Induced Circular Dichroism of Disperse Red Dye in the Self-Assembled Nanoparticles Composed of Poly(γ-benzyl L-glutamate) and Poly(*N*-isopropylacrylamide) and Its Phase Transition by Temperature

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Introduction. Chiral recognition has long been attracting much attention due to its importance in the fields of biochemistry and biopharmacology. The optical activity induced by a chiral environment has been extensively studied in terms of the characteristics of chiral molecules in several systems. In particular, interest has been focused on the induction of optical activity through the interaction of reactive guest molecules, such as azo compounds,[1] diazirin chromophore,[2] bilirubin,[3] cyanine dyes,[4] and acridine orange,[5] with the host molecules such as cyclodextrins,[1−4] cyclophane,[6] DNA,[7] and helical polypeptides.[8] Furthermore, it was recently reported that the chiral supramolecular structure was formed through the association of organic molecules such as aromatic compounds and dyes.[9] The host molecules are capable of interacting with particular guests through covalent links or various noncovalent interactions. In this case, circular dichroism (CD) spectroscopy is a powerful probe capable of detecting the binding geometry and conformational change.[10] The host−guest complex shows an induced CD (ICD) in the UV/vis region of the guest molecules.

In a previous study, we reported that the CD of merocyanine dye (MD) as the guest was induced by the chiral poly(γ-benzyl L-glutamate) (PBLG) as the host in self-assembled nanoparticles composed of diblock copolymer based on PBLG as the core and poly(ethylene oxide) (PEO) as the shell.[11] Also, the effect of temperature on the conformational change of poly(*N*-isopropylacrylamide) (PNIPAAm) in the diblock copolymeric nanoparticles composed of PBLG and PNIPAAm was studied.[12]

Disperse red (DR), well-known to undergo a trans−cis photoisomerization, has a second-order nonlinear property.[13]

In this study, we report on the ICD of the DR dye in the diblock copolymeric nanoparticles and phase transition of DR incorporated in thermosensitive PBLG/PNIPAAm nanoparticles with temperature changes. In particular, differences in the phase transition of DR between PBLG/PNIPAAm and PBLG/PEO nanoparticles with temperature changes will be compared.

It is of particular interest to investigate an ICD in the chiral microenvironment because chiral molecule assemblies have recently been reported to have a strong enhancement for nonlinear optical properties.[14] We expect that a nonlinear optical chromophore incorporated into the chiral microenvironment may have potential applications as a nonlinear optical device.

Results and Discussion. The PBLG/PEO (GE) and PBLG/PNIPAAm (GN) diblock copolymers were similarly prepared as previously reported.[15] The amphiphilic diblock copolymers containing PBLG as a hydrophobic part and PEO or PNIPPAm as a hydrophilic part are self-assembled in aqueous media as the core−shell type nanoparticles reported earlier.[12]

DR was prepared by modification of disperse red 1 (DR1), and its structure is shown in Figure 1.

The compositions and sizes of GE and GN nanoparticles are shown in Table 1. The sizes of the nanoparticles are dependent on the organic solvents and their mixed composition.[12] In particular, THF/DMF (7/3: v/v) system enables GE and GN nanoparticles to form the smallest sizes. The sizes of the DR-loaded polymeric nanoparticles at room temperature were 214.8 ± 120 and 349 ± 23.1 nm for GE and GN nanoparticles, respectively. The particle sizes increased with loading of DR, suggesting that DRs were incorporated into the PBLG cores in the core−shell type nanoparticles through hydrophobic interaction.[16]

UV spectra of DR loaded into GE and GN nanoparticles at 4 °C are shown in Figure 2. DR by itself showed a typical absorption in a monomeric state with a $\pi-\pi^*$ transition near λ_{max} 480 nm in mixed organic solvent (THF/DMF: 7/3 v/v), while the absorption band of DR in GE and GN nanoparticles appeared at around λ_{max} 400 at 4 °C in water, an indication of a blue shift. This result suggested that DRs loaded in GE and GN nanoparticles formed H-aggregates aligned in a face-to-face stacking form[17] where a new band resulted from excitonic interaction between the transition moments of DR. CD spectra in Figure 3a,b showed a strong split ICD curve in the UV/vis absorption region of DR. The observed ICD spectra of the DR matched its UV/vis absorption spectra precisely. The achiral DR exhibits Cotton effects induced by the chiral microenvironment of PBLG core in the self-assembled core−shell type GE and GN nanoparticles. The interaction between the excited states of DR gave the ICD peak with biphasic Cotton effects on the basis of exciton coupling[18] at centered 390 nm which coincided with the λ_{max} of the excited absorption band. Linear dichroism is not considered to affect the CD spectra because no changes in CD spectra were observed with the rotation of quartz cell in the CD measurement. Moreover, the magnitude of ICD of H-aggregated DR increased with the increase in DR concentration as well as the hydrophobic PBLG core content in the GE and GN nanoparticles (data not shown). When compared to the content of PBLG core contained in the GE and GN nanoparticle at the constant concentration of DR, the magnitude of ICD also increased with an increase in hydrophobic PBLG core in the nanoparticles, indicating that hydrophobic inter-

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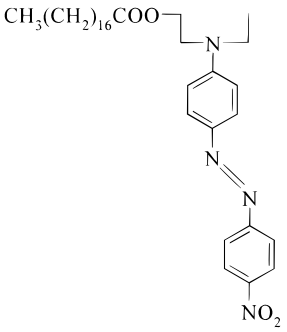

Figure 1. Chemical structure of DR.

