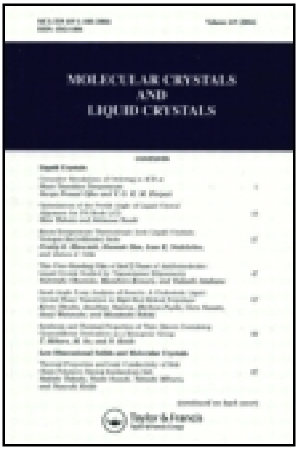

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PREPARATION OF J-AGGREGATED MICROCRYSTALS OF PSEUDOISOCYANINE

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Abstract J-aggregated microcrystals of 1,1'-diethyl-2,2'-cyanine bromide [pseudoisocyanine bromide (PIC)] was prepared by salting-out in saturated potasium bromide aqueous solution, reprecipitation in hexane and recrystallization in polymers at room temperature. J-band of microcrystals from aqueous conditions was sharp and blue-shifted compared with those from hydrophobic conditions. The size of the former microcrystals was smaller than that of the latter ones.

Keywords: microcrystals, J-aggregates, pseudoisocyanine, photophysics

INTRODUCTION

Microcrystals are an intermediate state between bulk crystals and isolated molecules, and are interested in both chemical and physical properties. For example, they are expected to have some striking characteristics in the field of catalysis,[1] microelectronics,[2] and photoelectoronics.[3] Microcrystals of semiconductors, metals and ceramics are generally prepared in both vapor and liquid phases. Their optical and electronic properties are known to be different from those of bulk crystals.[4] However evaporation method is not applicable to all the organic compounds because of their instability at elevated temperature. Recently, we have reported that varieties of organic microcrystals could be easily obtained by the simple reprecipitation method under mild conditions.[5] In the case of a merocyanine dye, we have been able to obtain the water dispersion which looks like a solution. The merocyanine is known to form J-aggregates, which show a sharp and red-shifted absorption band compared with the monomer. After ammoniac treatment of this dispersion, we obtained dispersion of J-aggregates. From the observation by a scanning electron microscope (SEM) and powder X-ray diffraction patterns of the J-aggregated merocyanine, it was found that the J-aggregated merocyanine was microcrystals. In order to examine the generality of the fact, preparation of microcrystals of 1,1'-diethyl-2,2'-cyanine bromide [pseudoisocyanine bromide (PIC)] is worth investigating. PIC is known to show extraordinarily sharp J-band absorption under severe conditions such as low temperature, i.e. 77 K,[6,7] and highly concentrated solution.[8] Its large third-order optical nonlinearlity has recently been reported.[9] In this paper, we describe the preparation methods of PIC J-aggregated microcrystals under the various conditions at ambient temperature.

EXPERIMENTAL

The reprecipitation method which we have performed so far was that ethanol solution of organic compounds was dropped into vigorously stirred water, and then microcrystals were reprecipitated and dispersed in water. Since PIC is soluble in water, the same reprecipitation method as above could not be applied for PIC. Thus, we modified the reprecipitation method in water to following two ways. In the first case, saturated water solution of salt was used instead of water and PIC ethanol solution was dropped into the solution resulting in the precipitation of PIC by salting-out effect, i.e. the salting-out method. In the second case, PIC ethanol solution was dropped into *n*-hexane in which PIC is not soluble, i.e. the reprecipitation method in an organic solvent. In addition, we also examined the preparation of microcrystals by recrystallization in polymers.

Under a typical experimental condition, 100 μl of PIC ethanol solution (3.1 $\times$ 10^{-3} M) was dropped into 10 ml of stirred saturated (c.a. 5 M) potassium bromide aqueous solution in the case of salting-out, and into 10 ml of stirred *n*-hexane in the case of reprecipitation method. In the case of the recrystallization in polymers, PIC and polymers, i.e. gelatin and poly(methyl methacrylate) (PMMA), were dissolved in a solvent under a heating condition. The concentration of PIC in 5% water solution of gelatin was 0.5×10^{-2} M. PIC molar ratio per PMMA weight was 7.3×10^{-6} mol/g in benzene solution. The PIC-polymer solution was cooled to room temperature. Spin-coating on glass substrates was performed for fabricating thin film samples.

Visible absorption spectra were measured by a Shimadzu UV-240 spectrophotometer. The size of microcrystals were investigated by a SEM (Hitachi S-900) or an optical microscope (OLYMPUS BH 2-UMA). In the SEM observation, samples were decorated by platinum. Powder X-ray diffractions were recorded on a Shimadzu XD-D1 diffractometer.

