Study on Compatibility of Fullerene C$_{60}$ Derivative with Polymers and Estimation of Electron Trapping Ability

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Fullerene C$_{60}$ has poor compatibility with polymers. Therefore, it is difficult to control the aggregation state in a polymer. To improve the compatibility with polymers, a bismalonate segment in which has 2-(2-methoxyethoxy)ethyl groups was introduced to a C$_{60}$ skeleton. As a result, the C$_{60}$ derivative showed high compatibility with several polymers, and it was easy to obtain the polymer films that C$_{60}$ skeletons were dispersed homogeneously. The polyvinylcarbazole (PVK) based film containing either C$_{60}$ or the C$_{60}$ derivative (C$_{60}$ skeleton: 1 wt%) was prepared and the electron charges trapped by the C$_{60}$ skeletons were estimated. In consequence, the collected charges of the C$_{60}$ derivative were approximately twice as large as those of C$_{60}$. This result was speculated that the photocarrier generation efficiency of the C$_{60}$ derivative was higher than that of C$_{60}$, or the hopping conduction was not occurred easily in the PVK based film containing the C$_{60}$ derivative.

Key words: transient photocurrent method, fullerene C$_{60}$, compatibility with polymers, electron trapping ability

1. INTRODUCTION

Fullerene C$_{60}$ has characteristic electric and optical properties[1] owing to the truncated icosahedral molecular structure with the conjugated double bonds extended three dimensionally, and there have been many researches on the properties of both C$_{60}$ and conjugated polymer/C$_{60}$ composites for the past decade. For example, an efficiency of photocarrier generation in polyvinylcarbazole (PVK) is increased with C$_{60}$ doping[2]. However, since C$_{60}$ shows strong aggregate property, poor solubility in organic solvents, and low compatibility with polymers, it is difficult to disperse high concentration of C$_{60}$ homogeneously in the polymers. Therefore, in order to endow C$_{60}$ skeleton with high solubility in organic solvents and high compatibility with polymers, chemical modification methods of C$_{60}$ have been extensively studied. For instance, Hummelen *et al.* prepared the C$_{60}$ derivative 1-(3-methoxycarbonyl)propyl-1-phenyl [6,6] C$_{61}$ (PCBM) which was soluble in organic solvents[3]. And using PCBM/conjugated polymer systems, bulk hetero junction photovoltaic devises have been developed[4]. Hummelen and Heeger reported the photovoltaic devise of poly(*p*-phenylenevinylene) (PPV) derivative (MEH-PPV) together with PCBM[5]. This device showed higher power conversion efficiency than the device of MEH-PPV/C$_{60}$. Martens *et al.*[6] reported that the cluster size of PCBM dispersed in the PPV derivative (MDMO-PPV) film was less than 100 nm. The morphologies of PCBM in other conjugated polymers were described in the recent review[4]. On the other hand, the C$_{60}$ derivative which has long ether chains also showed high compatibility with conjugated polymers. Li *et al.* fabricated the photovoltaic devices that consisted of the PPV derivative (MEH-PPV) and the C$_{60}$ derivative with hydrophilic triethylene glycol ether

parts[7]. Furthermore, some C$_{60}$ derivative with ether chains such as the C$_{60}$ derivative 1 which has 2-(2-methoxyethoxy)ethyl ether chains was investigated for an electron beam resist material[8]. However, there have been few researches on other optical properties of conjugated polymers together with the C$_{60}$ derivative which has ether chains.

