Φ_{et}^T and k_{et}^T values for the present electron transfer reactions were estimated to be 1.1×10^6 M^{-1} s^{-1}, 0.64 and 6.8×10^5 M^{-1} s^{-1}, respectively.

By assuming that the oxidation potential of PVCz is the same as that of EtCz (1.18 V vs. SCE) [26], the free energy change for the present electron transfer reaction via $^3C_{60}^*$ is calculated to be 1.35 kcal mol^{-1}, an endothermic reaction. Such a positive free energy change for the reaction is responsible for the quite slow reaction rate. In Fig. 4, electron transfer rates between $^3C_{60}^*$ and various amine donors including PVCz and EtCz in benzonitrile were plotted against the free energy changes for the reactions. Solid line indicates a calculated curve using semi-empirical Rehm–Weller equation [27]. Quite a good fit was observed among the experimental data and the theoretical curve.

It is interesting to note that the k_{et}^T value of PVCz is larger than that of EtCz by a factor of 7.5, which is far greater than the experimental error of our instruments. Carbazole moiety of PVCz is expected to take various stacking structures with neighboring carbazole moieties. In such polymer chains, generated radical cations are expected to take more energetically relaxed form, which will decrease the free energy change for the electron transfer reaction. Tsujii et al. evaluated the stabilization energy of the carbazole radical cation in PVCz by charge delocalization to be 0.5 ± 0.1 eV [19].

Itaya et al. reported that the charge separation did not take place between $^3C_{60}^*$ and PVCz in the film [8]. The different behavior from our present result can be attributed to low dielectric constant of PVCz ($\varepsilon = 3.38$), which places charge separated states at more higher energy level relative to $^3C_{60}^*$, predicting more endothermic reaction than the reaction in benzonitrile ($\varepsilon = 25.2$).

The transient absorption band of $C_{60}\cdot^-$ shows decay over several ten microseconds after the generation by the electron transfer reaction. The decay of $C_{60}\cdot^-$ can be attributed to the back electron transfer between $C_{60}\cdot^-$ and PVCz$\cdot^+$ or EtCz$\cdot^+$. By applying the second-order plot to the absorption-time profile of $C_{60}\cdot^-$, the rate constant for the back-electron transfer reaction was estimated to be 4.4×10^9 or 6.7×10^9 M^{-1} s^{-1} for the reaction with PVCz or EtCz, respectively. Slow back electron transfer of PVCz than EtCz may indicate migration of the generated hole
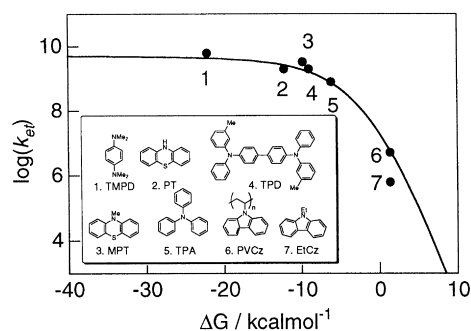

Fig. 4. Relation between free energy change for the electron transfer (ΔG_{et}) and k_{et}^T of C_{60} and various amine donors. Inset: molecular structure of the donors. TMPD: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine PT: phenothiazine MPT: *N*-methylphenothiazine TPD: *N,N'*-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine TPA: triphenylamine.
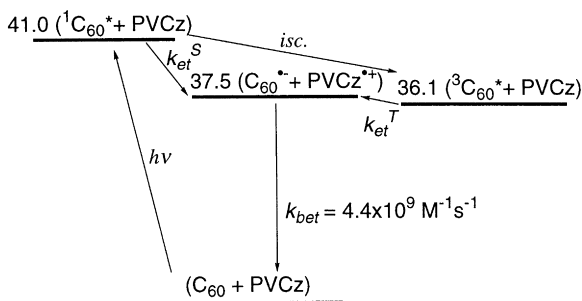
Fig. 5. Schematic energy diagram for the electron transfer via $^{1}C_{60}^{*}$ or $^{3}C_{60}^{*}$. Numbers indicate energies relative to the ground state (in kcal mol^{-1}).

along PVCz polymer chain. The reaction rates at the diffusion-controlled rates are quite reasonable, since sufficiently negative free energy changes of ca. -37.5 kcal - mol^{-1} are expected for the back electron transfer reactions.

