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Induced circular dichroism of merocyanine dye in the self-assembled polymeric nanoparticles

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Abstract

The core–shell type nanoparticles composed of poly(γ-benzyl-L-glutamate) (PBLG) as hydrophobic inner core and poly(ethylene oxide) (PEO) as hydrophilic outer shell are formed from organic solution of the block copolymer by the diafiltration method. Amphiphilic merocyanine dyes (MDs) were self-assembled in the self-assembled copolymeric nanoparticles which provide a chiral microenvironment as red-shifted aggregates (J-aggregates). Also, the circular dichroism (CD) of MD was induced in the self-assembled copolymeric nanoparticles with negative and positive Cotton effect in the range of 575–625 nm whose crossing point matched $\lambda_{\max}$ in the UV region of MD. This result indicated that the PBLG chains and MDs were associated together to form spherical nanoparticles by hydrophobic interaction and the chiral PBLG core in the self-assembled copolymeric nanoparticles induced CD of J-aggregated MD. The helix sense of induced circular dichroism (ICD) of MD in the copolymeric nanoparticles was affected by the helix sense of PBLG in the copolymeric nanoparticles. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Nanoparticle; Merocyanine; Induced circular dichroism

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1. Introduction

The circular dichroism induced by a chiral environment has been extensively studied with characteristic of chiral compound. Induced circular dichroism (ICD) has been observed in several systems. Schuster et al. reported an ICD in cyanine borate penetrated ion pairs [1]. Also, it was reported that aggregates of dyes and aromatic molecules gave an ICD spectra in the UV or visible region [2]. Especially, the ICD system that has been much more widely studied is interested in the induction of optical activity by entrapping reactive species as the guest molecules, such as anionic azo compounds [3], diazirin chromophore, [4] bilirubin [5] and achiral cyanine dyes [6] in the host molecules such as cyclodextrins [3–6], cyclophane [7,8] and a helical peptide [9]. The host–guest complex formed by covalent link or physical interaction shows an ICD in the UV or visible region of the guest molecules.

Merocyanine dye (MD) is characterized by a polymethin chain connecting a nitrogen and an oxygen. It shows unique molecular stacks, so-called J-aggregates [10,11], which exhibit a narrow absorption peak red-shifted from that of a monomeric dye. Recently, MD has attracted much attention in the field of solar energy conversion due to the striking photoconductive properties [12,13]. In addition, J-aggregated MDs have been applied to nonlinear optical materials [14].

In the previous work, we reported conformational transition of nanoparticles composed of diblock copolymer based on poly(γ-benzyl-L-glutamate) (PBLG) as the core and poly(ethylene oxide) (PEO) as the shell. It was found that α-helical sense of PBLG in the nanoparticles transfers from the right-handed form to the left-handed one with the incorporation of PEO in the PBLG homopolymer nanoparticles [15].

In this study, we report an ICD of MD in the self-assembled polymeric nanoparticles. This study provides a particularly interesting approach to investigate an ICD in the chiral microenvironment. It may be expected that the J-aggregated MDs incorporated in the chiral microenvironment may show novel nonlinear optical properties.

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Table 1
Particle size distribution of nanoparticles and MD-loaded nanoparticles (the nanoparticles were prepared by the mixture of THF/DMF(7/3: v/v)) against PBLG chain length

Sample	PBLG content in mol%	$\bar{M}_n$	Nanoparticles without the loading of MD (nm)	Nanoparticles with the loading of MD (nm)
GE-1	60.5	103,700	182.4 ± 38.4	261.5 ± 99.8
GE-2	40.0	51,800	159.1 ± 33.2	247.0 ± 86.2
GE-3	12.4	20,400	132.0 ± 25.9	214.0 ± 120

2. Experimental

2.1. Materials

Amine-terminated PEO ($M_w = 12\,000$) was supplied from Nippon Oil and Fats Co., Ltd, Japan. γ-benzyl-L-glutamate-*N*-carboxyanhydride (γ-BLG-NCA) was synthesized from γ-benzyl-L-glutamate using triphosgene. The PBLG ($M_w = 6000$) was purchased from Sigma and used without further purification. Merocyanine dye was supplied from Nippon Kankoh Shikiso Kenkyusho, Okayama, Japan. Hexane, terahydrofuran (THF), dimethyleneformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMAc) and 1,4-dioxane were purchased from Aldrich and dried with molecular sieve.