Therefore, in this research, electron trapping ability in the PVK/C$_{60}$ derivative 1 system was estimated using a transient photocurrent method and compared with that of PVK/C$_{60}$ system.
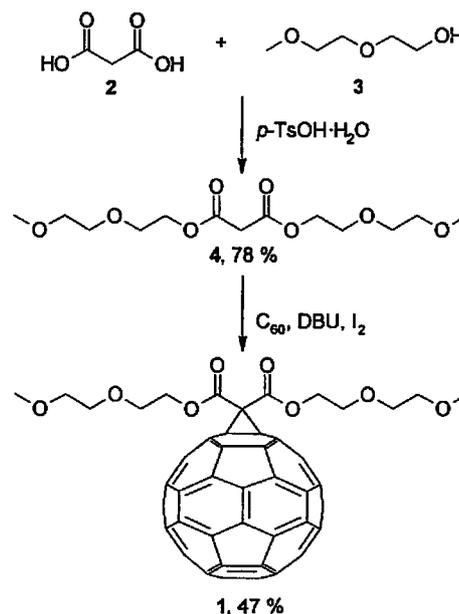
Scheme 1   Synthesis of C$_{60}$ derivative 1.

2. EXPRIMENTAL

2.1 Synthesis

The C_{60} derivative 1 was synthesized according to Scheme 1.

All solvents, starting materials and reagents were used without further purification.

Both ^{1}H NMR and ^{13}C NMR spectrum were measured with a Vrian Gemini 300 spectrometer.

2.2 Preparation of bis(2-(2-methoxyethoxy)ethyl)malonate 4.

A solution of malonic acid 2 (13.10 g, 126 mmol), 2-(2-methoxyethoxy)ethanol 3 (36.98 g, 300 mmol) and p-toluenesulfonic acid monohydrate (1.48 g, 7.8 mmol) in benzene (30mL) was heated and refluxed removing generated H_2O by a Dean-Stark trap. After heating for 35 h, the reaction mixture was washed up with 60 mL of saturated $NaHCO_3$ and 60 mL of brine. After dried over Na_2SO_4, the solvent was removed to gave the bismalonate 4 (30.38 g, 78 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.32 (t, 4 H, CH$_2$OCO), 3.73 (t, 4 H, OCH$_2$CH$_2$OCO), 3.7–3.6 (m, 4 H, CH$_3$OCH$_2$CH$_2$O), 3.6–3.5 (m, 4 H, CH$_3$OCH$_2$CH$_2$O), 3.47 (s, 2H, OCCH$_2$CO), 3.39 (s, 6H, CH$_3$O). ^{13}C NMR(75 MHz, CDCl$_3$): δ 166.99, 72.29, 70.95, 69.31, 65.02, 59.53, 41.73.

2.3 Preparation of C_{60} derivative 1

Bis(2-(2-methoxyethoxy)ethyl) malonate 4 (66.0 mg, 0.21 mmol), DBU (67.0 mg, 0.44 mmol), and iodine (50.6 mg, 0.20 mmol) was added to a solution of C_{60} (284.2 mg, 0.39 mmol) in toluene (300 mL) . After stirred at room temperature for 24 h, the reaction mixture was purified by a silica gel column chromatography (initial solvent; toluene, second solvent; toluene/ethyl acetate 10:1, final solvent; toluene/ethyl acetate 10:4) to give the C_{60} derivative 1 (103.5 g, 47 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.67 (t, 4 H, CH$_2$OCO), 3.89 (t, 4H, OCH$_2$CH$_2$OCO), 3.7–3.6 (m, 4 H, CH$_3$OCH$_2$CH$_2$), 3.6–3.5 (m, 4 H, CH$_3$OCH$_2$CH$_2$), 3.39 (s, 6H, CH$_3$O). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.51, 145.20, 145.15, 144.86, 144.65, 144.59, 143.86, 143.05, 142.99, 142.95, 142.16, 141.84, 140.90, 139.05, 71.88, 70.63, 68.77, 66.20, 59.15.

