Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Time Rsponse of Crystallization of Impurity Controlled Tetrabenzo- [a, cd, j, Im]perylene Film

Satoshi Iwashima [a] , Tadanobu Sawada [a] , Junji Aoki [b a] & Hiroo Inokuchi [c a]

[a] Department of Chemistry, Faculty of Science and Technology, Meisei University, Hino-shi, 191, Tokyo, Japan

[b] Department of Chemistry, Faculty of Science, Toho University, Funabashi-shi, 274, Chiba, Japan

[c] The Institue for Molecular Science, Okazaki-shi, 444, Aichi, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Satoshi Iwashima , Tadanobu Sawada , Junji Aoki & Hiroo Inokuchi (1981): Time Rsponse of Crystallization of Impurity Controlled Tetrabenzo- [a, cd, j, Im]perylene Film, Molecular Crystals and Liquid Crystals, 73:3-4, 223-230

To link to this article: http://dx.doi.org/10.1080/00268948108072336

Mol. Cryst. Liq. Cryst., 1981, Vol. 73, pp. 223–230
0026-8941/81/7304–0223$06.50/0

Printed in the United States of America

Time Response of Crystallization of Impurity Controlled Tetrabenzo-[a, cd, j, lm]perylene Film†

SATOSHI IWASHIMA and TADANOBU SAWADA

Department of Chemistry, Faculty of Science and Technology, Meisei University, Hino-shi, 191 Tokyo, Japan

and

JUNJI AOKI

Department of Chemistry, Faculty of Science, Toho University, Funabashi-shi, 274, Chiba, Japan

and

HIROO INOKUCHI

The Institute for Molecular Science, Okazaki-shi, 444, Aichi, Japan

(*Received March 17, 1981; in final form March 30, 1981*)

Crystals with quantitative additions of adding quantitatively VEB or iso-VEB to TBP were prepared, and the time response of the absorption and fluorescence spectra were examined for their thin films evaporated at room temperature, 100°C, 130°C and also 140°C.

The crystallization rate was found to depend on the purity of the specimen and also on the substrate temperature. Furthermore, we confirm that the purity of TBP estimated in our previous paper[1] is reasonable, and that the crystallization rate can be used as a new monitor of purity.

INTRODUCTION

We found that the crystallization rate of Tetrabenzo[a, cd, j, lm]perylene (TBP) (a in Figure 1) film depends on its purity,[1] the rate being estimated on the basis of the absorption and fluorescence spectra as shown in Table I.

In this study, we present the rate determination for impurity controlled TBP films by means of the absorption and fluorescence spectra; the amount of

† Preparation of High-Purity Organic Compounds XIV. Part XIII. S. Iwashima, H. Honda, J. Aoki and H. Imokuchi, *Mol. Cryst. Liq. Cryst.*, **59**, 207 (1980).

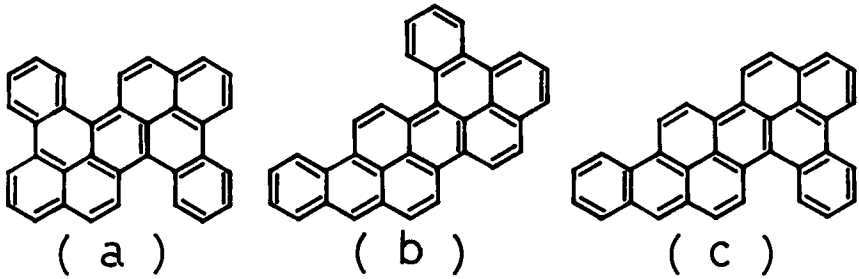

FIGURE 1 Structural formulas of Tetrabenzo[a, cd, j, lm]perylene (a), Violanthrene-B (b) and iso-Violanthrene-B (c).

impurity, violanthrene-B(VEB) or iso-violanthrene-B (iso-VEB) (b & c in Figure 1), affects strongly the crystallization rate as described in a previous report.[1]

EXPERIMENTAL

Materials (TBP, VEB and Iso-VEB)

The synthesis of TBP was carried out by heating benzanthrone with copper powder, zinc chloride and sodium chloride.[2] As described in the previous paper,[1] crude TBP separated from the reaction mixture was further purified. The most purified specimen is denoted as TBP [$MC_2NaC_2R_2$], where [R_1] is the recrystallization from xylene, [M] is the purification with maleic anhydride, [C_1] is the chromatographical purification over activated alumina, [C_2]

