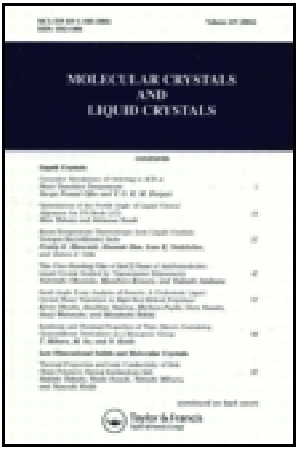

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Photochemical Behavior of Polymethylene Bis(p-Phenylenediacrylate)

Toshiki Komatsu [a] [b] , Hirochika Sakuragi [b] , Jun'Ichi Nagasawa [a] & Fusae Nakanishi [a]

[a] National Institute of Materials and Chemical Research, Tsukuba, Ibaraki, 305-8565, Japan

[b] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan

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Synthesis and Photochemical Behavior of Polymethylene Bis(*p*-Phenylenediacrylate)

TOSHIKI KOMATSU[a,b], HIROCHIKA SAKURAGI[b],
JUN'ICHI NAGASAWA[a] and FUSAE NAKANISHI[a]

[a]*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305–8565, Japan; and* [b]*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305–8571, Japan*

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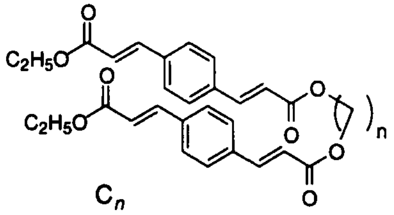
Polymethylene bis(*p*-phenylenediacrylate) with various alkyl chains were synthesized to clarify the relationship between emission behavior and structure both in solution and in crystal. In both states a unique emission behavior was found which was caused by solvents effect and alkyl chain length.

Keywords: *p*-phenylenediacrylate; bichromophoric system; fluorescence

INTRODUCTION

Photochemical dimerization has been paid attention based on not only scientific but also industrial interests. Cinnamic acid is one of the best examples that have three types of crystal giving different reactivity [1]. The authors have investigated *p*-phenylenediacrylic acid (*p*-PDA) derivatives which are bifunctionals of cinnamic acid and bichromophoric system. Taking advantage of bifunctionality, the photopolymerization of *p*-PDA derivatives has been studied. We have synthesized poly(vinyl alcohol) (PVA) bearing ethyl hydrogen *p*-phenylenediacrylate (*p*-PDA$_m$C$_2$)[2]. The photoreactivity of this polymer (PVA–*p*-PDA$_m$C$_2$) was found to be very high among the photopolymers reported [3]. We have concluded that the high reactivity is due to the formation of aggregation of side chains of *p*-PDA$_m$C$_2$.



C_n

For further investigation of the phenomena from the viewpoint of chemical structure and emission behavior, the more simplified new bichromophoric system, polymethylene bis-(*p*-(2-ethoxy carbonyl)vinyl)cinnamate (C*n*) was designed and synthesized.

This C*n* consists of two *p*-phenylenediacrylates bound various lengths of alkyl chain and expected formation of aggregates. In this report the fluorescence of C*n* both in solution and in crystal is measured under different conditions and the relationship between structure and emission behavior are described.

EXPERIMENTAL

The C*n*s (n=2~11) were prepared by the reactions of ethyl hydrogen *p*-phenylenediacrylate with 1,ω-dibromoalkanes in the presence of potassium carbonate. The products were purified by crystallization from toluene and subsequently from 2-propanol. The structure was confirmed by NMR spectroscopy and elementary analysis.

Fluorescence spectra were measured with a JASCO FP-777 spectrofluorometer with a Hoya U-340 and Corning 0-52 glass filters if necessary. Fluorescence spectrum measurements are carried out in a 10-mm rectangular cell. Measurement of fluorescence spectra of crystals was carried out using the specific sample folder. The sample was sandwiched in two quartz plates and used for fluorescence measurement.