2.4 Preparation of polymer/C_{60} derivative 1 films and polymer/C_{60} films

The C_{60} derivative 1 (10.9 mg, 10.6 μmol) and polystyrene (PS) (10.8 mg; M.W. 208000) were dissolved in toluene (10.9 mL) to prepare the solution contained 1 mg/mL (0.12 wt%) of C_{60} derivative 1 and PS, respectively. A solution of the C_{60} derivative 1 (2.1 mg, 2.0 μmol) and polymethylmethacrylate (PMMA) (2.0 mg; M.W. 1380000) in toluene (2.0 mL), a solution of C_{60} (11.0 mg, 2.0 μmol) and PS (11.2 mg) in toluene (11.0 mL), and a solution of C_{60} (2.0 g, 2.8 μmol) and PMMA (1.9 mg) in toluene (2.0 mL) were also prepared in a similar manner. Each solution was cast on an indium tin oxide (ITO) electrode and dried naturally. The obtained films were consist of 50 wt% of C_{60} derivative 1 or C_{60}, and 50 wt% of polymer matrix, namely the ratio of C_{60} derivative 1 or C_{60} to polymer was 1:1 (w/w).

Dispersibility of the C_{60} derivative 1 in the PS or PMMA was compared with that of C_{60} by examination under an optical microscope.

2.5 Measurements of transient photocurrent method

A 1 cm^2 of ITO electrode with read electrode was made by acid etching from ITO coated glass.

The PVK/C_{60} derivative 1 film and the PVK/C_{60} film were formed on a square ITO electrode as follows. PVK (229.4 mg; M.W. 66100) and N-ethylcarbazole (155.4 mg, 79.6 mmol) were added to the 15 mL toluene solution of the C_{60} derivative 1 (5.6 mg 5.4 μmol) and heated in a sample tube until all of the substances were dissolved. Then, the solution was concentrated blowing N_2 gas to a viscous solution. The solution of the PVK/C_{60} system was prepared in a similar manner.

The concentrated solution was cast on the square ITO electrode and dried on a hotplate raising the temperature gradually from 45 °C to 120 °C. And then, after heating at 130 °C for 2 days in an oven, the film was dried under reduced pressure at 40–50 °C for 4 h. The obtained films were estimated to contain 1.39×10^{-5} mmol/g (1.4 wt%) of the C_{60} derivative 1 and 1.39×10^{-5} mmol/g (1 wt%) of C_{60}, respectively.

The cell for the measurement of the transient photocurrent method was prepared as follows (Fig. 1).

Two obtained films on the ITO electrode were heated at 200 °C to be softened and contacted closely each other opposite using preheated weight of stainless steal block. The cell thickness was adjusted with Teflon spacer (50, 75, 100, 125, 150μm). Finally, the cell was cooled down gradually.

The typical procedure of the transient photocurrent measurement is described below.

The cell was set on measuring equipment shown in Fig. 2, and then an electric field of 20 kV cm^{-1} was applied irradiating light with a wavelength of 500 nm. In case that the energy of the irradiated light was lager than
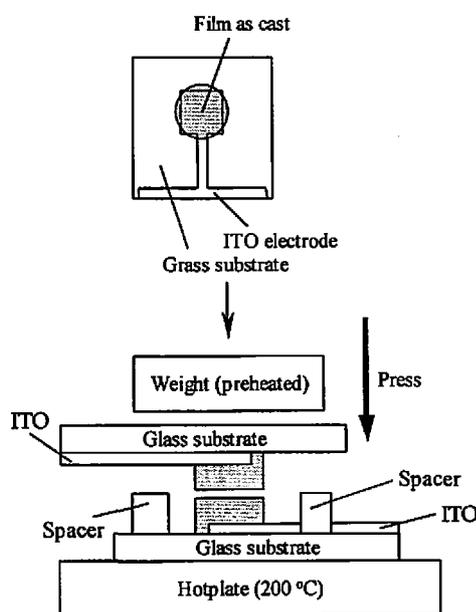

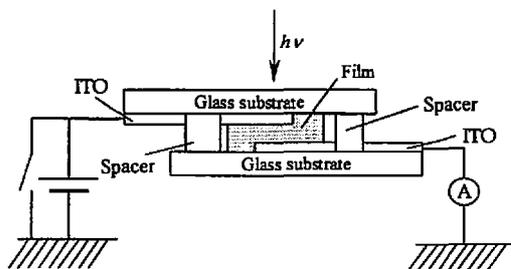Fig. 1   The schematic illustration of preparation process of the cell for the transient photocurrent method.