TABLE I

Time response of the crystallization of impurity controlled TBP films

	TBP sample	Temperature (C°)	Period (hour)†	Concentration of impurity (mol/mol) (estimated)
RT-film	[R_1]	Room Temperature	∞	10^{-1}
	[MC_1]		24	10^{-4}
	[MC_2]		24	10^{-5}
	[$C_2NaC_2R_2$]		9	10^{-6}
	[$MC_2NaC_2R_2$]		0	10^{-8}
HT-film	[$C_2NaC_2R_2$]	100	9	10^{-6}
		130	3	
		135	0	
		140	0	
	[$MC_2NaC_2R_2$]	130	0	10^{-8}
		140	0	

† The time required to form the crystalline film from amorphous film.

is the chromatographical procedure over activated carbon-activated alumina, [Na] is treatment with metallic sodium in 2,2'-dioxydiethyl ether and [R_2] is recrystallization from benzene and then from xylene.

Synthesized VEB and iso-VEB were separated from the reaction mixture by column chromatography method, and purified by means of recrystallization and sublimation in high vacuum.[2,3]

Preparation of TBP-VEB and TBP-iso-VEB crystals and measurement of their spectra

Benzene solution of TBP (0.07 mol/1) was mixed with that of VEB in definite proportion. The solvent was evaporated slowly on a steam bath and then was excluded from the mixture completely in a vacuum of 10^{-4} Torr. The crystal obtained was molten under an atmosphere of 1/2 Torr of argon. Thus the TBP-VEB crystals [$10^{-3} \sim 10^{-8}$ mol (VEB)/mol (TBP)] were prepared. TBP-iso-VEB crystals ($10^{-3} \sim 10^{-8}$ mol/mol) were also prepared in a similar manner.

The thin films of the crystals, their thickness being $0.2 \sim 0.25$ μm, were prepared on quartz plates at room temperature (abbreviated as RT-films). By the same procedure, the TBP-VEB thin films were prepared on quartz plates which were kept at 100°C, 130°C and 140°C, respectively (abbreviated as HT-films).

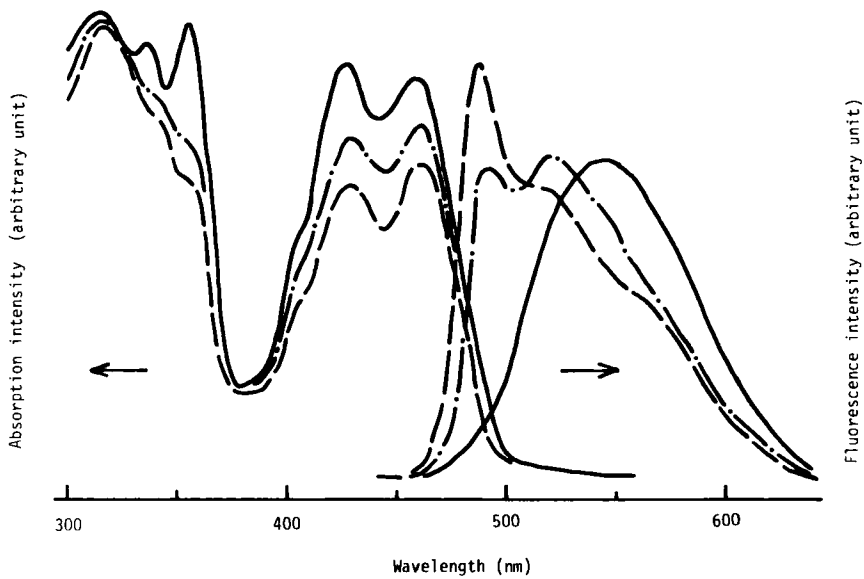

FIGURE 2 Time response of the absorption and fluorescence spectra of TBP-VEB (10^{-5} mol/mol) thin film evaporated at room temperature. ——: immediately after evaporation; —·—: after 3 hr. - - - - -: after 9 hr.

Measurement The absorption and fluorescence spectra of the TBP-VEB and TBP-iso-VEB films were measured at room temperature at 0, 1,2, 3, 5, 7, 9, 24, 48, and 72 hours after the sample preparation with a Shimadzu Double-40 Multiconvertible Spectrometer and with a Hitachi TYPE-3 Fluorescence Spectrometer.