Table 1. Particle Size Distribution of Nanoparticles and DR-Loaded Nanoparticles against PBLG Chain Length[a]

sample	PBLG content (mol %)	$\bar{M}_n$	nanoparticles without DR (nm)	nanoparticles with DR (nm)
GN	21	13 500	349 ± 23.1	402 ± 30
GE	12.4	20 400	132.0 ± 25.9	214.0 ± 120

[a] MW of PNIPAAm: 9000; MW of PEO: 12 000. The nanoparticles were prepared using the mixture of THF/DMF (7/3: v/v).

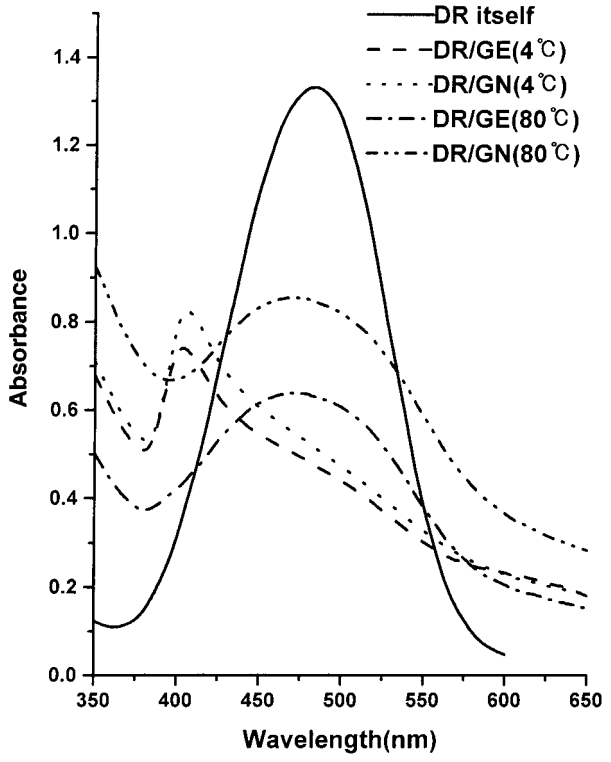

Figure 2. UV spectra of DR loaded in GE and GN nanoparticles at 4 °C and after heating from 4 to 80 °C [DR: 68 μM; GE/DR and GN/DR (10/1: w/w)].

action predominated over the driving force of H-aggregate of DRs in the nanoparticles. In addition, the $\pi-\pi$ interaction of the DR might be necessary to maintain stable stacking structures between the chromophores. And, taking into account the steric hindrance of DRs on molecular association, they might preferentially be packed as trans type in nanoparticles. Interestingly, it was found that the helix screw of ICD of DR in the GE nanoparticles was in a reverse position to that of DR in the GN nanoparticle. As was already reported,[19] the α-helix screw of GE nanoparticles was dependent on the content of PEO in the PBLG/PEO block copolymer while that of GN nanoparticles was not

