Electron-Transfer Quenching Accompanied by Highly Efficient Energy Migration in Polymer Langmuir-Blodgett Films¹

Toru Yatsue and Tokuji Miyashita*

Department of Molecular Chemistry and Engineering, Tohoku University, Aoba Aramaki, Aoba-ku, Sendai 980-77, Japan

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Copolymers of N-dodecylacrylamide (DDA), which has the excellent property to form LB film, and 2-(9carbazolyl)ethyl acrylate (CzEA) with various copolymer compositions were prepared to investigate the electron transfer quenching of the excited carbazole chromophore in LB film assembly. The copolymers form a stable condensed monolayer and LB film in a wide range of copolymer compositions. In LB films, the emission spectra show only the structured emission characteristic of the monomeric carbazole chromophore at 350 nm and no excimer emission whereas the corresponding N-vinylcarbazole copolymer LB films in the previous study show strong emission from excimer which acts as an energy trapping site. For the quenching study, the DDA-CzEA monolayer are in direct contact with the mixed monolayer of barius stearate and stearyl viologen quencher. The emission of the excited carbazole was quenched effectively by a small amount of the viologen quencher in the mixed monolayer. The quenching efficiency was varied linearly by the mole fraction of carbazole chromophore in the copolymer monolayer. The effective electron-transfer quenching is attributed to the highly efficient energy migration between carbazole chromophores, which is assisted with a regular alignment of carbazole chromophore and no excimer formation in the copolymer LB films. The plots of $\ln(I_0/I - 1)$ (I in the presence of and I_0 in the absence of the quencher) vs distance (R) between the quenchers gave a linear relationship. The mechanism of electron transfer quenching in the LB film assembly is discussed on the basis of electron-tunneling and energy migration.

Introduction

Photosynthesis in green plants provides life energy on earth by changing solar energy to chemical energy in thylakoid membranes. This efficient photoenergy conversion system consists of regular molecular array systems in organized molecular assemblies made of amphiphilic molecules such as phospholipids, where an efficient energy transfer and electron transfer are performed.² Various molecular organized assemblies have been attempted to realize an efficient photoenergy conversion system from the viewpoint of artificial photosynthesis.³⁻⁸ Supramolecules in which donor and acceptor molecules/components are covalently linked were synthesized to examine key parameters of electron transfer process.9,10 Langmuir-Blodgett (LB) film is also one of the fascinating molecular assemblies to fabricate a controllable molecular array for efficient electron transport.^{6,11–13} Electron transfer process, however, in a solid matrix is complicated due to an irregular distribution and/or an aggregation of probe molecules. In this respect, the LB technique is the best tool for a basic research of electron transfer process in solid systems. The distance between donor and acceptor molecules and the two-dimensional density can be controlled at a molecular level for the study of the electron transfer process by using the LB technique.

The incorporation of photofunctional chromophores into LB films has been tried by various methods. Amphiphilic chromophores having an ability of LB film formation have been synthesized.^{14,15} As a more general method, a physical mixing of the chromophore with a long alkyl-chain fatty acid forming a stable LB film is employed.^{16,17} Recently, we proposed a copolymerization method to incorporate various functional chromophores into polymer LB films as a comonomer of

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N-dodecylcrylamide (DDA) which has an excellent ability to form a stable LB film.¹⁸⁻²⁰

In the previous study,²¹ we have succeeded in preparing stable polymer LB films containing the carbazole chromophore, which is known to show a wide range of photofunctions. $^{22-26}$ as the form of copolymer of DDA with N-vinylcarbazole (VCz). Electron transfer from the excited carbazole chromophore in the copolymer monolayers to a stearyl viologen (SV) acceptor and stearylpyridinium derivatives incorporated in the adjacent monolayer has been studied in LB film assemblies using an emission quenching method. It was found that very effective quenching takes place due to the energy migration between the carbazole chromophores which are aligned regularly in the copolymer monolayer. We have proposed a quenching scheme where the quenching in the monolayer is determined by the result of the competition of energy transfer to the energy trapping site (excimer formation site) or to the carbazole chromophore just facing to the quenchers (Scheme 1). To achieve more efficient electron-transfer systems, it is required to design a molecular assembly where an energy trapping site is not formed; that is, there is no excimer formation site in the copolymer monolayer. Recently Yamamoto et al. reported that poly[2-(9-carbazolyl)ethyl methacrylate] (CzEMA) does not form an excimer, which acts as an energy trapping site, even in the solid state.^{27,28} According to the quenching mechanism shown in Scheme 1, if we could prepare the polymer LB films with the non-excimer-forming carbazole derivatives instead of N-vinylcarbazole, very effective electron transfer accompanied by highly efficient energy transfer would be realized.

