Photoinduced Electron Transfer between C_{60} and Poly(*N*-vinylcarbazole) by Laser Flash Photolysis

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The formation of a C_{60} radical anion due to photoinduced electron transfer between C_{60} and poly(*N*-vinylcarbazole) was observed by the excitation of poly(*N*-vinylcarbazole) at 355 nm whereas the photoinduced electron transfer did not take place by excitation of C_{60} at 532 nm.

The enhancement of the photoconductivity of poly(*N*-vinylcarbazole) (PVCz) film by doping with fullerene has been reported by Wang *et al.*[1,2] Similar doping effects of fullerene on the photoconductivity are also reported on poly(*p*-phenylene vinylene),[3] and poly(2,5-dialkoxy-*p*-phenylene vinylene).[4] These results show possibilities for the development of fullerene-based polymeric photoconductors. The photoconductivity is due to the effect of the fullerene on the charge generation and the charge transport processes in the polymeric system. Wang pointed out that the charge generation process could be due to either the excitation of fullerene or the direct excitation of fullerene–carbazole CT complexes, but it is difficult to distinguish between these two possibilities using the gain spectra of the photoconductivity. Laser flash photolysis is effective in investigating the initial step of the charge-generation. Here we report on the photoinduced electron transfer between C_{60} and PVCz in solution by observing the formation of radical ions of C_{60} and PVCz. The mechanism of the photoinduced electron transfer was discussed on the basis of the transient absorption spectra and the absorption–time profiles of radical ions in the near IR region.

C_{60} (99.9% purity) was obtained from Texas Fullerene Corp. PVCz was prepared by radical polymerization using azobisisobutyronitrile as an initiator ($M_w = 94.8 \times 10^4$, $M_w/M_n = 3.33$). C_{60} and PVCz were dissolved in benzonitrile, and deaerated with nitrogen before measurements. The solution was excited by a Nd : YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 355 nm and 532 nm. The absorption-time profiles were detected with a Ge-APD module (Hamamatsu) using a xenon flash lamp as a probe beam. All experiments were carried out at 20 °C.

The following pathways [eqns. (1)–(6)] can be considered in the photoinduced electron transfer between C_{60} and PVCz.

$$C_{60}^* + \text{PVCz} \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (1)$$

$$C_{60}^* + \text{PVCz} \rightarrow (C_{60}\text{–PVCz})^* \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (2)$$

$$^{T}C_{60}^* + \text{PVCz} \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (3)$$

$$C_{60} + \text{PVCz}^* \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (4)$$

$$C_{60} + \text{PVCz}^* \rightarrow (C_{60}\text{–PVCz})^* \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (5)$$

$$(C_{60}\text{–PVCz})^* \rightarrow C_{60}^{\cdot -} + \text{PVCz}^{\cdot +} \quad (6)$$

The excitation of fullerene and the direct excitation of fullerene/carbazole CT complexes correspond to eqns. (1) and (6), respectively. Eqns. (1), (2) and (3) *via* C_{60} excited state and eqns. (4) and (5) *via* PVCz excited state can be distinguished by changing the excitation wavelength. The laser flash photolysis was carried out using two excitation wavelengths; at 355 nm C_{60} and PVCz have absorption bands and at 532 nm only C_{60} has an absorption band. The photoinduced electron transfer *via* C_{60} triplet [$^{T}C_{60}^*$; eqn (3)] has been reported for systems of fullerene–low molecular weight donors which have low oxidation potentials. The quenching rate constants were determined by the pseudo-first order plots of $^{T}C_{60}^*$ decay.[5,6]

The transient absorption spectra obtained by laser flash photolysis of 0.1 mmol dm^{-3} C_{60} in the presence of 3 mmol dm^{-3} (concentration based on carbazole repeating unit) PVCz in benzonitrile are shown in Figs. 1 and 2 for the laser excitations at 355 and 532 nm, respectively. Fig. 1 shows a sharp absorption band at 1060 nm,which is assigned to a C_{60} radical anion on the basis of the absorption spectra of a C_{60} radical anion reported by Sida *et al.* in a γ-irradiated glassy matrix at 77 K[7] and by Asmus *et al.* using a pulse radiolysis technique.[8,9] The direct excitation of C_{60} alone in benzonitrile at 355 nm did not show the transient absorption of C_{60} radical anion, and the intense triplet–triplet absorption of C_{60} with a sharp peak at 740 nm was only observed at 400–850 nm. This result suggests that the C_{60} radical anion is formed by the electron transfer between C_{60} and PVCz in the case of the laser excitation at 355 nm.