RESULTS AND DISCUSSION

Room temperature (RT) film

Absorption and fluorescence spectra of TBP-VEB thin films containing 10^{-5} mol/mol of VEB, as an example, are shown in Figure 2. The absorption peaks in the wavelength region between 300 nm and 360 nm became broad with time. The intensities of peaks at 430 nm and 460 nm were reversed with the passage of time. On the other hand, the broad fluorescence maximum peak appeared at 545 nm immediately after sample preparation, and the peak-shift to 488 nm occurred in 9 hours. These results resemble those of TBP [MC_2] and TBP [$C_2NaC_2R_2$]. Furthermore, time response of the absorption spectra varied much less than that of the fluorescence spectra. Therefore, the fluorescence spectra can be used as an index of the crystallization rate.

Time response of fluorescence spectra of TBP-VEB film containing 10^{-4}, 10^{-6} and 10^{-8} mol/mol of VEB are shown in Figure 3. Immediately after sample preparation, the broad maximum peaks were observed in the region of 540 nm. However, characteristic changes of such specimens occurred as a function of time. After 3 hours, the fluorescence peak of the specimen, contained 10^{-8} mol/mol of VEB, was shifted to 488 nm and the intensity in the wavelength region longer than 500 nm decreased. After that no further change was observed. This fluorescence spectrum was very similar to that of high-purity TBP [$C_2NaC_2R_2$].

On the other hand, for specimens of 10^{-6} and 10^{-4} mol/mol of VEB content, the fluorescence spectra, similar to that of high-purity TBP, were observed in 9 hours and 1 day, respectively. These findings show that the crystallization rate of TBP film (RT-film) was decreased with increasing the impurity (VEB) content. An increase of the impurity (VEB) in the specimen decreased the intensity of the 488 nm peak as compared with that of the wavelength region longer than 500 nm. The time response of the fluorescence spectra of 10^{-5} mol/mol of VEB content film were intermediate between those of 10^{-4} and 10^{-6} mol/mol films, and those of 10^{-7} mol/mol TBP-VEB film were intermediate between those of 10^{-6} and 10^{-8} mol/mol films.

As shown in Figure 4, the time response of the fluorescence spectra of TBP-iso-VEB crystals were similar to those of TBP-VEB crystals. The peak-shift occurred in 1, 7 and 24 hours after sample preparation for specimens containing 10^{-8}, 10^{-6} and 10^{-4} mol/mol of iso-VEB, respectively.