3.3. Electron transfer via $^{1}C_{60}^{*}$

Due to high oxidation potential of carbazole, electron transfer via $^{3}C_{60}^{*}$ proceeded slowly compared with other amine donors such as TMPD. However, electron transfer via $^{1}C_{60}^{*}$ is expected to proceed more rapidly, because the singlet energy of C_{60} is larger than the triplet energy by 4.9 kcal mol^{-1}. The free energy change for the electron transfer via $^{1}C_{60}^{*}$ is calculated to be -3.5 kcal mol^{-1} as shown in the schematic energy diagram (Fig. 5), which predicts the rapid electron transfer close to the k_{diff}.

Fig. 6 shows the decay profile of the fluorescence around 700 nm observed for benzonitrile solution containing C_{60} (0.1 mM) and PVCz (24 mM). In the presence of PVCz, the decay profile shows two-components: From the time-resolved fluorescence spectra, fast decaying main component can be attributed to the fluorescence of C_{60} [28], while the slow one may be fluorescence tail of PVCz or impurity, since PVCz is also excited under the present experimental condition. The decay rate of the fast component was accelerated with the concentration of PVCz. The acceleration of the decay of $^{1}C_{60}^{*}$ can be usually attributed to electron transfer via $^{1}C_{60}^{*}$ (Eq. (2)).
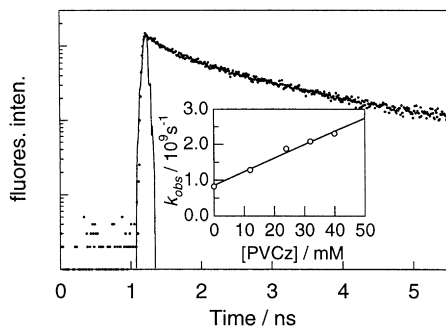

Fig. 6. First-order plot of a fluorescence decay profile of C_{60} (0.1 mM) in the presence of PVCz (24 mM) in BN. Inset: relation between observed decay rates of $^{1}C_{60}^{*}$ (k_{obs}) and the concentration of PVCz.
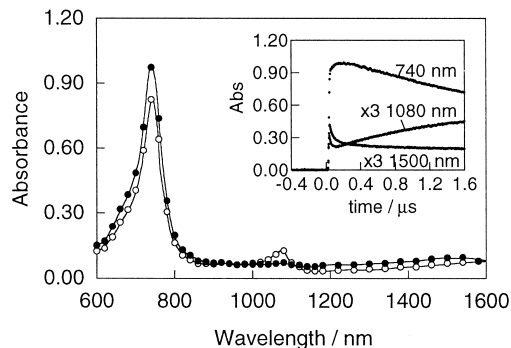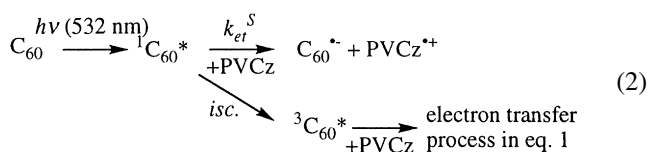

Fig. 7. Transient absorption spectra observed by the 355 nm-laser irradiation of C_{60} (0.1 mM) in the presence of PVCz (3 mM; monomer unit) in deaerated benzonitrile at 100 ns (filled circle) and 1.0 μs (open circle). Inset: absorption-time profiles at 1500, 1080 and 740 nm.

$$C_{60} \xrightarrow{h\nu \ (532 \ nm)} {}^{1}C_{60}^{*} \xrightarrow[+PVCz]{k_{et}^{S}} C_{60}^{\bullet-} + PVCz^{\bullet+}$$
$$\xrightarrow{isc.} {}^{3}C_{60}^{*} \xrightarrow[+PVCz]{} \text{electron transfer process in eq. 1} \tag{2}$$

