Photophysical and Photochemical Behavior of Triplet Excited State of C_{60} in Unimer Micelle

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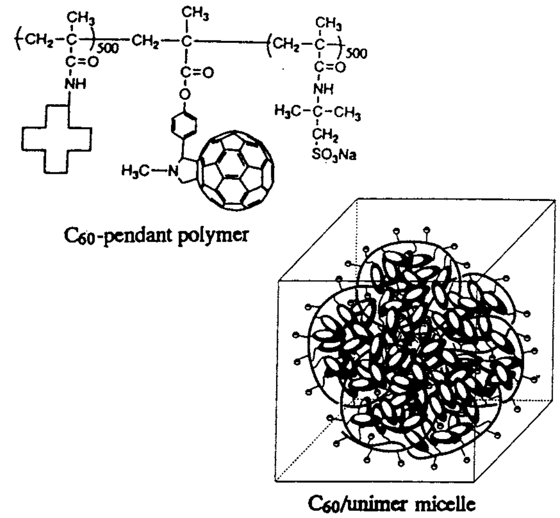
Photophysical and photochemical properties of C_{60}-pendant polymer in aqueous solution, in which C_{60} was covalently incorporated into polymer cluster (C_{60}/unimer), have been studied by transient absorption spectroscopy. $^3C_{60}$*/unimer was quenched by O_2 in two routes; the initial fast decay component was increased by addition of a detergent. From these observations, kinetic models for the quenching are proposed.

Photoexcited fullerenes act as both good energy-transfer and electron-transfer reagents.[1] In the presence of O_2, the triplet excited states of fullerenes transfer their energy to the ground state oxygen, yielding singlet oxygen with high efficiency.[2] Although most of the photochemistry of fullerenes have been performed in organic solvents, the importance of the photochemistry of fullerenes in aqueous solution has been pointed out from the standpoint of bio-activity of photo-excited fullerenes.

Since pristine fullerenes are insoluble in water, it is difficult to study the properties of fullerenes in aqueous solution. Some efforts have been paid to dissolve fullerenes in aqueous solution. The inclusion complex of C_{60} into a water-soluble host molecule of γ–cyclodextrin (γ-CD) exhibits high solubility in water.[3] It is reported that fullerenes dissolve slightly both in micellar solution and in water-soluble polymer solution.[3] In the previous paper, the synthesis and photophysical properties of the C_{60}-pendant polymer (Scheme 1) have been reported.[4] In the C_{60}-pendant polymer, the hydrophobic group inside surrounds the C_{60}-moiety, while the hydrophilic group outside exposes to water interface forming highly constrained micro-cluster; i.e., C_{60}-unimer micelle.[4]



Scheme 1.

Since molecular weight of polymer was evaluated to be around 1.5×10^5, a C_{60}-moiety is expected to be included in each polymer chain.[4] In the present laser photolysis study, the concentration of the C_{60}-moiety in aqueous solution was adjust to be 2.0×10^{-5} mol dm^{-3}. Nanosecond time-resolved absorption spectra were measured by combination of exciting source [THG (355 nm) of a Nd: YAG laser (fwhm 6 ns)] and monitoring light system using InGaAs detector. All the samples for the laser flash photolysis were deaerated by argon bubbling for 10 min before measurements. The O_2-concentration was controlled by O_2 bubbling.

In the steady-state absorption spectrum of C_{60}/unimer micelle in aqueous solution, the observed broad and blue-shifted absorption bands compared with those of the pristine C_{60} and pyrrolidino-substituted C_{60} in organic solvents suggested that there exists strong hydrophobic interaction between C_{60}-moiety and surrounding aliphatic groups in the polymer.[4] The fluorescence band of C_{60}/unimer micelle appeared at 560 nm, which is broader and blue-shifted compared with those of the pyrrolidino-substituted C_{60} in THF.[4] Although quantum yield of C_{60}/unimer micelle is similar to that of pristine C_{60} in benzene, lifetime of C_{60}/unimer micelle is twice as longer as that of pristine C_{60} in benzene.[4]