On the other hand, the C_{60} radical anion was not observed by laser excitation at 532 nm as shown in Fig. 2. Only the absorption peak of $^{T}C_{60}^*$ appears at 740 nm and no absorption peak is seen at wavelengths longer than 800 nm. This result indicates the absence of pathways shown in eqns. (1), (2) and

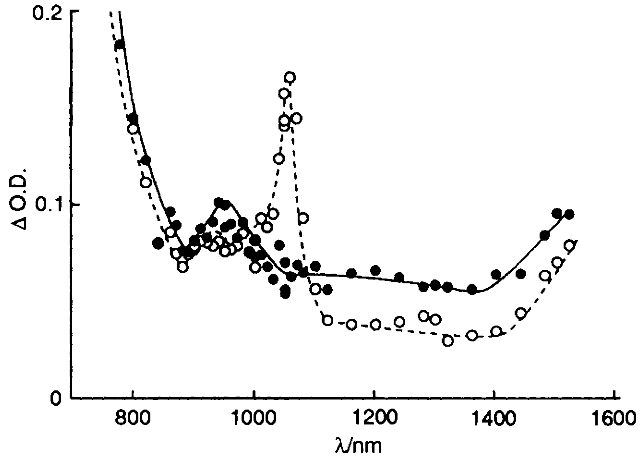

Fig. 1 Transient absorption spectra obtained by laser flash photolysis of 0.1 mmol dm^{-3} C_{60} in the presence of 3 mmol dm^{-3} PVCz in benzonitrile; (●) 20 ns and (○) 1 μs after laser excitation at 355 nm

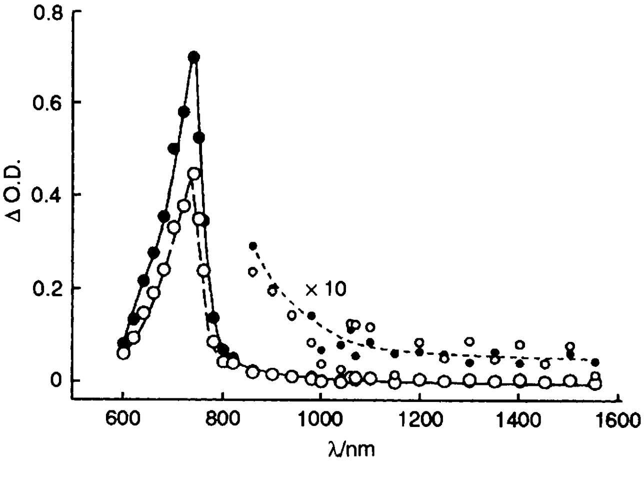

Fig. 2 Transient absorption spectra obtained by laser flash photolysis of 0.1 mmol dm^{-3} C_{60} in the presence of 3 mmol dm^{-3} PVCz in benzonitrile; (●) 20 ns and (○) 1 μs after laser excitation at 532 nm

(3) where the photoinduced electron transfer takes place *via* the C_{60} excited state. The direct excitation of C_{60} does not give radical ions of C_{60} and PVCz in solution.

Fig. 3 shows the transient absorption spectra obtained by laser flash photolysis of 3 mmol dm^{-3} PVCz in benzonitrile. The PVCz radical cation was formed by the direct excitation of PVCz in a polar solvent, which is similar to low molecular weight carbazole derivatives.[10] In Fig. 3, the absorption bands at 740 nm and near 1500 nm can be assigned to the radical cation of the carbazole unit and the charge resonance band formed between the carbazole radical cation and neutral carbazole unit, respectively.[11] In Fig. 1, such absorption bands are overlapping with those of the C_{60} radical anion and $^{T}C_{60}^{*}$.

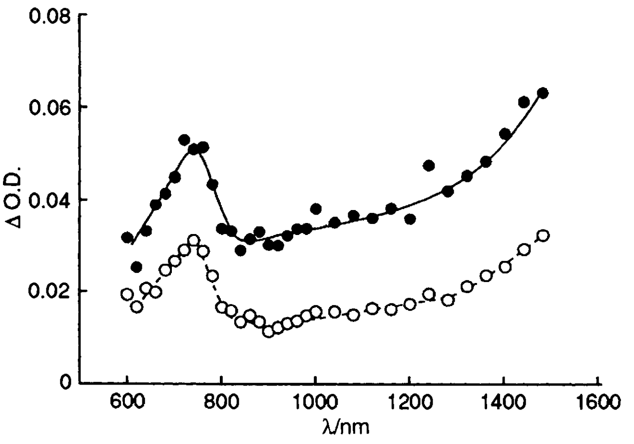

Fig. 3 Transient absorption spectra obtained by laser flash photolysis of 3 mmol dm^{-3} PVCz in benzonitrile; (●) 20 ns and (○) 1 μs after laser excitation at 355 nm