In the present work, therefore, we have tried to fabricate the monolayer and LB films from the DDA copolymer with 2-(9carbazolyl)ethyl acrylate (CzEA) (Chart 1) and investigated the electron transfer quenching of the excited carbazole chromophore by viologen quencher in the LB assembly to compare

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SCHEME 1



with the results in the previous work. Very effective electron transfer quenching accompanied by highly efficient energy migration was observed, and the quenching mechanism proposed in the previous study can be confirmed.

Experimental Section

Materials. 2-(9-Carbazolyl)ethyl Acrylate (CzEA). 2-(9-Carbazolyl)ethyl acrylate (CzEA) was prepared from the reaction of acryloyl chloride with 9-(2-hydroxyethyl)carbazole in the presence of triethylamine in dichloromethane. 9-(2-Hydroxyethyl)carbazole was prepared from the following; a DMF solution of carbazole and ethylene carbonate is refluxed in the presence of a small amount of sodium hydroxide. After being cooled to room temperature, the reaction mixture is extracted with benzene. White crystalline 9-(2-hydroxyethyl)carbazole was obtained by recrystallization from hexane.

DDA-CzEA Copolymers. The copolymers were prepared by free-radical polymerization of N-dodecylacrylamide (DDA) with CzEA in benzene at 60 °C with 2,2'-azobis(isobutyronitrile) as a thermal initiator. The copolymers are purified by dissolution in chloroform, followed by filtration and precipitation in a large excess of acetonitrile. The molar ratios of the CzEA in the copolymers were determined by measuring nuclear magnetic resonance (NMR) spectroscopy and UV-visible absorption spectra. The number average molecular weights were measured by gel permeation chromatography (GPC); the molecular weights for the copolymers with the CzEA mole fraction of 31.3, 20.8, 15.4, 9.1, and 5.3% are 4.0×10^4 , 3.3×10^4 , 2.7×10^4 , 1.3×10^4 , and 0.9×10^4 , respectively.

Preparation of Langmuir–Blodgett Films. An automatic working Langmuir trough (Kyowa Kaimen Kagaku HBM-AP with a Wilhelmy-type film balance) was used for the measurements of surface pressure–area isotherms (π –A isotherms) and preparation of LB films. All copolymers were dissolved in chloroform (spectroscopic grade) at a concentration of about 10^{-3} M and spread on a water surface. The mixtures of stearyl viologen (SV) with stearic acid were spread on the water subphase containing BaCl₂ (3 × 10^{-5} M) and KHCO₃ (4 × 10^{-4} M) at 19 °C from a solution of chloroform containing 5% methanol. Distilled water (Millipore Milli-QII) was used. The



Figure 1. Surface pressure – area isotherms of DDA-CzEA copolymer monolayers at 19 °C.

quartz slides used for the deposition of monolayers are previously cleaned in boiling H_2SO_4 -HNO₃ (2:1) solution, and made hydrophobic with dichlorodimethylsilane, and are coated in advance by poly(*N*-dodecylacrylamide) LB film with four layers to prepare uniform surface and to remove the influence of bare quartz slide. Fluorescence spectra and UV-visible absorption spectra were measured with a Hitachi 850 spectrofluorophotometer and a Shimadzu UV-365 UV-visible spectrophotometer, respectively.

Results and Discussion

Monolayer and Multilayers Formation. The DDA-CzEA copolymers with various copolymer compositions were spread on water surface from chloroform solution. The π -A isotherms for the copolymers at 19 °C are shown in Figure 1. The isotherms have a steep rising in surface pressure and also have a high collapse pressure, which decreased with an increase in CzEA mole fraction in the copolymers. It is apparent that the DDA-CzEA copolymers form stable and condensed monolayers on the water surface in the same manner as the DDA copolymers with N-vinylcarbazole. The average limiting surface areas per monomer in the copolymers are estimated by extrapolating the steep region of the isotherms to zero surface pressure. The average surface area increases almost linearly with CzEA mole fraction (Figure 2). The area for CzEA monomer can be calculated from the average areas by assuming the area of DDA to be 0.28 nm²/monomer.²⁰ The obtained area for CzEA monomer is around 0.4 nm²/molecule regardless of the mole fraction of CzEA in the copolymers. This means that the CzEA is dispersed having its own surface area in the copolymer monolayers. The surface area is consistent with the value estimated from the CPK (space-filling) model where the polymer chain is laid horizontally on the water surface and the dodecyl alkyl chains and the carbazole ring are oriented vertically to the water surface (Figure 3). The copolymer monolayers can be transferred onto a solid support at 25 mN/m by both downward and upward strokes at a dipping speed of 10 mm/min with a transfer ratio of unity (Y-type deposition). The copolymer LB films with various CzEA mole fractions are safely obtained.

