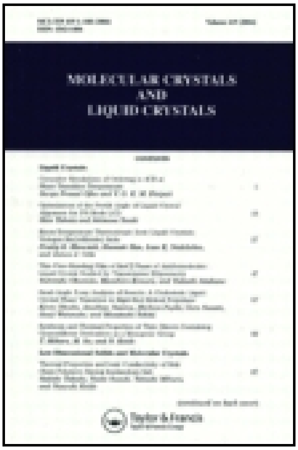

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Condensed States and Optical Properties of the Densely Dissolved Organic Compounds in Polymer Matrices by Coprecipitation

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Abstract Association of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI) molecules has been revealed in polymer matrices [poly(methyl methacrylate), poly(benzyl methacrylate), etc.], comparing it with association states in appropriate solvents ranging from a dilute concentration ($\sim 10^{-5}$ mol/l) to a saturated one, and in a crystal grown in methanol. The association state was investigate by means of optical-absorption and emission spectroscopy, emission lifetime analysis, ^{13}C-NMR spectroscopy and small angle X-ray scattering. Properties of DODCI molecules in polymer matrices were controlled by varying side-chain substituents of the polymers, and DODCI contents.

Keywords: diethyloxadicarbocyanine iodide (DODCI), aggregates, X-ray scattering, spectroscopy, polymers, association, coprecipitation

Introduction

In recent years, optical properties of associated molecules, e.g., J- and H-aggregates, have been widely investigated because electronic states in the associate, typically known as molecular exciton, excimer, etc., exhibit very interesting phenomena.[1] Such investigation has also been stimulated by a measurement that analyzes the ultrafast response of the associate to incident light.[2] Condensed states of these molecular systems may been investigated by analyzing spectroscopic data.[3] A mesoscopic system composed of organic molecules from several ten to ten thousand molecules is a matter of current interest as well because of its new optical properties quite different from those of a single molecule and a bulk crystal.[4]

A single organic molecule dispersed in a solvent or a polymer matrix, exhibits photoresponsive properties such as photo-absorption and photo-emission. This yields novel photochemistry and photophysics such as solvatochromism,[5] laser oscillation[6], etc. Furthermore, in some cases of molecular association of organic dyes, photo-absorption and emission induced by the association, ranging from a dimeric molecule to a crystalline aggregate of more than ten thousand molecules, become observable. In these systems, optical properties of associated molecules strongly depend on states of dispersion such as size and order of the associate, and interactions between solvents, polymer matrices and solute molecules.

Association states in macromolecular systems have rarely been clarified at present, because a clear direct observation of the associates smaller than ten thousand molecules has hardly been successful by any methods, e.g., transmission electron microscope observation, atomic force microscope measurement, etc. Even if the direct observation was possible, the exact state of association would commonly be screened by statistical fluctuation.

We believe, therefore, the practical approach to investigate the association state in organic macromolecular systems is not to explore a single absolutely reliable determination method but to use various correlations between optical properties, SAXS, NMR, and so on, in continuously controlled molecular association from a monomolecule to a bulk crystal. Optical properties (absorption, emission spectrum and emission lifetime) of a dilute solutions of DODCI were almost identical to those of dilutely ($\sim 10^{-5}$ mol) dissolved polymer films. In densely ($\sim 10^{-1}$ mol) dissolved films, on the other hand, the properties are similar to those of a bulk crystal. Based on the results mentioned above, organic molecular systems were prepared with the following working hypothesis. 1) In a system with strong interactions between solute molecules and matrices, orderliness of each solute molecule will be disturbed, where optical responses may be determined mainly by interface properties between solute molecules and matrices instead of bulk properties of solute molecules. 2) In a system with weak interactions between solute molecules and matrices, on the contrary, orderliness of each solute molecule will be enhanced toward self-organization, where optical responses may be determined mainly by the bulk properties and size effects instead of the interface properties. 3) Degree of interactions between solute molecules and matrices are controlled by selecting suitable side-chain substituents of polymers.