From the relation between the decay rate of $^{1}C_{60}^{*}$ and the concentration of PVCz (inset of Fig. 6), the bimolecular quenching rate of $^{1}C_{60}^{*}$ (k_{q}^{S}) was estimated to be 3.8×10^{10} M^{-1} s^{-1}, quite a fast process due to the negative free energy change for the electron transfer via $^{1}C_{60}^{*}$. Fluorescence of C_{60} was also quenched in the presence of EtCz: The k_{q}^{S} value was estimated to be 4.3×10^{10} M^{-1} s^{-1}.

The electron transfer via $^{1}C_{60}^{*}$ was also confirmed in the nanosecond transient absorption spectra. The absorption-time profile of $C_{60}^{\bullet-}$ at 1080 nm (inset of Fig. 2) can be divided into two rising components: Fast rising component within the laser duration (fwhm 6 ns) is due to the electron transfer via $^{1}C_{60}^{*}$, while slowly rising component is due to the electron transfer via $^{3}C_{60}^{*}$. From the absorbance ratio of the fast and the slow rising components, contribution of the singlet route in the net charge generation is estimated to be ~20% when the 532 nm-laser light was irradiated to the solution containing C_{60} (0.1 mM) and PVCz (53 mM). From the estimated ratio of the absorbance, k_{et}^{T}, k_{q}^{S}, and intersystem crossing rate ($k_{isc} = 8.2 \times 10^{8}$ s^{-1}), electron transfer rate (k_{et}^{S}) and quantum yield for the electron transfer via $^{1}C_{60}^{*}$ ($\Phi_{et}^{S} = (k_{et}^{S} \times [PVCz])/(k_{r}^{S} + k_{nr}^{S} + k_{isc} + k_{q}^{S} \times [PVCz])$ where k_{r}^{S} and k_{nr}^{S} are radiative and non-radiative deactivation rate of $^{1}C_{60}^{*}$, respectively) are calculated to be 2.2×10^{9} M^{-1} s^{-1} and 0.04, respectively. Small Φ_{et}^{S} value indicates the existence of other bimolecular deactivation processes of $^{1}C_{60}^{*}$ such as collisional deactivation. The contribution of the singlet route in the net charge generation should increase with the concentration of PVCz. In C_{60} doped PVCz film, electron transfer of charge transfer complex is dominant charge-generation mechanism [7,8].

3.4. Electron transfer via excited PVCz

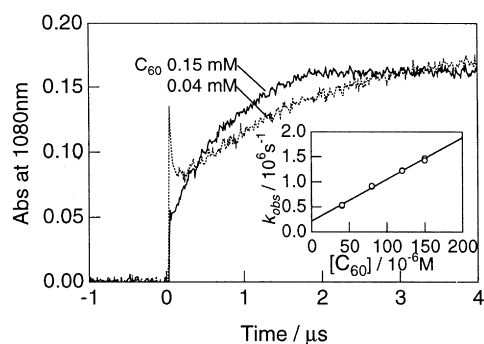When the 355 nm-laser light was irradiated to benzonitrile

Fig. 8. Absorption-time profiles at 1080 nm observed by the 355 nm-laser irradiation of C_{60} (0.15 or 0.04 mM) and PVCz (5 mM) in benzonitrile. Inset: relation between the first-order rate constants (k_{obs}) and the concentration of C_{60}.