RESULTS AND DISCUSSION

By the salting-out method, J-aggregates were obtained as good dispersion in salt solution. Obtained J-aggregates must be microcrystals since it is impossible to dissolve PIC in saturated salt solution. Though Tanaka and Iwasaki have

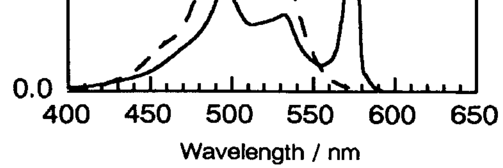


FIGURE 1 Absorption spectra of PIC J-aggregated microcrystals dispersed in saturated KBr solution (1) and aqueous PIC solution (2) at room temperature.

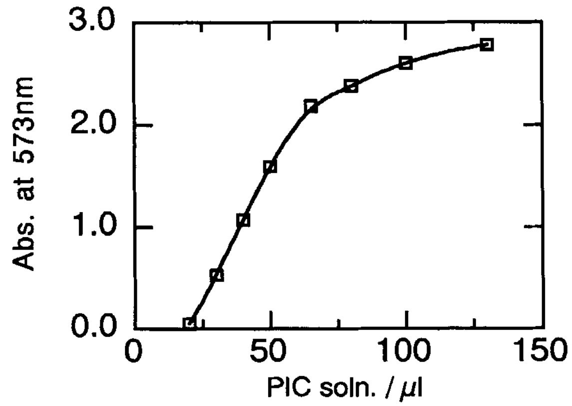


FIGURE 2 Relationship between added volume of PIC ethanol solution (3.1 × 10^{-3} M) to 10 ml of almost saturated KBr solution (4.2 M) and absorbance at 573 nm.

reported the preparation method of J-aggregates under the similar conditions,[10] they did not recognize this phenomenon as the formation of microcrystals. The dispersion was very transparent with almost no scattering, suggesting that the size of microcrystals was smaller than the range of the visible-light wavelengths. FIGURE 1 shows the absorption spectra of PIC aqueous solution and PIC-microcrystal dispersion at room temperature. The latter one clearly showed J-band at 573 nm and very small half width of about 5 nm. When the dropping amount of the PIC ethanol solution (3.1 × 10^{-3} M) to the constant volume (10 ml) of saturated salt solution was increased, J-band absorption increased as shown in FIGURE 2. In the case of non-saturated potassium bomide solution, higher concentration of potassium bromide gave stronger J-band absorption as shown in FIGURE 3. It turns out from FIGURE 3 that the minimum concentration of KBr for the starting of J-aggregation and/or microcrystallization increases with decreasing PIC amount. Though we tried to see the microcrystal size of the specimen after drying the dispersion, it was difficult to distinguish between PIC and potassium bromide microcrystals and the size of microcrystals could not be confirmed by SEM. However the size of microcrystals was surely less than

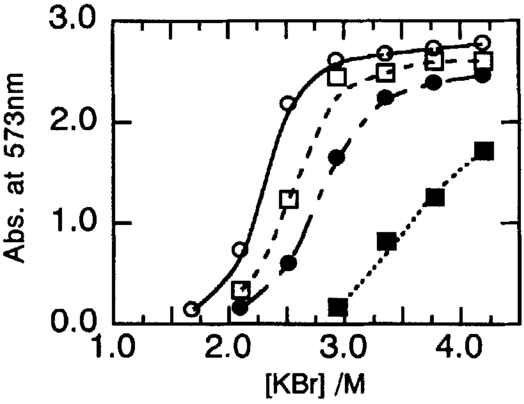


FIGURE 3 Relationship between concentration of KBr solution and absorbance at 573 nm. Added volumes of PIC ethanol solution to 10 ml of KBr solution were 130 μl(○), 100 μl(□), 80 μl(●), and 50 μl(■).

0.1 μm because all of the dispersion passed through the filter having the mesh of 0.1 μm.