2.2. Synthesis of PBLG/PEO (abbreviated as GE) diblock copolymer

GE copolymer was synthesized according to a similar method previously reported [16]. Briefly, GE block copolymers were obtained by the ring-opening polymerization of γ-BLG-NCA initiated by the α-methoxy-ω-amino PEO as a polymeric initiator in CH_2Cl_2 at room temperature for 72 h. After the characteristic absorption of BLG-NCA (1785, 1860 cm^{-1}) had disappeared in the IR spectrum (72 h), the reaction mixture was poured into a large excess of diethyl ether. The precipitated copolymer was dried in vacuum.

2.3. Preparation of nanoparticles containing MD

The nanoparticles were prepared by the diafiltration method according to a similar method previously reported [16]. Briefly, the block copolymer and dye solution dissolved in a mixture of 2.5 ml of THF/DMF (7/3: v/v) was dialyzed against distilled water using cellulose membrane tubing (12,000 molecular weight cutoff) to remove the organic solvent at room temperature.

2.4. Mesurement of CD

The CD spectra were measured at room temperature using JASCO J-715 spectropolarimeter equipped with a quartz cell having a path length of 10 mm. The UV spectra were obtained with UVIKON 923 (Kontron Instrument) at

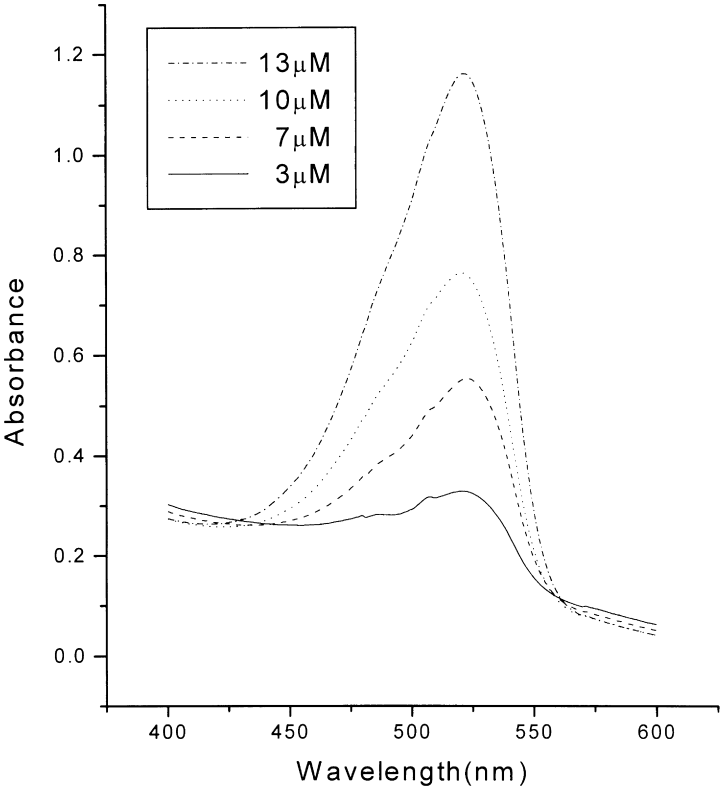

Fig. 1. UV spectra of MD with various concentrations of MD in THF/DMF (7/3: v/v) solution.