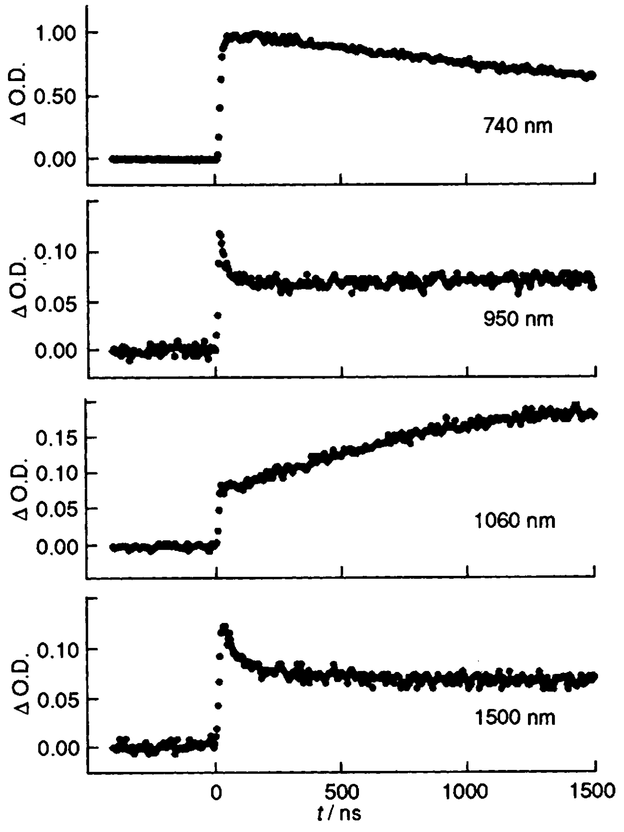

Fig. 4 The absorption–time profiles obtained by laser flash photolysis of 0.1 mmol dm^{-3} C_{60} in the presence of 3 mmol dm^{-3} PVCz in benzonitrile; laser excitation at 355 nm

The absorption–time profiles obtained by laser excitation at 355 nm are shown in Fig. 4. The absorption bands at 740, 1060 and 1500 nm correspond to those of $^{T}C_{60}^{*}$, C_{60} radical anion, and PVCz radical cation, respectively. The absorption of the C_{60} radical anion at 1060 nm shows a rather slow growth. If direct excitation of fullerene/carbazole CT complexes occurs, then the C_{60} radical anion should be produced immediately after laser flash photolysis. There is a difference between our dilute solution system and the C_{60}-doped PVCz film system reported by Wang *et al.* No CT band was observed for 0.1 mmol dm^{-3} C_{60}–3 mmol dm^{-3} PVCz in benzonitrile. These results indicate the absence of pathways shown in eqn. (6) *via* C_{60}/PVCz CT complexes in the case of the photoinduced electron transfer in solution.

The pathways *via* PVCz* are suggested from the above results. However, the slow growth of the C_{60} radical anion cannot be caused by direct electron transfer from PVCz* to C_{60} as expressed in eqn. (4) since the lifetime of PVCz* is within 10 ns. A remaining possibility of the electron transfer pathway is shown in eqn. (5) *via* (C_{60}–PVCz)* exciplexes. The emission spectrum of C_{60}–PVCz in benzonitrile showed no exciplex emission, which may be due to the low fluorescence quantum yield of the exciplexes. In Fig. 4, a fast decaying component at 950 nm within 50 ns after the laser pulse may be attributed to the absorption of (C_{60}–PVCz)*. However, the slow growth of the C_{60} radical anion at 1060 nm does not correspond to the fast decay at 950 nm. Another intermediate which has lifetime corresponding to the growth of the C_{60} radical anion must be considered. Such an intermediate may be formed *via* (C_{60}–PVCz)* exciplexes. As one of the possibilities, the ion-pair-like structure of a C_{60} radical anion and PVCz radical cation can be expected as an intermediate state between (C_{60}–PVCz)* exciplexes and the solvent-separated radical ions in solution. However, the broad absorption bands of $^{T}C_{60}^{*}$ and the PVCz radical cation make it difficult to determine the nature of the transient absorption band of the intermediate.

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