Therefore we examined the reprecipitation in *n*-hexane. Microcrystals obtained were also in J-aggregates. Because PIC is not soluble in *n*-hexane, crystallization occurred just after the addition of the PIC solution into *n*-hexane. FIGURE 4 shows the absorption spectrum of the PIC dispersion in *n*-hexane. The

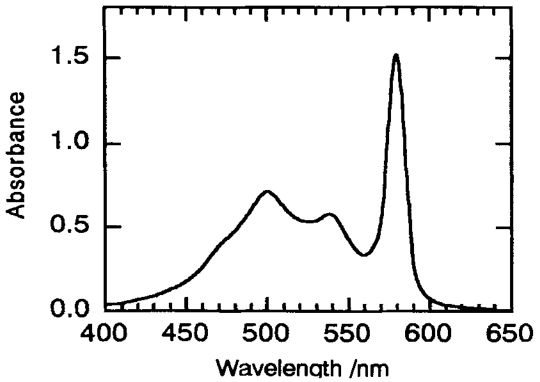


FIGURE 4 Absorption spectrum of PIC J-aggregated microcrystals prepared by reprecipitation method in *n*-hexane at room temperature.

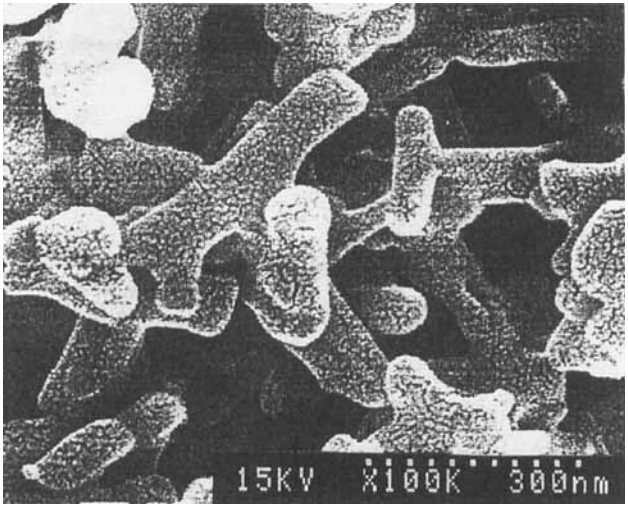


FIGURE 5 SEM photograph of PIC J-aggregated microcrystals prepared by reprecipitation method in *n*-hexane.

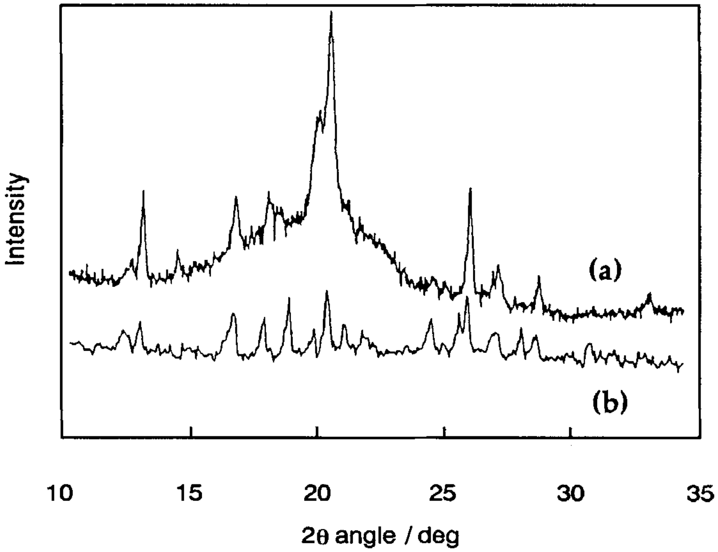


FIGURE 6 X-ray diffraction patterns of PIC J-aggregated microcrystals prepared by reprecipitation method in *n*-hexane (a) and PIC bulk crystals (b). A broad peak around 20° in 2θ angle due to the Millipore® filter used for collecting microcrystals overlaped with those from microcrystals in (a).

J-band was located at 580 nm and was somewhat red-shifted from that of salting-out J-aggregates. The half width of the J-band was 15 nm. The sizes of microcrystals were found to be about 100 nm to 1 μm by the SEM observation (FIGURE 5). The powder X-ray diffraction patterns clearly indicated that they were crystals (FIGURE 6).