Experimental

Sample preparation

Commercially available 3,3'-diethyloxadicarbocyanine iodide (DODCI; Exciton) was used without further purification. Six polymers were employed in the present experiments: poly(methyl methacrylate) (PMMA, MW=12,000; Aldrich), poly(2-hydroxypropyl methacrylate) (PHPMA, MW=93,000; Aldrich), poly(benzyl methacrylate) (PBzMA, MW=54,000; Aldrich), poly(phenyl methacrylate) (PPhMA, MW=170,000; SCIENTIFIC POLYMER PRODUCTS), poly(Styrene) (PS, MW=430,000; Aldrich) and poly(vinyl chloride-co-vinyl acetate) (VYHH; Union Carbide Co.). DODCI was dissolved in polymer matrices by coprecipitation of DODCI with polymer using an acetone/n-hexane mixture.[7] The powder made by coprecipitation was dried for two days under ultra high vacuum ($\sim 10^{-5}$ Pa) at just bellow the glass transition temperature of the polymer.[8] Formation of thinfilm was performed by the Hot-press method.[9] A single crystal was grown in an evacuated pyrex tube by slow evaporation of methanol from a solution.[10]

Apparatus

High-resolution solid-state ^{13}C-NMR spectroscopy was performed using a JEOL GSH-200 spectrometer at the resonance frequency of 50.23 MHz.[11] Small angle X-ray scattering (SAXS) was measured for associated DODCI molecules in polymer matrices using a 3-slit goniometer with a rotating Cu anode (50 kv, 300 mA)(RINT-1500; Rigaku Co.).[12] X-ray diffraction for the crystal and DODCI dispersed polymers was measured by a conventional diffractometer (50 kv, 300 mA)(RINT-2500; Rigaku Co.) Absorption spectroscopy over visible and ultraviolet wavelength regions was carried out on a commercial spectrophotometer (U-3400; HITACHI); emission spectroscopy on a commercial fluorescence spectrophotometer (MPF-4; HITACHI). Time resolved emission analysis was performed by the time-correlated single-photon counting (TC-SPC) method in both nsec and psec region: a Neon gas discharge lamp was employed for a nsec region (10 nsec pulse),[13] and a dye laser in combination with a mode-locked Nd:YAG laser (Spectra Physics, series 3000) for a psec region (5 psec pulse).[14]

Results and Discussion

Optical Properties of DODCI molecules in various states

Typical spectra of absorption, excitation, and emission in a dilute methanol solution (OD$\sim$1) are shown in Fig. 1. DODCI molecules in solvents exhibited a small (~25 nm) stokes shift. Blue shifts of absorption peak wavelength with the increase in a static dielectric constant (ε) were observed for both protonic and aprotic solvents: for $CHCl_3$ (absorption λ_{max}~592 nm, ε^{20}: 4.8), and for H_2O (576 nm, ε^{20}: 80.4), except for DMSO (589 nm, ε^{20}: 36.8). These blue shifts were also observed in the DODCI family; 3,3'-Diethyloxacarbocyanine Iodide, 3,3'-Dimethyloxacarbocyanine Iodide, 1,1'-Diethyl-2,2'-cyanine [Iodide, Bromide, and Chloride]. Though the blue shift occurs, an electronic transition of DODCI may be a π-π^* transition, judging from the very large extinction coefficient of the longer wavelength absorption.

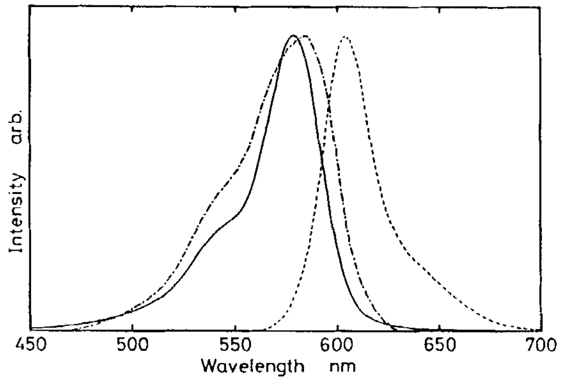

Fig. 1. Absorption(——), excitation (-•-) and emission (······) spectra of a dilute (OD=1) methanol solution of DODCI.

Table I. Absorption, excitation and emission maximum wavelengths, and emission lifetime of DODCI in a methanol solution, in a polymer, and in a crystal.

DODCI/Matrix	λ_{max}[nm]			τ [psec (650nm)]	
	absorpt.	excit.	emission	τ_1; τ_2	Ne
MeOH Solution OD=1 ($4x10^{-6}$M)	579	580	601		1100
PMMA; $1x10^{-3}$mol	586	590	600	; 1839	
$1x10^{-1}$mol[a]	594/690	594	613/720	180 ; 1370	
Crystal powder[b]	---	---[e]	740	< 40;	
Crystal powder[c]	---	---[e]	640	< 40;	
Crystal[d]	---	---[e]	780	200;	

a)Made by the hot-press method after coprecipitation. b)Made by reprecipitation from an acetone solution to n-hexane. c)Made by reprecipitation by injection of an acetone solution into vacuum. d)A ground crystal from a commercial reagent. e)There were no peaks but intensity gradually increased toward the emission peak.