Fig. 2   The sketch of the cell for measurement of transient photocurrent method.

Fig. 3   Optical microscope images (×3000). (a) PS film containing 50 wt% of C_{60} derivative 1. (b) PMMA film containing 50 wt % of C_{60} derivative 1. (c) PS film containing 50 wt% of C_{60}. (d) PMMA film containing 50 wt% of C_{60}.

the band gap of C_{60} (1.8 eV), excitons (hole-electron pairs) were formed by photoexcitation. In the presence of a hole conductive material, the generated holes moved to ground by the applied electric field. Consequently, the remnant electrons were collected by the C_{60} skeletons in the film. When the photocurrent got to constant, the applied electric field was aborted simultaneously with shutting down the light irradiation. After these operations, small amount of residual holes initially moved to the direction of ground, and then, the electrons trapped by C_{60} skeletons moved to the same direction. Therefore, the current corresponding to the movement of the electrons was detected later than that of the holes by the galvanometer. The total charges of the electrons trapped by the C_{60} skeletons were estimated by integrating the current curve from the moment when the current first became 0 A (when the holes were removed completely) to the time when the electrons finished to move (50 seconds later).

3. RESULTS AND DISCUSSION

3.1 Dispersibility of the C_{60} derivative 1 in polymers

Fig. 3 shows the optical microscope images of the PS/C_{60} derivative 1 film, the PMMA/C_{60} derivative 1 film, PS/C_{60} film, and PMMA/C_{60} film. Since compatibility of C_{60} with polymers was low, needle crystals and aggregated clusters of C_{60} molecules were observed in both PS film and PMMA film containing 50 wt% C_{60} (Fig. 3 c and d). In contrast, 50 wt% of the C_{60} derivative 1 was dispersed homogeneously in both PS and PMMA, and no aggregated clusters of C_{60} skeletons and/or crystals were formed (Fig. 3 a and b).

These results show that compatibility of C_{60} skeleton with polymers was improved drastically owing to the introduced hydrophilic ether chains.

3.2 Estimation of electric charges trapped by the C_{60} skeletons

The electron trapping ability was estimated on the basis of the collected electron charges by C_{60} skeletons.

In the transient photocurrent measurement, both of the C_{60} skeletons and the charge transfer complexes between the C_{60} skeletons and carbazole groups were excited to excited states by the light with a wavelength of 500 nm and excitons (hole-electron pairs) were formed. In the presence of carbazole moieties, the generated holes moved to ground and were removed from the film by the applied electric field and the remnant electrons were trapped by the C_{60} skeletons to cause the residual potential at the film. After aborting the applied electric

field simultaneously with shutting down the light irradiation, the current which cancelled out the residual potential run through the film. Therefore, the electron tapping ability of the C_{60} skeleton could be estimated by measuring of this current.

The results of transient photocurrent measurement for the PVK/C_{60} derivative 1 system and the PVK/C_{60} system are summarized in Table I and Table II, respectively. Although the number of C_{60} skeletons in the PVK/C_{60} derivative 1 film was nearly equal to that in the PVK/C_{60} film, the collected charges of the C_{60} derivative 1 were approximately twice as large as those of C_{60}. This result was speculated that the photocarrier generation efficiency of the C_{60} derivative 1 was higher than that of C_{60} or the hopping conduction was not occurred easily in the PVK/C_{60} derivative 1 film.

The photocarrier generation was scarcely occurred both inside of the C_{60} derivative 1 clusters and the C_{60} clusters caused by recombination due to the instability of the C_{60} cation[9]. Therefore, most of the photocarriers were generated at the interface between the clusters of the C_{60} skeletons and the hole conductive molecules (the carbazole moieties). Since the interface area increases in proportion as the cluster size of the C_{60} skeletons becomes smaller, the photocarrier generation efficiency of the C_{60} derivative 1 was considered to become higher than that of C_{60} owing to its high dispersibility in PVK.