J-aggregated microcrystals dispersed in *n*-hexane have a tendency to cohere within several minutes to give precipitated mass of PIC. In order to avoid cohesion of dispersed microcrystals, we examined to recrystallize PIC as microcrystals in polymer matrices. Saeva and Olin have reported the formation of J-aggregates in the ethyl cellulose matrix.[11] We extended the polymer system, to gelatin as a hydrophilic polymer and PMMA as a hydrophobic polymer. Consequently, the microcrystals in both systems showed J-band absorption. The size of microcrystals depended on a sort of polymers and condition of recrystallization. In gelatin, J-band absorption was very narrow (6 nm in half width) at 573 nm (line 1 in FIGURE 7). No clear microcrystal images were found by optical microscopic observation, suggesting that the size of microcrystals was less than several hundred nanometer. On the other hand, microcrystals in PMMA were generally several micrometers and larger than those in gelatin. J-

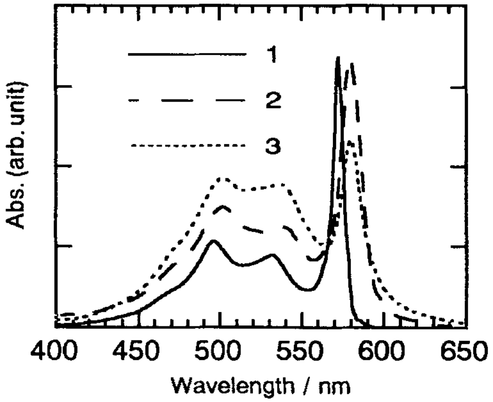
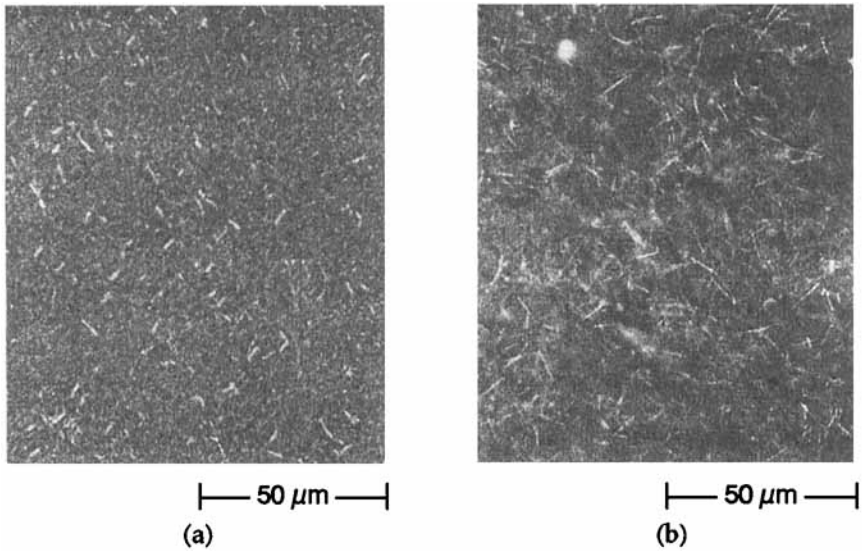


FIGURE 7 Absorption spectra of PIC J-aggregated microcrystals prepared by recrystallization in gelatin by spin-coating (1), in PMMA by spin-coating (2), and in PMMA by slow evaporation (3).



(a) (b)

FIGURE 8 Optical micrograph of J-aggregated microcrystals in PMMA.
(a) evaporation by spin-coating
(b) slow evaporation

band absorption of microcrystals in PMMA became broad (15 nm in half width) and absorption maximum was located at 580 nm. Since the evaporation rate was considered to be one of the main factor to determine the crystal size of PIC in this polymer system, the size of PIC microcrystals in PMMA with different evaporation rates was examined. In the fast evaporation rate by spin-coating method, the size of microcrystals tended to be 1-3 μm. And, in slow evaporation rate under natural evaporation condition, the size was fairly large, i.e. mainly 5-10 μm and partially more than 10 μm. These optical micrographs were shown in FIGURE 8. These microcrystals showed clear dichroism under the crossed-nicols condition. Though these J-aggregates in polymers were stable in the dark at room temperature, they were not stable under exposure to the room light or high temperature.

In conclusion, PIC J-aggregates were obtained as microcrystals by the salting-out method, the reprecipitation method and recrystallization in polymers at room temperature. The extremely sharp J-band was observed under the aqueous preparation conditions, i.e. the salting-out method and recrystallization in gelatin, and the broad and red-shifted J-band was obtained under hydrophobic conditions, i.e. the reprecipitation method in *n*-hexane and recrystallization in PMMA. The size of the former microcrystals was smaller than that of the latter ones, implying that smaller crystals may absorb shoter wavelengths with a sharper spectrum. The studies on the relationship between the size and other physical properties of these J-aggregated microcrystals are currently in progress.

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