solution containing C_{60} and PVCz, appreciable $C_{60}{}^{\cdot-}$ generation was observed even at low concentration of PVCz (Fig. 7). In the present experimental condition, ca. 10% of photons are absorbed by PVCz (3 mM). From the absorption-time profile at 1080 nm (inset of Fig. 7), the generation rate of $C_{60}{}^{\cdot-}$ was estimated to be 1.2×10^6 s^{-1} which is larger than the reaction rate of $^3C_{60}^*$ with PVCz($= k_q^T \times$ [PVCz], [PVCz] = 3 mM) by a factor of 600. The participation of $^3C_{60}^*$ in the net $C_{60}{}^{\cdot-}$ generation in the present experimental condition was calculated to be 16% from the estimated k_{et}^T and Φ_{et}^T. Quite fast generation of $C_{60}{}^{\cdot-}$ at the low concentration of PVCz indicates different electron transfer mechanism other than that via $^3C_{60}^*$. The finding is also supported by the fact that the decay rate of absorption band due to $^3C_{60}^*$ at 740 nm was not accelerated with an increase in the concentration of PVCz in <20 mM. On the contrary, the generation rate of $C_{60}{}^{\cdot-}$ was accelerated with an increase in the concentration of C_{60} as shown in Fig. 8. Furthermore, a linear relationship was observed between the generation rate and the concentration of C_{60} (inset of Fig. 8), indicating pseudo-first order reaction between ground-state C_{60} and other species with high donor-ability. From the slope of the inset of Fig. 8, the reaction rate was estimated to be 8.3×10^9 M^{-1} s^{-1},
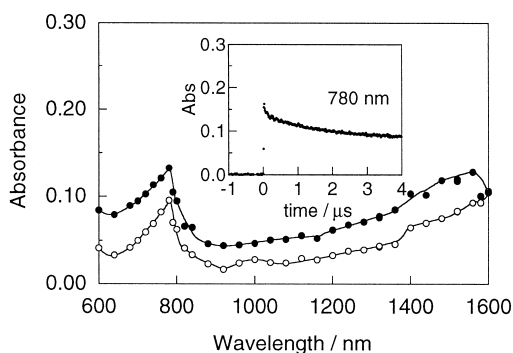

Fig. 9. Transient absorption spectra observed by the 355 nm-laser irradiation of PVCz (3 mM; monomer unit) in deaerated benzonitrile at 250 ns (filled circle) and 2.5 μs (open circle). Inset: absorption-time profile at 780 nm.

indicating the diffusion-controlled reaction. As for the reaction between C_{60} and EtCz induced by the 355 nm-laser excitation, acceleration of the generation rate of $C_{60}{}^{\cdot-}$ with a concentration of C_{60} was also observed; the bimolecular reaction rate was estimated to be 6.2×10^9 M^{-1} s^{-1}.

As an appropriate reaction mechanism for the reaction by the 355 nm-excitation, following two mechanisms can be expected: (1) solvated electron-capture by C_{60}; and (2) electron transfer via ^{3}PVCz*. Taking the concentration of PVCz and the reaction rate via $^3C_{60}^*$ into account, contribution of $^3C_{60}^*$ to the present electron transfer is negligibly small.

Fig. 9 shows the transient absorption spectra observed by the 355 nm-laser irradiation to benzonitrile solution containing only PVCz. Immediately after the laser irradiation, absorption bands around 1600 and 780 nm were observed. Both transient absorption bands can be attributed to PVCz$\cdot^+$ as indicated previously. The generation of PVCz$\cdot^+$ can be attributed to the photo-ejection from singlet excited PVCz (Eq. (3)).

$$\text{PVCz} \xrightarrow{h\nu \ (355 \ \text{nm})} \text{PVCz}^* \rightarrow \text{PVCz}\cdot^+ + e_{\text{solvated}} \tag{3}$$

An absorption due to solvated electron in benzonitrile may be hidden by the broad absorption of PVCz$\cdot^+$. Therefore, fast rise within the laser duration observed in an absorption-time profile in the near-ir region (for example, profiles at 1500 and 1080 nm in inset of Fig. 7) can be attributed to the formation of charge resonance band of PVCz$\cdot^+$. The time profile of PVCz$\cdot^+$ at 780 nm shows gradual decay after the laser pulse which can be attributed to the recombination with solvated electron, indicating relative long lifetime of the solvated electron. Therefore, solvated electron-capture process by C_{60} (Eq. (4)) is an appropriate mechanism for the present electron transfer reaction.

$$C_{60} + e_{\text{solvated}} \rightarrow C_{60}{}^{\cdot-} \tag{4}$$

This process is considered to be competing with the charge recombination between solvated electron and PVCz$\cdot^+$.