Triplet excited states of C_{60}/unimer micelle were investigated by transient spectroscopy. Laser irradiation of C_{60}/unimer micelle in aqueous solution generates a broad transient absorption band at 640 nm as shown in Figure 1. The transient absorption band can be attributed to the triplet excited state of C_{60}/unimer micelle ($^3C_{60}$*/unimer micelle), since the absorption band was quenched in the presence of O_2, a typical triplet ener-

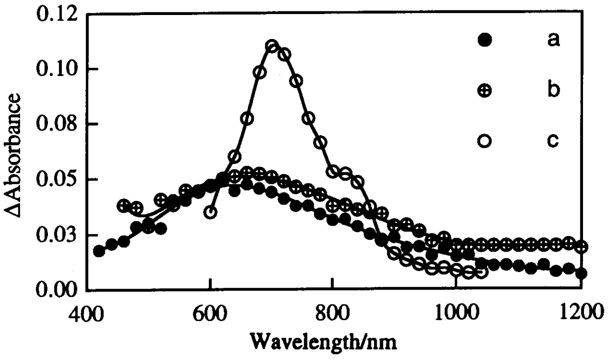


Figure 1. Transient absorption spectra at 1 μs after THG laser irradiation of (a) C_{60}/unimer micelle (50 mg dm^{-3}) in water, (b) C_{60}/unimer micelle in the presence of $C_{12}E_6$ (0.3×10^{-3} mol dm^{-3}) in water, and (c) N-methylphenylpyrrolidine substituted C_{60} in benzene.

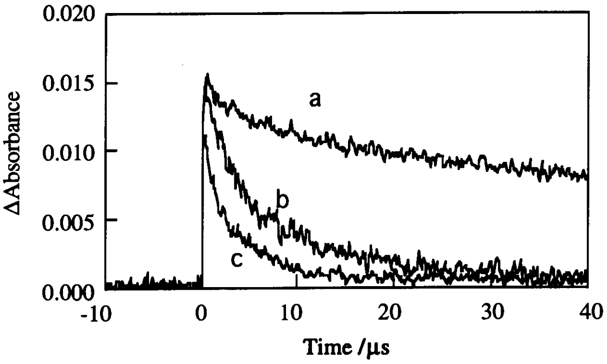


Figure 2. Decay time-profiles; (a) $^3C_{60}$*/unimer micelle in Ar-saturated aqueous solution, (b) $^3C_{60}$*/unimer micelle in O_2-saturated solution, and (c) $^3C_{60}$*/unimer micelle in O_2-saturated solution in the presence of $C_{12}E_6$ (0.3×10^{-3} mol dm^{-3}).

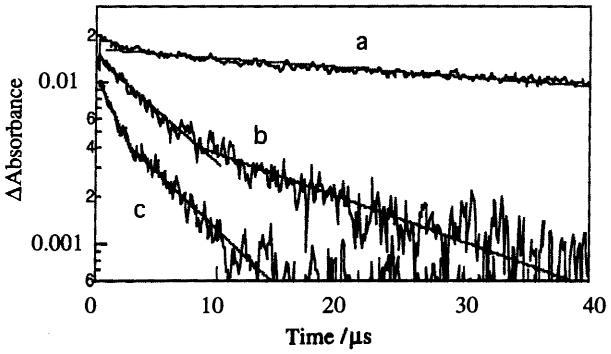


Figure 3. First-order plots of decay-time profiles of $^3C_{60}$*/unimer micelle; (a)-(c) correspond to (a)-(c) in Figure 2.

gy quencher for pristine C_{60}. The peak position is blue-shifted by 100 nm and 60 nm, respectively, compared with those of pristine $^3C_{60}$* (740 nm)[5] and the triplet state of *N*-methylphenylpyrrolidine substituted C_{60} (700 nm) in benzene.[5] On addition of a detergent (dodecyl hexaethylene glycol monoether; $C_{12}E_6$) in order to destroy the unimer micelle, the transient absorption spectrum was similar to that of $^3C_{60}$*/unimer micelle, although a slight shift of the peak position to longer wavelength region was observed.