In order to roughly view occurrence of molecular association, absorption, excitation, and emission maximum wavelengths of DODCI in a dilute (OD~1) methanol solution, in polymer films made by the hot-press method (DODCI/polymer film), and in crystal forms (ground, and powdered by reprecipitation) were measured.(Table I) Absorption and emission λ_{max}, and emission lifetime (τ_{em}) in the dilute MeOH solution agreed well with the reported ones.[15] In a dilute DODCI/PMMA film, somewhat longer wavelength shift in absorption λ_{max} and longer τ_{em} were observed compared with those in the solution, which could result from 'solvent effects' including solid matrices as well as liquid solvents. In a dense DODCI/PMMA film, an additional new peak

Table II. Optical properties of DODCI molecules as functions of both polymer types and DODCI contents.

Matrix (conc.;M)	λ_{max}[nm]			τ_{em}[psec] τ_1; τ_2	Remarks
	absorpt.	excit.	emission		
PBzMA 54k					$PhCH_2$, C=O
1 x10^{-1}	---	599	616/715	190 ; 1210	
5 x10^{-2}	601/693	605	626/720	; 1003	
1 x10^{-2}	601/449	607	622/697	; 1091	
1 x10^{-3}	600/419	605	611	; 1839	
PMMA 12k					CH_3, C=O
1 x10^{-1}	594/690	594	613/720	180 ; 1370	
7.5x10^{-2}	590/655	593	615/718	188 ; 1142	
5 x10^{-2}	592/688	592	612	130 ; 1520	
1 x10^{-2}	590/708	596	615	100 ; 1680	
1 x10^{-3}	586	590	600	; 1839	
1 x10^{-4}	---	590	599	--	
PS 430k					Ph
1 x10^{-1}	---	614	685	115 ; 440	
1 x10^{-2}	---	615	617	166 ; 430	
1 x10^{-3}	603	610	618	; 1878	
PPhMA170k					PhO, C=O
1 x10^{-1}	613	662	646	86 ;	
1 x10^{-2}	598	636	629	; 1111	
1 x10^{-3}	597	607	621	; 1914	
VYHH					CH_3COO
1 x10^{-1}	---	664	645	114 ; 856	
5 x10^{-2}	---	643	643	260 ; 893	
1 x10^{-2}	---	618	622	; 2772	
1 x10^{-3}	593	595	609	31 ; 1002	
1 x10^{-4}	594	595	606	40 ; 1090	
1 x10^{-5}	594	596	604	72 ;	
PHPMA 93k					OH, CH_3, C=O
1 x10^{-1}	590/490	647	618/642	130 ; 800	
2.5x10^{-2}	588	602	617/641	; 1235	
1 x10^{-2}	588	620	617	; 1790	
1 x10^{-3}	588	595	611	; 2470	

appeared in both absorption and emission spectra, and an additional fast decay component (τ_1) in τ_{em} was also observed. In a crystal, whose properties depended strongly on a preparation method, emission λ_{max} shifted to wavelengths much longer than that in the dense DODCI/PMMA film, and a very short τ_{em} was observed. Though emission λ_{max} in the crystal form seemed to depend on particle size of the powder, which can be presumed by microscopic observation, the properties in the dense DODCI/PMMA film, on the whole, became close to those in the crystal.

Effect of local environment in the polymer matrices on the association state of DODCI molecules was varied both by changing side-chain substituents of polymers and DODCI contents.(Table **II**) A typical phenomenon may be observable in a densely dissolved region for emission λ_{max}, where the additional new emission over 700 nm appeared in both PBzMA and PMMA film; this also corresponded to the appearance of the fast component of τ_{em} (τ_1). Origin of the new emission and τ_1 might be due to some kind of DODCI association in polymer matrices with the coexistence of DODCI monomer dissolved in the matrix. Intensity of the additional new emission in PMMA and PBzMA was enhanced remarkably at a low temperature bellow 10 K while the emission from DODCI monomer in the polymer film was not enhanced so much. These results indicate that the association in the dense DODCI/polymer possesses a significant orderliness.