The emission spectra of the copolymer LB films (four layers) for the copolymer with various CzEA contents are shown in Figure 4. The structured fluorescence around at 350 nm can be assigned to the emission for the locally excited state of the carbazole chromophore.^{29,30} No excimer emission around 420



Figure 2. Average surface area per monomer and the calculated limiting surface area for CzEA monomer as a function of CzEA mole fraction.



Figure 3. A probable orientation of DDA-CzEA monolayer on the water surface.

nm is observed for the copolymer LB films even with a high content of CzEA (31.3%) as expected from the results of Yamamoto et al. The emission spectra are not changed with the number of layers. For the DDA copolymers with VCz in the previous study a strong excimer emission is observed in LB film even at 12.5% mole fraction of VCz.²¹ Moreover, the excimer emission increases with the number of deposited layers due to energy transfer to a small amount of excimer formation site (the nearest VCz-VCz pair) via energy migration between the carbazole chromophores.²¹ The reason why the DDA-CzEA copolymer does not show excimer emission can be explained by a free rotation of ethyl group linked to the carbazole chromophore. The results from the π -A isotherms and the fluorescence spectroscopy indicate that the carbazole chromophore can be incorporated into DDA polymer LB films with a molecular dispersion in the monolayer, and uniform



Figure 4. Emission spectra of various DDA-CzEA copolymers in LB films (four layers).



Figure 5. Schematic illustration of the structure of LB film assembly for quenching.

copolymer LB films with no energy trapping site (no excimer formation site) can be fabricated.

Electron Transfer Quenching for DDA-CzEA Copolymer in the LB Film Systems. The electron transfer from the photoexcited carbazole chromophore in DDA-CzEA copolymers to viologen acceptor was investigated by the emission quenching method using the LB film assembly shown in Figure 5, where foure DDA homopolymer monolayers are coated on a bare quartz slide and then the DDA-CzEA copolymer monolayer, stearyl viologen monolayer mixed with barium stearate, and finally again four the homopolymer monolayers are coated. It is confirmed in the previous study that the mixed monolayer of stearyl viologen (SV) with barium stearate (St) forms a stable condensed monolayer for more diluted mixture than $St/SV^{2+} = 5/1$ molar ratio. The intensity of the monomer emission at 350 nm from the excited carbazole in the DDA-CzEA copolymer monolayer decreased by the presence of SV in the mixed monolayer in the LB assembly. The emission quenching is due to electron transfer from the photoexcited



Figure 6. Plots of relative emission intensity (I/I_0) against viologen density.

carbazole to the viologen quencher; this process is an exothermic process ($\Delta G = -2.13$ V).

$$Cz^* + SV \rightarrow Cz^{*+} + SV^{*+}$$
(1)

The extent of the decrease in the emission intensity due to the electron transfer quenching depended on the two-dimensional density of the viologen in the monolayer, which can be varied by the mixing ratio of the stearyl viologen with the inert barium stearate (St). The relative steady state emission intensities I/I_0 (I in the presence and I_0 in the absence of the viologen, that is, the emission intensity for the monolayer covered with the barium stearate monolayer with no SV) plotted against the density of the viologen quencher for the copolymer monolayers with various CzEA contents are shown in Figure 6. Apparently, I/I_0 decreases in the presence of a small amount of SV, indicating that very effective quenching occurs. The I/I_0 value depends on the two-dimensional density of SV. Moreover, the quenching efficiency increases with the mole fraction of CzEA, in the order of DDA-CzEA (5.3%) < DDA-CzEA (15.4%) < DDA-CzEA (31.3%). This order is reasonable, because the probability that the carbazole chromophore just facing viologen quencher is excited should increase with the mole fraction of CzEA. In the previous work on the N-vinylcarbazole (VCz) copolymers, however, the quenching efficiency was not correlated linearly with the mole fraction of VCZ. The quenching for the copolymer with 12.5% VCz content was the most effective, compared with that for the copolymer with 31.3 or 6.4% VCz content. This is explained by the mechanism shown in Scheme 1; that is, the excited energy absorbed by the carbazole chromophore is migrated between the carbazole chromophores in the DDA-VCz copolymer monolayer, and when the migrating energy arrives at the carbazole facing to the viologen quencher, electron transfer quenching may occur. On the other hand, when the migrating energy arrives at an energy trapping site (an excimer formation site), the energy would be trapped. Therefore, the quenching efficiency is determined from the results of competition of the energy migration to the carbazole facing to SV quencher and the energy trapping at the excimer formation site. The monotonic increase in the quenching efficiency with the mole fraction of CzEA in the present work supports the quenching mechanism in Scheme 1. We can therefore conclude that the effective electron-transfer quenching accompanied by highly efficient energy migration can be realized in the DDA-CzEA copolymer LB films.