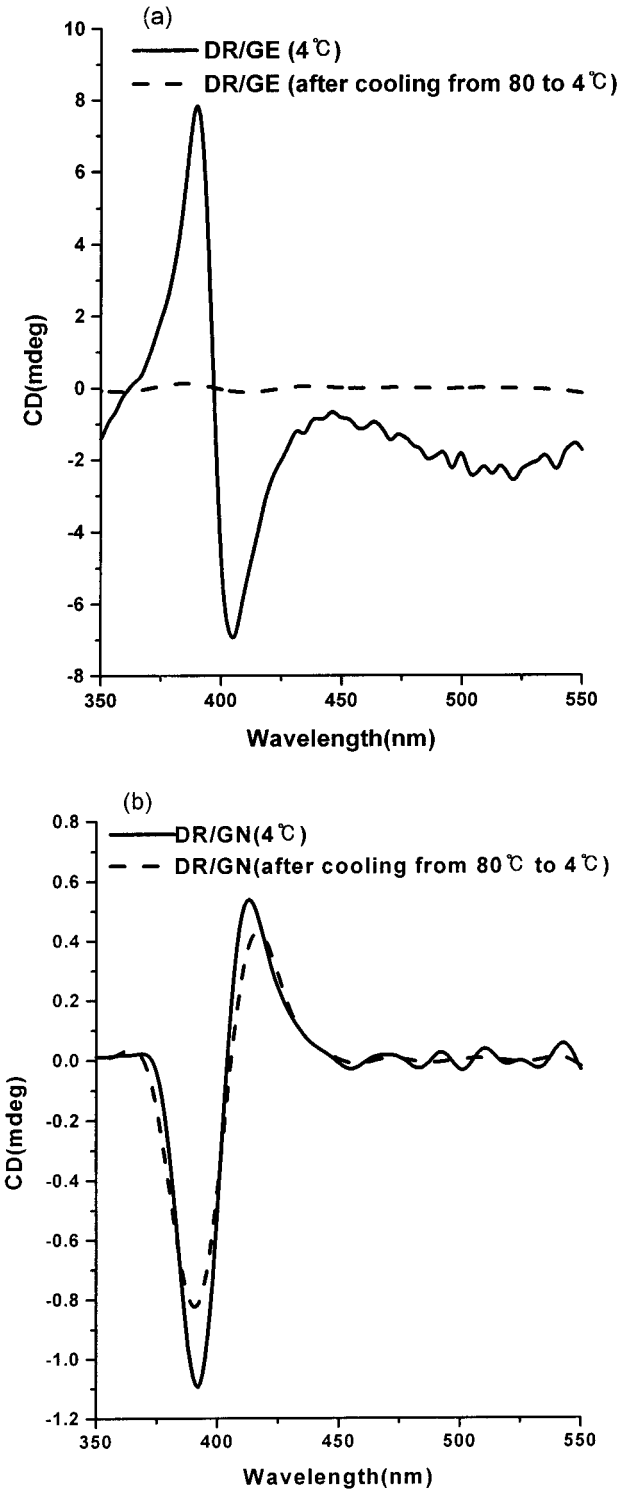

Figure 3. CD spectra of DR loaded in GE and GN nanoparticles at 4 °C and after cooling from 80 to 4 °C [DR: 68 μM; GE/DR and GN/DR (10/1: w/w)].

dependent on the content of PNIPAAm in the PBLG/PNIPAAm block copolymer. Thus, the helix screw of PBLG core in the GE nanoparticle is a left-handed form, while that of PBLG cores in the GN nanoparticle is a right-handed form. This suggested that the PBLG core of GE and GN nanoparticles, each with an inverse α-helix screw, affected the helix screw of ICD of DR in nanoparticles.[11]

As shown in the UV absorption spectra of Figure 2, DRs in GE and GN nanoparticles after heating 4−80

°C were converted from well-ordered stacking structures to the monomeric states and disordered aggregates with a little blue shift compared to the monomeric peak in organic solvent, resulting in an order−disorder phase transition in solution.[20] In particular, the H-aggregates in GE and GN nanoparticles abruptly changed into the monomeric state and disordered aggregates at around the phase transition temperature (T_c). This result indicated that the mobility of long hydrophobic alkyl chains in the DRs increased before the conformational change of DRs occurred in the nanoparticles and that the conversion is concerned with the increase in the mobility of the alkyl chain, as have already been reported.[21] Also, no ICD of DR was observed in GE and GN nanoparticles over T_c (data not shown), suggesting that the heating led the well-ordered H-aggregates of DRs in the nanoparticles to the disordered aggregates with loss of orientation, resulting in the disappearance of ICD. It could be supposed that the micellar structures of the GE block copolymer would be disrupted after heating, and the DRs in the nanoparticles came out into the aqueous media.

Figure 3a,b shows the CD spectra of DR loaded in the GE and GN nanoparticles after cooling from 80 to 4 °C. The absorption bands at approximately 400 nm were recovered with little decrease in intensity for both GE and GN nanoparticles (data not shown). However, no ICD was detected in the GE nanoparicles. Very interestingly, in contrast to the GE nanoparticle, the ICD curve of DR in the GN nanoparticles reappeared as the original ICD at 4 °C although the magnitude of the DRs in the CD spectrum decreased compared to the original at 4 °C. The result suggested that the disordered aggregates of DRs could be retained in GN nanoparticles due to the compacted thermosensitive PNIPAAm shell above the LCST[22] (lower critical solution temperature) and were reoriented into the well-ordered stacking structure after cooling at 4 °C, an indication of H-aggregates.

Conclusively, the PBLG chains in the GE or GN nanoparticles and DRs bonded together to form spherical nanoparticles through hydrophobic interaction during diafiltration. The chiral PBLG core in the self-assembled core−shell nanoparticles induced the CD of H-aggregated DR. The ICD and order−disorder phase transition in the nanoparticles were affected by the temperature accompanying the orientation change of DRs in the nanoparticles. In contrast to DR in the GE nanoparticles, the DR in the GN nanoparticles is more stable to temperature changes due to the conformational change of the PNIPAAm chain from an expanded type to a compact type above the LCST of PNIPAAm, resulting in a reversible ICD and order−disorder phase transition.

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