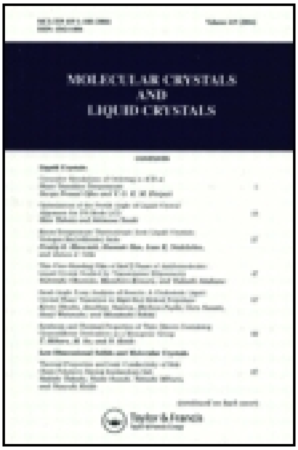

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Tetsuya Kunisawa [a], Tomoo Sato [a] & Yoshiro Yonezawa [b]

[a] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-01, JAPAN

[b] Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto 3, Sumiyoshi-ku, Osaka, 558, JAPAN

To cite this article: Tetsuya Kunisawa, Tomoo Sato & Yoshiro Yonezawa (1997): Fabrication and Optical Properties of J-Aggregate of Cyanine DYE in Thin Polymer Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 169-172

To link to this article: http://dx.doi.org/10.1080/10587259708032274

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 169–172
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FABRICATION AND OPTICAL PROPERTIES OF J-AGGREGATE OF CYANINE DYE IN THIN POLYMER FILMS

TETSUYA KUNISAWA, TOMOO SATO AND YOSHIRO YONEZAWA[†]
Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, JAPAN
[†]Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto 3, Sumiyoshi-ku, Osaka 558, JAPAN

Abstract Polymer films containing cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine chloride (PIC), were fabricated by dropping aqueous solutions of the dye and the water-soluble polymer on the quartz plate and drying. The aggregation state of PIC in thin polymer films was dependent on the kind of polymers. The aggregation state could be controlled by varying the amount of anionic sites on the polymer chain or by mixing two kinds of polymers.

INTRODUCTION

Characteristic properties of the J-aggregate (JA), e.g., the sharp absorption band and resonance fluorescence, have interested the researchers in wide disciplines.[1,2] Because of the remarkable nonlinear optical properties, studies on the fabrication and optical properties of JA in polymer matrices have advanced in recent years.[3-6] Polymer films are regarded as a useful matrix for opto-electronic device because of its high stability and simple fabrication procedure compared with LB films. In this study, we tried to fabricate polymer films containing JA by dropping aqueous solutions of the water-soluble polymer and quinocyanine dye, 1,1'-diethyl-2,2'-cyanine chloride (PIC), on the quartz plate and drying. When sodium alginate (SA) or carboxymethyl cellulose sodium salt (CMC) was used as the matrix, JA was easily formed. In case of polymethacrylic acid (PM), PIC molecules were incorporated in the forms of monomer and dimer. In addition, we tried to control the aggregation state of dye molecules by mixing SA with PM, or by changing the amounts of anionic site on CMC.

EXPERIMENTAL

Structural formulas of PIC and polymers used in this study are given in Figure 1. PIC was purchased from the Japanese Research Institute for Photosensitizing Dyes Co. SA was obtained from Nacalai Tesque Co. CMC was made in Daicel Chemical Industries. Ltd. PM was purchased from Scientific Polymer Products Inc. These polymers possess COO^- groups as the anionic site. SA was purified by recrystallization method.[3]

The mixed aqueous solution of polymer and PIC was dropped on one side of the quartz plate ($10\times40\times1$ mm^3 in size) by the amount of 0.05 ml cm^{-2} and dried in a desiccator for 1-2 days. The film thickness was 1-2 μm. The concentrations of polymer and dye in aqueous solutions were 0.5 wt% and 2.5×10^{-5} mol dm^{-3}, respectively. The absorption spectra were recorded on a UV-260 spectrophotometer (Shimadzu Seisakusyo Co.). Measurements of the fluorescence spectra were carried out with a PMA-10 system (Hamamatsu Photonics Co.) attached to a fluorescence microscope XF-EFD2 (Nikon Co.). The excitation wavelength for fluorescence measurements was 365 nm. The absorption and fluorescence spectra were measured at room temperature in air.

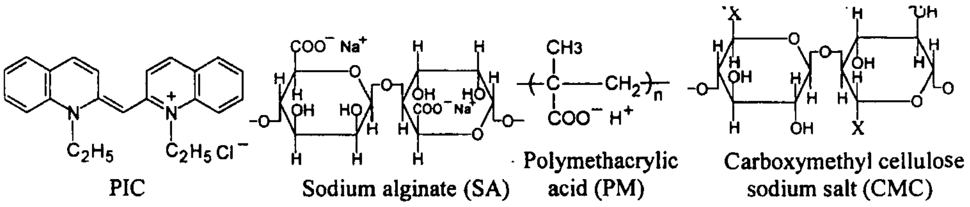
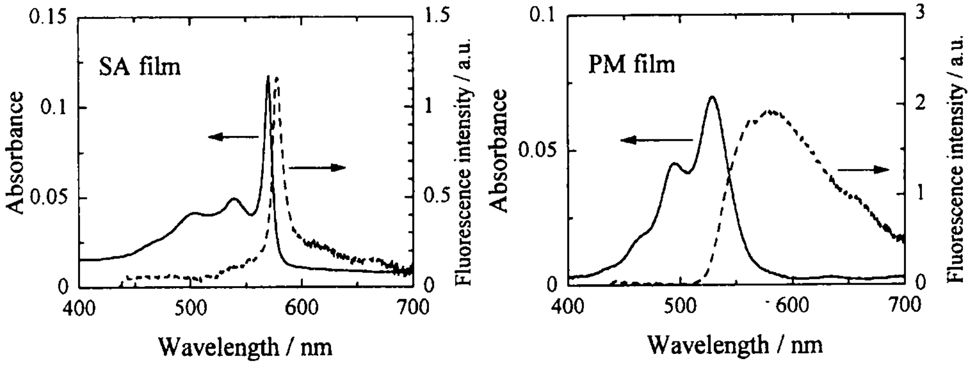