The absorption time-profile of $^3C_{60}$*/unimer micelle in Ar-saturated aqueous solution (curve a in Figure 2) can be fitted by two components: Initial fast decay part with lifetime of 10 μs is 15% and later slow decay part with lifetime of 67 μs is 85%. The lifetime of the slow decay component of $^3C_{60}$*/unimer micelle is longer than that of pristine $^3C_{60}$* (26 μs). On addition of the detergent ($C_{12}E_6$) in Ar-saturated aqueous solution, the decay of $^3C_{60}$*/polymer was also two components; each lifetime was similar to the respective lifetime of $^3C_{60}$*/unimer micelle, indicating that micro-environment around $^3C_{60}$*/unimer micelle is not completely destroyed by the detergent.

As fast decay component of $^3C_{60}$*/unimer micelle, there are some possibilities; one is energy transfer to O_2, which remained in the unimer micelle after Ar-bubbling. The other possibility is the triplet-triplet annihilation process, when more than one C_{60} moieties are included in a micelle.

The decay rate of $^3C_{60}$*/unimer micelle was accelerated on addition of O_2 to aqueous solution (decay curve b in Figures 2 and 3). From the first-order plots of the decay curve b, the first order decay rate constants of the fast decay (70 %) and slow decay (30 %) were evaluated to be 1.5×10^5 s^{-1} and 4.8×10^4 s^{-1}, respectively. To explain the two decay processes, we propose two kinetic models for $^3C_{60}$*/unimer micelle. In the first kinetic model, the quick decay part is attributed to the reactive $^3C_{60}$*/unimer micelle, in which $^3C_{60}$* is present near the surface of the unimer micelle and the slow decay is attributed to the unreactive $^3C_{60}$*/unimer micelle, in which $^3C_{60}$* is present in the center of the unimer micelle. In this kinetic model, the second-order quenching rate constants (k_q) of $^3C_{60}$*/unimer micelle can be evaluated to be 1.2×10^8 and 3.7×10^7 mol^{-1} dm^3 s^{-1}, respectively, on the basis of O_2 concentration in aqueous solution (1.3×10^{-3} mol dm^{-3}). In alternative model, O_2 inside the unimer micelle reacts with $^3C_{60}$* in micelle more easily than O_2 outside the micelle, leading to the generation of the two different decay processes.

On addition of the detergent (curve c in Figure 2), the decay rates increase both in the fast component (3.7×10^5 s^{-1}) and slow component (1.5×10^5 s^{-1}). The increase in the fast decay component is due to the destroy of $^3C_{60}$*/unimer micelle by the detergent, exposing the $^3C_{60}$*-moiety to O_2-saturated aqueous solution. The slow decay component suggests the presence of the $^3C_{60}$*-moiety surrounded by the polymer chains ($^3C_{60}$* polymer). The k_q values were estimated to be 2.8×10^8 and 1.2×10^8 mol^{-1} dm^3 s^{-1} for the fast- and slow decays, respectively .

The decay rates of $^3C_{60}$*/unimer micelle and $^3C_{60}$* polymer were not accelerated on the addition of water-soluble electron donors such as *p*-anisidine (50 mmol dm^{-3}). Thus, photoinduced electron transfer via $^3C_{60}$*/unimer micelle and $^3C_{60}$*-polymer was not observed. Approach of the relatively large donor-molecules to $^3C_{60}$*/unimer micelle (or $^3C_{60}$*-polymer) was hindered by the polymer networks, whereas small molecules such as O_2 are accessible to $^3C_{60}$* in unimer micelle (or polymers), resulting in the quenching of $^3C_{60}$*.

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