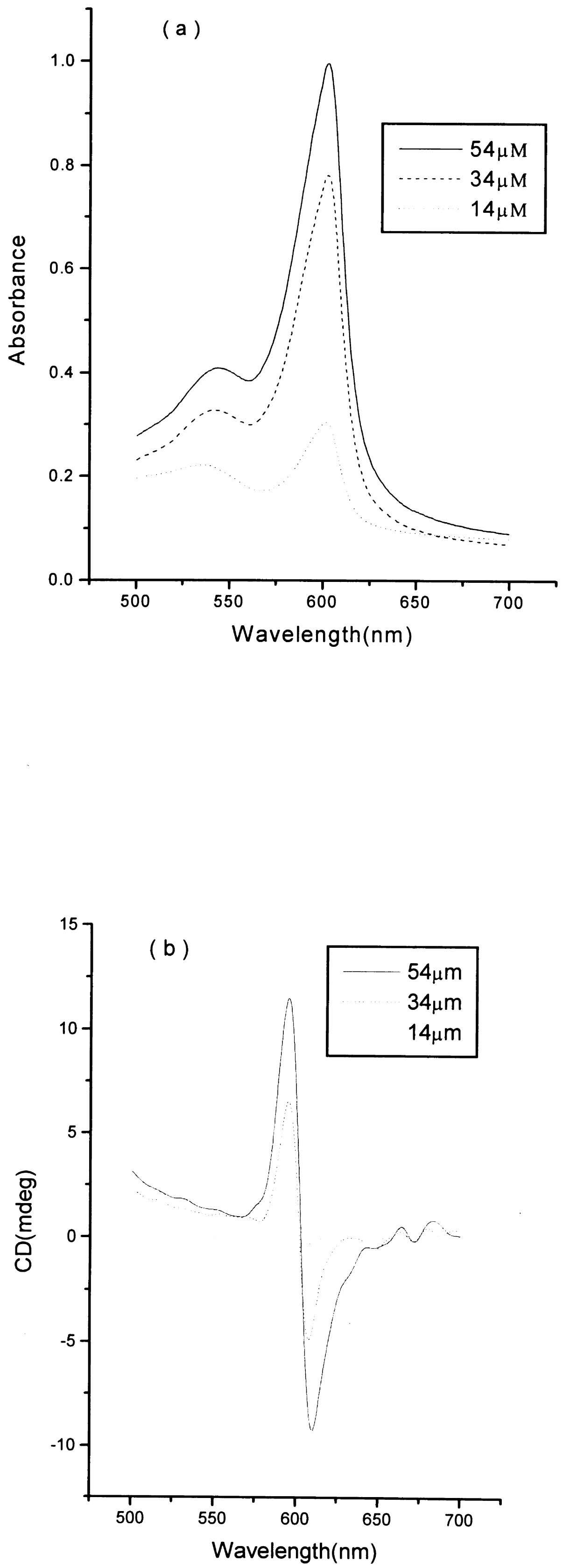

Fig. 2. UV(a) and CD(b) spectra of the MD loaded in the GE-3 nanoparticles according to the concentration of MD.

room temperature. The particle sizing experiments were performed using ELS-8000 (Otsuka Electronics).

3. Results and discussion

The PBLG/PEO diblock copolymer (abbreviated as GE) was prepared by a similar method as reported previously [16]. The amphiphilic diblock copolymers containing PBLG as a hydrophobic part and poly(ethylene oxide) as a hydrophilic one are self-assembled in aqueous media as the core–shell type nanoparticles as already reported [17,18]. The hydrophobic drugs can be entrapped in the nanoparticles core through the hydrophobic interaction [19].

Table 1 shows sizes of polymeric nanoparticles and MD-loaded polymeric ones prepared by diafiltration method [15]. They showed that the sizes of the nanoparticles were dependent on the chain length of hydrophobic PBLG, indicating that the more the PBLG content the larger the size of the nanoparticles. Also, the sizes of the nanoparticles are dependent on the organic solvents and their mixed composition (not shown in data). Especially, THF/DMF (7/3: (v/v)) system enables GE nanoparticles to form the smallest size among the organic solvents. The particle sizes of the MD-loaded polymeric nanoparticles at room temperature were 261.5 ± 99.8, 247.3 ± 86.2 and 214.8 ± 120 nm for GE-1, GE-2, and GE-3, respectively. As compared to the particle size of nanoparticle without MD, the sizes of nanoparticles increased after loading MD into the PBLG core. It may be supposed that MDs were loaded into the PBLG cores through the hydrophobic bonding.

Fig. 1 shows UV spectra of the MD solution (THF/DMF:7/3 in volume) against concentration of MD. This result indicated that the absorption maximum of MD appeared at 520 nm, indicating that MDs existed as monomeric state in solution.

Fig. 2 shows UV(a) and CD(b) spectra of the MD in the GE-3 nanoparticles according to the concentration of MD. This result indicated that new absorption band at around 600 nm appeared with a shoulder at around 540 nm. It was already reported that J-aggregates of the MD appeared at 590 nm [20,21]. Therefore, it can be said that the MDs existed as the J-aggregates form in the nanoparticles and the absorption peak of MD was red-shifted. Also, the J-aggregates of MD in the nanoparticles are enhanced with an increase of MD concentration.

Two strong bands appeared in the CD spectra (Fig. 2(b)) at around J-aggregates of MD shown in the UV spectra, an indication of ICD of the MD by chiral PBLG in the PBLG/PEO block copolymer. The observed ICD spectra of the MD matched its UV absorption spectra precisely. It can be said that achiral MD exhibits Cotton effects by the chiral microenvironment of PBLG core in the self-assembled core–shell type nanoparticles, and the interaction between the excited state of MDs in the chiral microenvironment gave an ICD curve with split Cotton effects on the basis of exciton