FIGURE 1 Structural formulas of cyanine dye and polymers. X sites on CMC are $-CH_2OCH_2COO^-\,Na^+$ or $-CH_2OH$ groups.

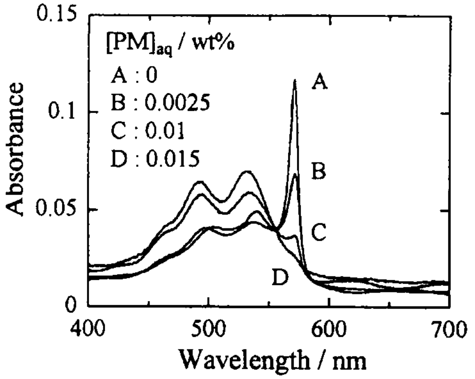
RESULTS AND DISCUSSION

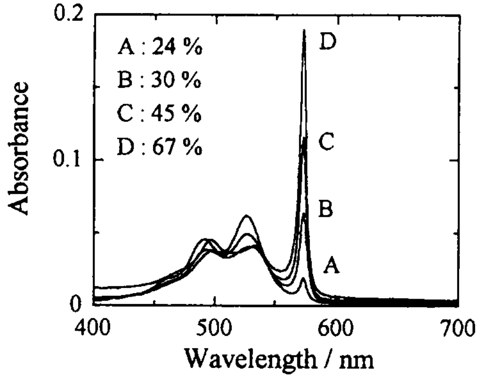
Absorption and fluorescence spectra of PIC in SA and PM films are shown in Figure 2. A sharp and intense peak at λ=570 nm in SA film (solid line) was assigned to the J-band. The full width at half maximum (FWHM) of the J-band was 9 nm. In the fluorescence spectra (dotted line), resonance fluorescence with small Stokes shift from the J-band was observed at λ=578 nm. These results demonstrate that PIC molecules were incorporated as JA in the SA film. According to the fluorescence microscope observation (100 magnification) with the color chilled CCD camera system (Hamamatsu

Phtonics Co.), JA of PIC were dispersed uniformly in the SA film. In the PM film, J-band was not observed. PIC molecules were incorporated as monomer and dimer, whose absorption maxima located at λ=529 nm and 494 nm, respectively. While PIC monomer in aqueous solutions was not fluorescent due to thermal deactivation, PIC in the PM film showed broad monomer fluorescence in the vicinity of 580 nm since fluorescence quantum yield in films was larger than that in aqueous solutions. We have shown the possibility that the aggregation state of cyanine dye could be controlled by changing the kinds of polymer matrices. The formation of JA in polymer films is assumed to be influenced by the secondary structure of the polymer as well as by the electrostatic interaction between cationic dye and COO^- groups on the polymer chain.



FUGURE 2 Absorption and fluorescence spectra of PIC in polymer films.





FUGURE 3 Absorption spectra of PIC in polymer films composed of SA and PM in various amounts of PM.

FUGURE 4 Absorption spectra of PIC in CMC films in various S.

We attempted to control the amount of JA in the following ways. First, we prepared the polymer films made of both SA and PM. Absorption spectra of PIC in the polymer films with varying amount of PM are shown in Figure 3. The concentrations of SA and PM in aqueous solution before drying were 0.5 wt% (constant) and 0-0.015 wt%, respectively. The formation of JA was suppressed in the presence of a small amount of PM. The conformation of SA would be influenced by PM. Second, we prepared the CMC films with varying amounts of carboxymethyl groups on CMC. We represent the ratio of carboxymethyl groups by S (%)=$100\alpha/(\alpha+\beta)$, where α and β are the number of $-CH_2OCH_2COO^-\ Na^+$ and $-CH_2OH$ groups at X site on CMC (Figure 1). Absorption spectra of PIC in CMC films with S; 24-67 %, are given in Figure 4. The J-band intensity increased unequivocally with the increase in the number of anionic groups.

In summary, we fabricated the polymer films containing JA of PIC molecules in the convenient method and controlled the formation of JA by changing the kinds of polymer matrices and the number of anionic groups. The stability of JA in the SA films was better than in LB films. Absorbance at the J-band decreased very gently and it reduced by half after 15 weeks. On the other hand, the stability of JA in LB films last only several days. Thus the polymer films would be useful for practical applications of JA to, e.g., novel optical materials.

ACKNOWLEDGEMENT

The authors are grateful to Daicel Chemical Industries. Ltd. for a gift of CMC.

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