TIME RESOLVED FLUORESCENT ANALYSIS FOR SEALED HEATING OF DIMETHYL-β-CYCLODEXTRIN AND NAPHTHALENE SYSTEM

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ABSTRACT

The inclusion process of naphthalene into heptakis-(2,6-di-*O*-methyl)-β-cyclodextrin (DMβCD) during the sealed heating was investigated by using solid state time resolved fluorescent analysis. Fluorescence lifetimes of naphthalene in naphthalene crystals and in inclusion complex with DMβCD prepared by coprecipitation were determined 59 ns and 88 ns, respectively. Fluorescence lifetime of naphthalene monomer becomes longer after inclusion complex formation. Fluorescence lifetimes of naphthalene monomer and excimer in the sealed heating complex were determined about 80 ns and 100 ns, respectively. By setting the observing wavelength of time resolved fluorescent analysis at 355 nm, the formation and the decay of the excimer state of naphthalene during the sealed heating process were successfully confirmed.

1. INTRODUCTION

For the sealed-heating of naphthalene and heptakis-(2,6-di-*O*-methyl)-β-cyclodextrin (DMβCD), we have already reported that two types of the complexes were obtained, which were different from the inclusion compound obtained by the coprecipitation method.(1) Powder X-ray diffractometry and solid state fluorescence analysis can be used to distinguish between the sealed heated complexes, the coprecipitated complex, and the physical mixture, while they are not enough to the complete distinction.

Time resolved fluorescence analysis is one of the effective techniques to investigate the microenvironment of the molecule. Nelson and Warner used the fluorescence lifetime data to investigate the ability of CD complexation in the presence of alcohols to shield fluorophores from interactions with quenchers.(2)

The aim of this study was to clarify the inclusion process by the sealed heating of naphthalene and DMβCD using time resolved fluorescence analysis, and to contrast the different approaches.

2. MATERIALS AND METHODS

250 mg mixture of amorphous DMβCD and naphthalene (molar ratio = 1:1) was sealed in a 2.0 ml glass ampule, then heated at a definite temperature for 1 min-72 h.

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Amorphous DMβCD was prepared by grinding. The coprecipitate was prepared by heating the mixture of DMβCD aqueous solution and naphthalene ethyl ether solution. Fluorescence spectra were measured using an FP-770E spectrofluorometer (Japan Spectroscopic Co.) for solid sample. A spectrofluorometer (Horiba NAES-700) was used for solid state time resolved fluorescent analysis.

3. RESULTS AND DISCUSSION

Table 1 shows the fluorescence lifetimes and relative quantum yields of naphthalene in various specimens when the λobs was fixed at 341.0 nm where the emission maximum of naphthalene monomer was observed. In naphthalene crystals, the lifetime of 59.1 ns was observed, even as Hamai evaluated the lifetime of naphthalene monomer in aqueous solution as 40 ns. The lifetime of naphthalene monomer was determined as 88.3 ns in the coprecipitate where the molar ratio of naphthalene to DMβCD was 1.20. In the sealed heated specimens, the similar lifetime was obtained with the coprecipitate, indicating the inclusion of naphthalene molecule to DMβCD cavity, however, the lifetime of coprecipitate was slightly longer than that of sealed heated specimens. Mataga et al. determined the lifetime of naphthalene monomer in organic solvents as 120 ns in cyclohexane and 110 ns in n-hexane, respectively.[3] The elongation of lifetime of naphthalene by the inclusion formation could be related to the environmental changes of naphthalene molecule. The lifetime of 107 ns was obtained in the sealed heated specimen heated at 70°C for 15 min, when λobs was fixed at 390.0 nm. As Mataga et al. reported that the lifetime of naphthalene excimer in cyclohexane was 117 ns, the observed value, 107 ns, seems to be due to naphthalene excimer formed during sealed heating process.

The solid state fluorescence emission spectra of the sealed heated specimens heated at 70°C are shown in Fig. 1. The increase of heating time resulted in the shifting of the emission maximum from 341 nm to 390 nm. Table 2 shows the changes of fluorescence lifetime and relative quantum yield of naphthalene by sealed heating at 70°C when λobs was fixed at 355.0 nm. The shortest lifetime was considered as a result of stray, reflective or scattered light. The sealed heated specimens showed other two components with varied relative quantum yield. While in the physical mixture, only monomer component

Table 1. Fluorescence Lifetimes (τ) and Relative Quantum Yields (φ) of Naphthalene in Various Naphthalene-DMβCD Systems (λex = 262.7 nm ; λobs = 341.0 nm)

Sample		τ_1(ns)	ϕ_1(%)	τ_2(ns)	ϕ_2(%)	χ^2
Naphthalene Crystals		5.56	*5.6*	59.1	*94.4*	2.58
Coprecipitate		4.56	*2.6*	88.3	*97.4*	1.19
Sealed-heated at 90°C (Mixing Molar Ratio = 1:1)						
for	3 h	6.06	*5.0*	77.8	*95.0*	1.25
	24 h	4.75	*4.5*	78.3	*95.5*	1.60