On the other hand, one of the important factors in determining the efficiency of electron transfer in the film is the distance between two C_{60} skeletons.

The average distance of balls in a space is given by equation 1.

$$(\text{number density of balls})^{-1/3} = (\text{diameter of ball})   \quad (1)$$

Since the number density of C_{60} skeletons is approximately 8.2×10^{18} cm^{-3} and the diameter of C_{60} skeleton is 0.71 nm, the average distance between two C_{60} skeletons was calculated to be approximately 4.3 nm. It was reported that the charge carrier distances of polyvinyl acetate/polyvinylidene fluoride blends were in the range of 5.5–7.5 nm[10]. Therefore, electron transfer

Table I   Results of transient photocurrent method for the PVK/C$_{60}$ derivative 1 film.

Thickness/μm	Number of C$_{60}$ skeleton	Collected charges/nC	Number of remnant electron	Electron trapping probability/%
75	6.16×10^{16}	6236	3.89×10^{13}	0.063
100	8.22×10^{16}	11973	7.47×10^{13}	0.091
125	1.03×10^{17}	14159	8.84×10^{13}	0.086
150	1.23×10^{17}	16030	1.00×10^{14}	0.081

Table II   Results of transient photocurrent method for the PVK/C$_{60}$ film.

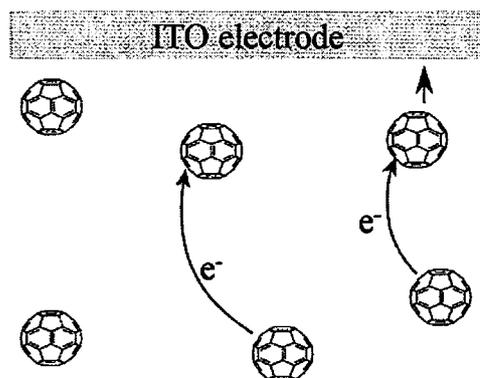| Thickness/μm	Number of C$_{60}$ skeleton	Collected charges/nC	Number of remnant electron	Electron trapping probability/%
50	4.09×10^{16}	2212	1.38×10^{13}	0.034
75	6.14×10^{16}	5368	3.35×10^{13}	0.055
100	8.19×10^{16}	6344	3.96×10^{13}	0.048
125	1.02×10^{17}	7113	4.44×10^{13}	0.043

Fig. 4   The illustration of hopping conduction in the PVK film. The average distance between two C$_{60}$ skeletons is approximately 4.3 nm. Electron hopping between the C$_{60}$ skeletons is enhanced by the π-conjugated system of the polymer.

through the film by hopping was expected to occur both in the PVK/C$_{60}$ derivative 1 film and the PVK/C$_{60}$ film (Fig. 4).

For the efficient electron transfer by hopping, the wave function of the hopping sites are required to overlap closely each other and it becomes difficult to occur in proportion as the overlap get smaller. As for the C$_{60}$ derivative 1, it was speculated that the wave function of the derivative was changed by chemical modification of the C$_{60}$ skeleton and overlap of the wave function between the C$_{60}$ derivatives 1 was smaller than that in case of C$_{60}$. Therefore, the trapped electrons were not easily transferred by hopping through the film and the collected charges of the C$_{60}$ derivative 1 were larger than those of C$_{60}$.

4. CONCLUSIONS

The C$_{60}$ derivative 1 dispersed homogeneously in polymers due to the long ether chains was synthesized and estimated the electron trapping ability using the transient photocurrent method. The collected charges of the C$_{60}$ derivative 1 were approximately twice as large as those of C$_{60}$. This result was speculated that the photocarrier generation efficiency of the C$_{60}$ derivative 1 was higher than that of C$_{60}$ owing to its high dispersibility or the hopping conduction was not occurred easily in the PVK/C$_{60}$ derivative 1 film.

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