Since the triplet energy of carbazole is reported to be 70.3 kcal mol^{-1} [25], which is much larger than that of C_{60}, sufficiently negative free energy change (-32.7 kcal mol^{-1}) is anticipated for the electron transfer from ^{3}PVCz* to C_{60} (Eq. (5)).

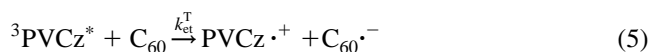$$^3\text{PVCz}^* + C_{60} \xrightarrow{k_{et}^T} \text{PVCz}\cdot^+ + C_{60}{}^{\cdot-} \tag{5}$$

Fig. 10 shows the absorption-time profiles at 440 nm of benzonitrile solution containing C_{60} and PVCz: PVCz is reported to show a triplet absorption band at 440 nm [29]. Since the absorption-time profile at 440 nm also includes the contribution of absorption bands of $^3C_{60}^*$ and PVCz$\cdot^+$, the time profile cannot be analyzed by a single exponential decay function. However, with an increase in the concentration of C_{60}, decay rate at 440 nm was accelerated as shown in Fig. 10. This indicates that the reaction takes place via ^{3}PVCz*, since contribution of $^3C_{60}^*$ should be very small in
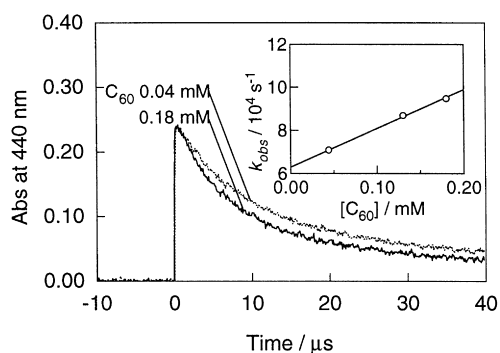
Fig. 10. Absorption-time profiles at 440 nm observed by the 355 nm-laser irradiation of C_{60} (0.18 or 0.04 mM) in the presence of PVCz (5 mM) in benzonitrile. Inset: relation between the first-order rate constants (k_{obs}) and the concentration of C_{60}.

the decay rate change under the present conditions. From the relation between the concentration of C_{60} and decay rates (inset of Fig. 10), which were estimated by applying the first-order decay function to the profiles in 0–10 μs of time-region, the bimolecular reaction rate was estimated to be $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The estimated reaction rate should be regarded as a tentative value because of the spectral overlap with other transient species.

Thus, the two mechanisms mentioned above may contribute to $C_{60}^{\cdot-}$ and PVCz$\cdot^+$ (or EtCz$\cdot^+$) generations. Perhaps, the contribution of electron transfer from ^{3}PVCz* may be small, since the estimated bimolecular quenching rate of ^{3}PVCz* ($1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is one-order smaller than the rate constant ($8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) estimated from the generation of $C_{60}^{\cdot-}$. The contribution of both possibilities will be changed by the solvent polarity, since in the less polar solvents photo-ejection process of PVCz will not take place much efficiently.

4. Conclusions

Electron transfer processes of C_{60} and PVCz in polar benzonitrile were quite different from that in solid PVCz films, in which electron transfer of charge transfer complex of C_{60} and PVCz is responsible for the generation of photo-induced carrier. Present results indicated that several photo-induced electron transfer processes other than photoexcitation of charge transfer complex also contribute to the charge generation processes of C_{60}-doped organic materials. The contribution of these processes to the charge generation should largely depend on the experimental conditions such as medium and the excitation wavelength. Furthermore, we confirmed different reactivity of PVCz and EtCz: Faster electron transfer and slower back electron transfer of PVCz are an interesting example of polymer effects in electron transfer.

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