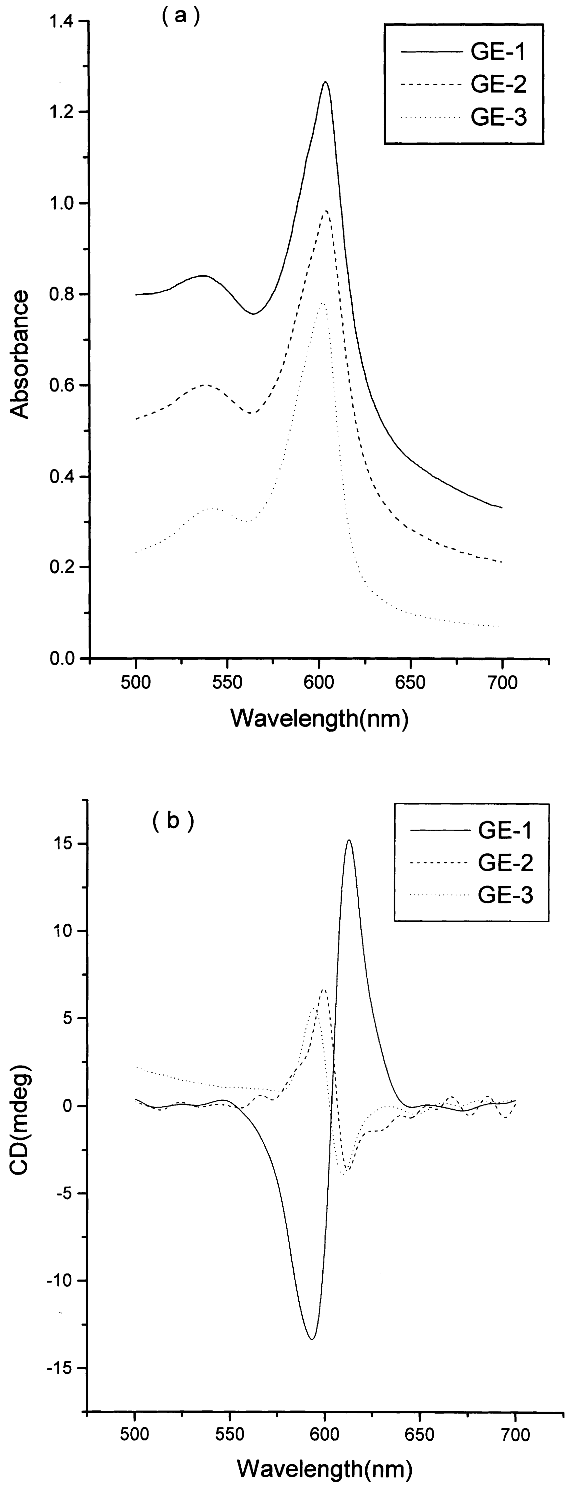

Fig. 3. UV (a) and CD (b) spectra of the MD loaded in the GE-1, GE-2 and GE-3 nanoparticles at a constant concentration of MD (MD contents per glutamate: GE-1; 17.6 wt%, GE-2; 26.8 wt%, and GE-3; 33.4 wt%).

coupling [22–24] centered at 600 nm. Also, the Cotton effect of MD was increased with an increase in the concentration of MD in the GE-3 nanoparticles. Taken into consideration the observed J-aggregate peak, it might be suggested that MD molecules were aligned with a small slip angle (α) [25].

Fig. 3(a) shows UV spectra of the MD in the nanoparticles according to the PEO content in the copolymer. This result shows that a strong absorption band at around 600 nm appears with a shoulder at around 540 nm for all copolymers, an indication of J-aggregates of MDs in the nanoparticles. The J-aggregates of the MDs in the nanoparticles are increased with an increase of PBLG content in the copolymer. It may be supposed that hydrophobic interaction between MD and PBLG in the nanoparticles is increased with an increase of PBLG content in the copolymer. Fig. 3(b) shows CD spectra of the MD in the nanoparticle according to the PEO content in the copolymer. This result indicates that the red-shifted aggregates of MDs are shown as the strong biphasic bands in the range of 575–625 nm whose crossing point coincided with the $\lambda_{\max}$ of major exciton band, indicating that PBLG in the core of the self-assembled nanoparticles induces CD of MD as the J-aggregates of MDs. Interestingly, helix sense of ICD of MD in the GE-1 nanoparticles was reverse to the helix one of MD in the GE-2 and GE-3 nanoparticles. It was already reported that the helix sense of the PBLG in the copolymer depended on the content of PEO in the copolymer [15]. Therefore, it can be said that the helix sense of the ICD of MD in the nanoparticles was affected by the helix sense of the PBLG in the nanoparticles. Generally, the helix sense of ICD has the opposite helix one to the chiral material, indicating a super-helix arrangement of the MD molecules [26].

Conclusively, MDs are self-assembled as the J-aggregates in the self-assembled nanoparticles. The CD of the MDs was induced by the chiral microenvironment of PBLG core in the self-assembled core–shell nanoparticles. The helix sense of the ICD of MD in the nanoparticles was affected by the helix sense of PBLG in the copolymer nanoparticles.

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