RESULTS AND DISCUSSION

It should be noted that fluorescence spectrum in solution was affected remarkably by solvents used. In benzene, as an example, C*n*s' solution (10^{-5} ~10^{-4} mol dm^{-3}) showed the monomer emission band (λ_{max} 371 nm). In protic solvents such as methanol and ethanol, however, the increase in

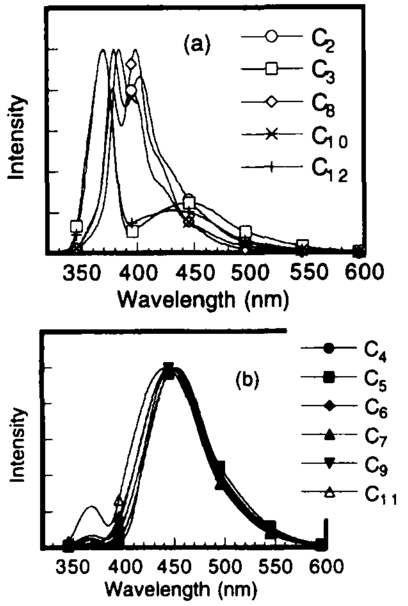


FIGURE 1 Fluorescence spectra on excitation of C*n* crystals by 305 nm light.

intensity at the longer wavelength region was remarkable for C_5 and C_7 (λ_{max} *ca.* 450 nm). This band can be ascribed to the emission from intramolecular excimers. Diethyl *p*-phenylenediacrylate (p-PDA$_d$C$_2$) showed intermolecular excimer emission at the same wavelength region in its higher concentrations than 0.1 mol dm^{-3} [4]. However, in the present concentration range lower than 10^{-4} mol dm^{-3}, the intermolecular interactions in the excited state could be neglected.

On excitation of the sample solutions with 355-nm light irradiating at the longer wavelength edge of the absorption band, the effect of alcohols was much more remarkable showing the emission peak at 450 nm.

C*n* crystals are relatively photostable, however, their emission behavior was found to be very interesting. Figure 1 shows the fluorescence spectra of C*n* crystals. In these crystals, the significant effect was observed on emission spectra depending on the alkyl chain length of C*n*.

In Figure 1(a), the C*n*s show the emission peak mainly at 375 nm and 400 nm. In all C*n*s shown in Figure 1(b) have the broad emission peak at 450 nm.

To explain these results, fluorescence spectrum data on other *p*-PDA derivatives including the polymer and the LB film are represented in Table I. The emission peak at 375 nm is the same as those of *p*-PDA derivatives in solution, which is due to the monomeric emission. The emission peak at 400

TABLE I Fluorescence peak of *p*-PDA derivatives in solutions and solid.

	λ_{max}(Solution :nm)	λ_{max}(Solid: nm)
PVA-*p*-PDA$_m$C$_2$	450 (CHCl$_3$)[2]	450 (Film)[2]
p-PDA$_d$C$_2$	375 (CHCl$_3$)[4]	400 (Crystal from Ethanol)
p-PDA$_m$C$_2$	375 (CHCl$_3$)	450 (Crystal from Ethanol)
p-PDA$_m$C$_{12}$	375 (CHCl$_3$)	430 (LB Film)[5]
C*n*	375 (CH$_2$Cl$_2$)	375~450 (Crystal)

nm is the same as observed in *p*-PDA$_d$C$_2$ of which crystal structure showed that *p*-PDA$_d$C$_2$ molecules are arranged in the stacking with no excimer formation. Therefore it is considered that the emission peaks observed in Figure 1(a) are due to monomeric species. The emission peak observed at 450 nm in Figure 1(b) was found in *p*-PDA$_m$C$_2$ crystal, the LB film of *p*-PDA mono dodecyl ester (*p*-PDA$_m$C$_{12}$) and PVA-*p*-PDA$_m$C$_2$ film. In these cases *p*-PDA chromophores are arranged side by side which leads to the excimer emission. Therefore it is suggested that C*n*s shown in Figure 1(b) have the similar molecular arrangement in crystals which can form excimers.

Thus depending on the alkyl chain length, the different emission behavior was found in the C*n* crystals, This fact suggests the possibility of control of molecular arrangement by alkyl chain length. Further study on crystal structure analysis of C*n* is under progress.

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