Figure 7. Plots of $\ln(I/I_0 - 1)$ as a function of distance (*R*) between viologen quenchers.

The following photochemical processes for the excited carbazole chromophore in the copolymer monolayer in the absence and presence of viologen quencher can be considered

$$Cz^* \xrightarrow{k_f} Cz + h\nu$$
 (2)

$$Cz^* \xrightarrow{k_d} Cz + kT$$
 (3)

$$Cz^* \xrightarrow{k_{q_1}} Cz^+$$
 (4)

where k_f , k_d , and k_{qt} are the rate constants for fluorescence, thermal deactivation, and quenching process of the excited carbazole, respectively. The quenching process is due to electron transfer of the excited CzEA to SV quencher via an electron-tunneling mechanism, because of the absence of diffusion in LB film. The relative emission intensity in the absence (I_0) and presence (I) of SV quencher is given as

$$I_0/I = 1 + k_{\rm qt}/(k_{\rm f} + k_{\rm d}) = 1 + k_{\rm qt} \tau_0 \tag{5}$$

where τ_0 is the lifetime of the excited CzEA in the absence of quencher. Recent studies³¹⁻³⁵ on electron transfer reaction in a rigid matrix suggest that rate constant for electron transfer via electron-tunneling mechanism depends exponentially on the distance (*r*) between the donor and acceptor

$$k_{\rm at} = k(0) \exp(-(r - R_0)/a)$$
 (6)

where a is the range parameter, which is related to the binding energy at the electron donor or barrier height, and R_0 corrects for the finite size of the reactants. From eqs 5 and 6, the following relation is obtained

$$\ln(I_0/I - 1) = -(r - R_0)/a + \ln(k(0)\tau_0)$$
(7)

The distance between CzEA and SV depends linearly on the distance of SV to SV (2*R*), which is calculated from the twodimensional density (n_q (molecules/nm²)) of SV in the monolayer matrix ($R = (n_q/\pi)^{-1/2}$ (nm)). The plots of $\ln(I_0/I - 1)$ vs *R* for the quenching in the LB films are shown in Figure 7. A good linear relationship was obtained for all the copolymer LB films, supporting eq 7. The half-quenching distance ($R_{1/2}$), which is defined as the distance giving half the emission intensity ($I/I_0 = 0.5$), was obtained from the plots in Figure 7. $R_{1/2}$ are collected in Table 1 together with the results for the Electron Transfer with Energy Migration in Polymer LB Films

TABLE 1: Half-Quenching Distance $(R_{1/2})$ for the Quenching of DDA-CZEA and DDA-VCz Copolymers in LB Films

DDA-CzEA		DDA-VCz	
carbazole content (%)	<i>R</i> _{1/2} (nm)	carbazole content (%)	<i>R</i> _{1/2} (nm)
31.3	3.1	31.3	1.9
15.4 -	2.3	12.5	2.8
5.3	1.4	6.4	

LB films of DDA-VCz copolymers. Apparently, the halfquenching distances for the DDA-CzEA LB films are larger than those for the DDA-VCz copolymer system, indicating that more effective quenching occurs in the DDA-CzEA LB films. The arrangement of carbazole chromophores along the polymer chain and the orientation of them in the LB film in the present polymer LB system would be favorable to the energy migration, resulting in the effective quenching.

In conclusion, efficient electron transfer accompanied by highly efficient energy migration can be realized using DDA-CzEA copolymer LB films, where the regular alignment of the carbazole chromophores without excimer formation, energy trapping site, and then the quenching mechanism proposed in the previous work was confirmed. As further extension, it is expected that the present polymer LB systems can be applied to efficient photoenergy conversion system in artificial photosynthesis.

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