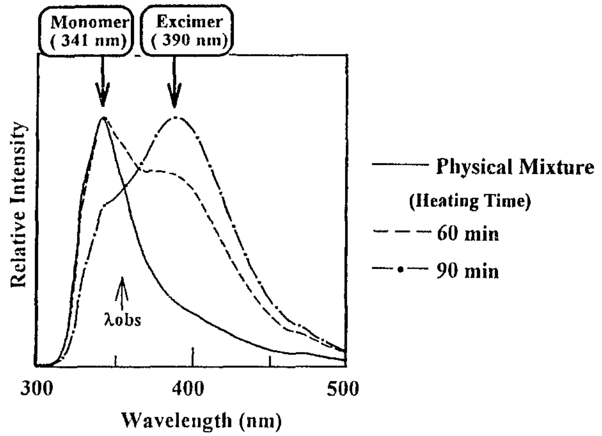

Fig. 1. Changes in Solid State Fluorescence Emission Spectrum of Sealed-heated Sample Heated at 70°C (λ_{ex} = 262.7 nm)

Table 2. Fluorescence Lifetimes (τ) and Relative Quantum Yields (φ) of Naphthalene in Sealed-heated Samples Heated at 70°C for Various Times (λ_{ex} = 262.7 nm ; λ_{obs} = 355.0 nm)

Heating Time	τ_{lamp} (ns)	ϕ_{lamp} (%)	$\tau_{monomer}$ (ns)	$\phi_{monomer}$ (%)	$\tau_{excimer}$ (ns)	$\phi_{excimer}$ (%)	χ^2
Physical Mixture	3.13	*3.9*	80.8	*96.1*	—	—	1.19
Sealed-heated for							
60 min	2.25	*6.8*	77.7	*56.6*	110	*36.6*	1.10
70 min	2.45	*7.4*	78.8	*61.3*	106	*31.3*	1.33
80 min	2.49	*6.4*	71.9	*41.9*	106	*51.7*	1.15
90 min	2.81	*8.4*	81.0	*42.3*	100	*49.3*	1.16

was observed. Figure 2 demonstrates the variation of monomer-excimer ratio in sealed heated specimens. The ratios were determined from solid state fluorescence spectra (Fig. 1) and relative quantum yield (Table 2) as well. With the increase of heating time, naphthalene excimer became major component. For the formation of naphthalene excimer, Smith et al. reported that the distance between two naphthalene molecules should be less than 3.7 Å.[4)] At the initial step of inclusion compound formation by sealed heating, naphthalene molecules had a certain molecular arrangement in which two naphthalene molecules presented in close distance. As the diameter of DMβCD was not so large to accommodate two naphthalene molecules and the stoichiometry of the inclusion compound was 0.87, two DMβCD and two naphthalene molecules should form the excimer complex. The results of time resolved fluorescence analysis when the specimen was sealed heated at 90°C are shown in Table 3. The amount of excimer complex decreased with the increase of heating time, indicating the formation of stable inclusion complex.

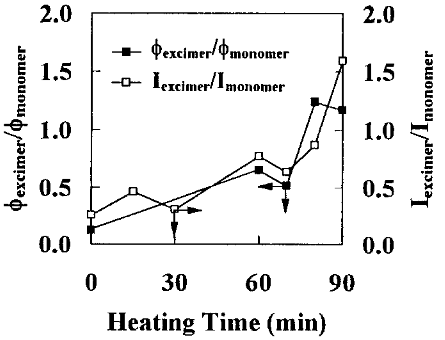

Fig. 2. Changes of $\phi_{excimer}/\phi_{monomer}$ and $I_{excimer}/I_{monomer}$ of Sealed-heated Samples Heated at 70°C

Table 3. Fluorescence Lifetimes (τ) and Relative Quantum Yields (φ) of Naphthalene in Sealed-heated Samples Heated at 90°C for Various Times (λex = 262.7 nm ; λobs = 355.0 nm)

Heating Time	τ_{lamp} (ns)	ϕ_{lamp} (%)	$\tau_{monomer}$ (ns)	$\phi_{monomer}$ (%)	$\tau_{excimer}$ (ns)	$\phi_{excimer}$ (%)	χ^2
Physical Mixture	3.13	*3.9*	80.8	*96.1*	—	—	1.19
Sealed-heated for							
30 min	2.88	*3.7*	81.4	*32.5*	95.7	*63.9*	1.07
40 min	2.81	*3.5*	70.7	*39.1*	100	*57.4*	1.04
50 min	2.95	*3.5*	73.8	*39.8*	101	*56.7*	1.09
60 min	3.38	*2.9*	73.9	*56.7*	100	*40.4*	1.21

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