Dispersed Conditions

Association sizes of DODCI molecules and interactions between DODCI molecules and polymer matrices were investigated by means of SAXS and solid-state ^{13}C-NMR spectroscopy, respectively. Diameters of the associated DODCI molecules were determined by the analysis of scattering profile with the assumption of a spherical shape scatterer. Sizes of the DODCI association in powdered crystals and in polymer films are summarized in Table **III**. An observable diameter range of the present apparatus is, on the whole, between 2 nm and 100 nm: if DODCI molecules are dissolved monomolecularly (smaller than 2 nm) or associated as large particles (larger than 100 nm), small angle scattering is not observable. X-ray diffraction from the films was also examined, which showed whether the associate have a crystal structure or not. Diameters of the DODCI association in the powdered crystal made by reprecipitation was equally distributed between 15 nm and 69 nm. In the polymer matrices, there are two types: diameter larger than 2 nmϕ with equally wide distribution, and diameter smaller than 2 nmϕ. In PHPMA and VYHH, there was no obvious association larger than 2 nmϕ. In PMMA and PBzMA, as a neat polymer without additive possesses a scatterer of ~7 nmϕ for PMMA and ~17 nmϕ for PBzMA, analysis of the diameter has some ambiguity. The existence of association larger than 2 nmϕ is thought to correspond with the additional new emission

Table III. Diameter of associated DODCI molecules measured by SAXS.

Matrix	Diameter [ratio] (nm) (%)	Diameter [ratio] (nm) (%)	Diameter [ratio] (nm) (%)
Powder[a]	14.53 [40.47]	33.82 [28.12]	68.77 [31.41]
PMMA film 〃 (neat)	8.04 [84.19] 7.13 [100]	33.36 [10.60]	63.93 [5.22]
PBzMA film 〃 (neat)	5.58 [59.13]	15.43 [24.80] 16.81 [100]	31.75 [16.08]
PS film 〃 (neat)	11.42 [57.07] < 2 [100]	36.84 [23.29]	73.32 [19.63]
PHPMA film 〃 (neat)	< 2 [100] 4.55 [100]		
VYHH film 〃 (neat)	2.4- [91.--] 2.41 [91.89]		

a) A powdered crystal made by reprecipitation from an acetone solution to n-hexane.

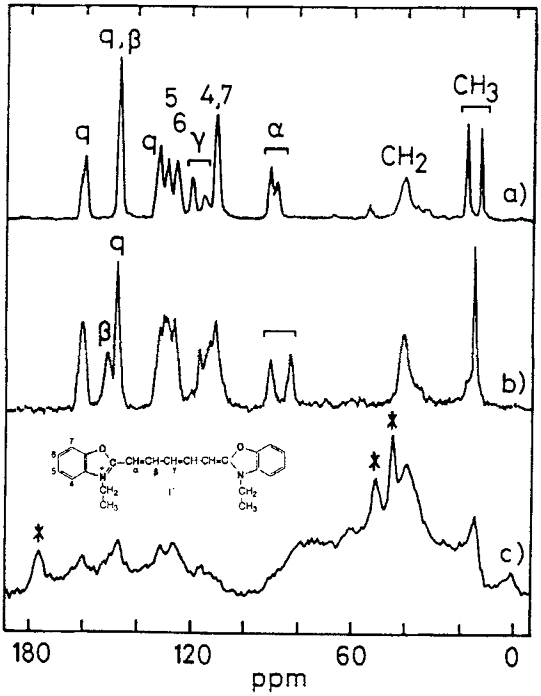

Fig. 2. ^{13}C-NMR spectra of DODCI in a crystal (a), in a powdered crystal made by reprecipitation (b), and in PMMA-d_8 (c). (✱) are peaks of PMMA-d_8.

over 700 nm in a dense region of both PBzMA and PMMA; similarly, correspondence exists between the scatterer smaller than 2 nmϕ and the absence of a new emission in both PHPMA and VYHH.

High resolution solid-state ^{13}C-NMR for DODCI in the ground crystal, in the powdered crystal made by reprecipitation, and in the deuterated PMMA (PMMA-d_8) film was measured (Fig. 2). Remarkable changes were observed between the ground crystal and the powder made by reprecipitation: a large lower field shift in β-CH= (146 ppm), and a doublet-to-singlet change in methyl carbon (CH_3). In the PMMA-d_8 film, several peaks disappeared: CH (125 and 111 ppm), γ-CH= (115 ppm) and α-CH= (88 and 90 ppm). The remarkable change in the polymer matrix will be interpreted by that some carbons of DODCI (CH, CH_2 and CH_3) feel an environmental atmosphere as in solution. These results indicate that the DODCI association in the polymer exhibits aspects of both solution and crystal.

Conclusion

The association of DODCI molecules in polymer matrices has been controlled by means of side-chain substituents of the polymers. The association state was reasonably elucidated by optical properties, SAXS and solid state ^{13}C-NMR chemical shifts with comparing these properties in various conditions. It has been concluded that the associate between about 15 nmϕ and 70 nmϕ can be produced in polymer matrices.

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