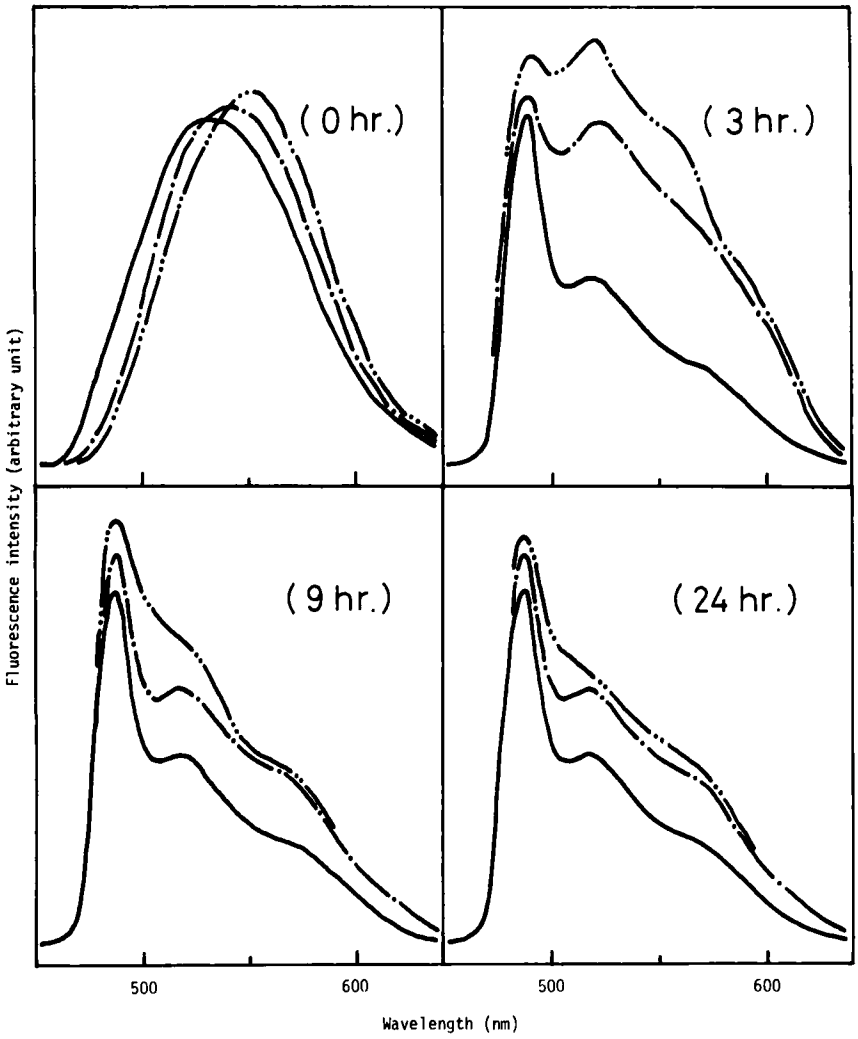

FIGURE 3 Time response of the fluorescence spectra of TBP-VEB thin film evaporated at room temperature. ———: 10^{-8} (mol/mol); —·—·—: 10^{-6}; —··—: 10^{-4}.

High temperature (HT) film

The time response of the fluorescence spectra of TBP-VEB films containing 10^{-4} mol/mol of VEB prepared at high temperature is shown in Figure 5. The shift of the fluorescence spectra similar to that of high-purity TBP occurred in 7, 9 and 24 hours after sample preparation for the films prepared at 140°C,

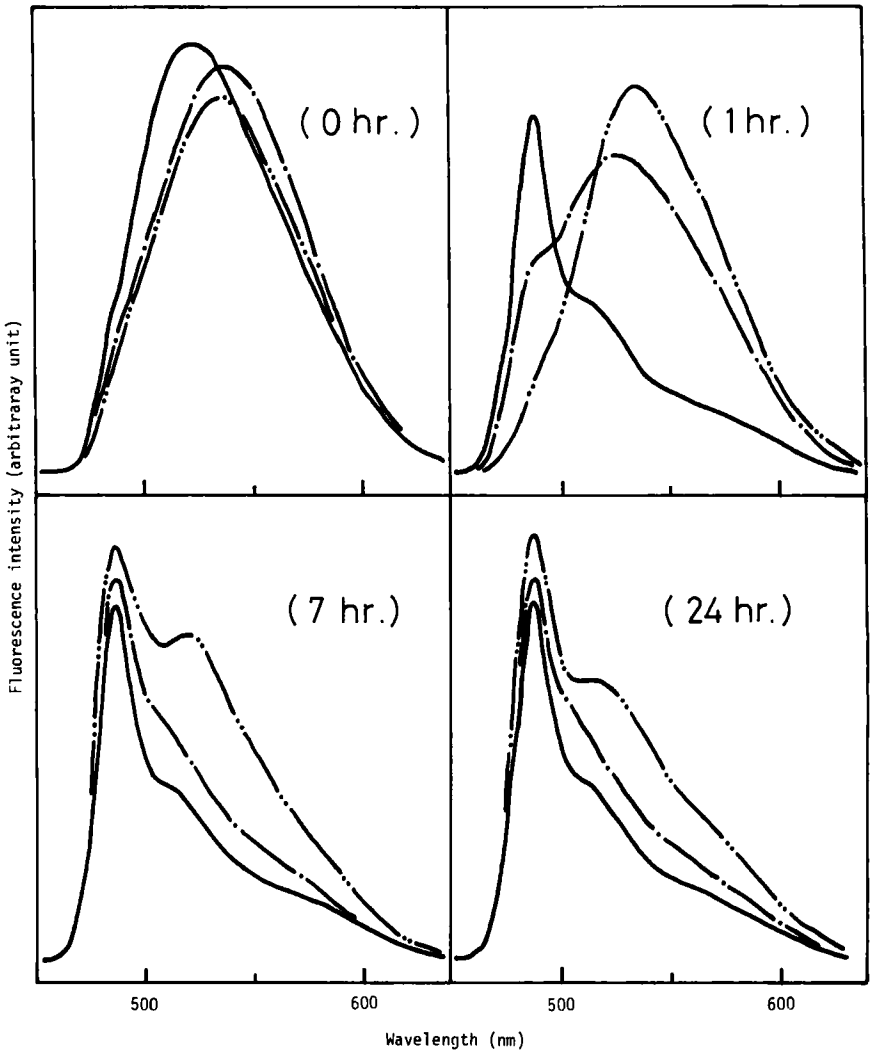

FIGURE 4 Time response of the fluorescence spectra of TBP-iso-VEB thin films evaporated at room temperature. ——: 10^{-8} (mol/mol); —·—: $^{10-6}$; —··—: 10^{-4}.

130°C and 100°C, respectively. On the basis of these results, it was found that the crystallization rate was increased with raising the substrate temperature higher that 130°C, almost independent of impurity content.

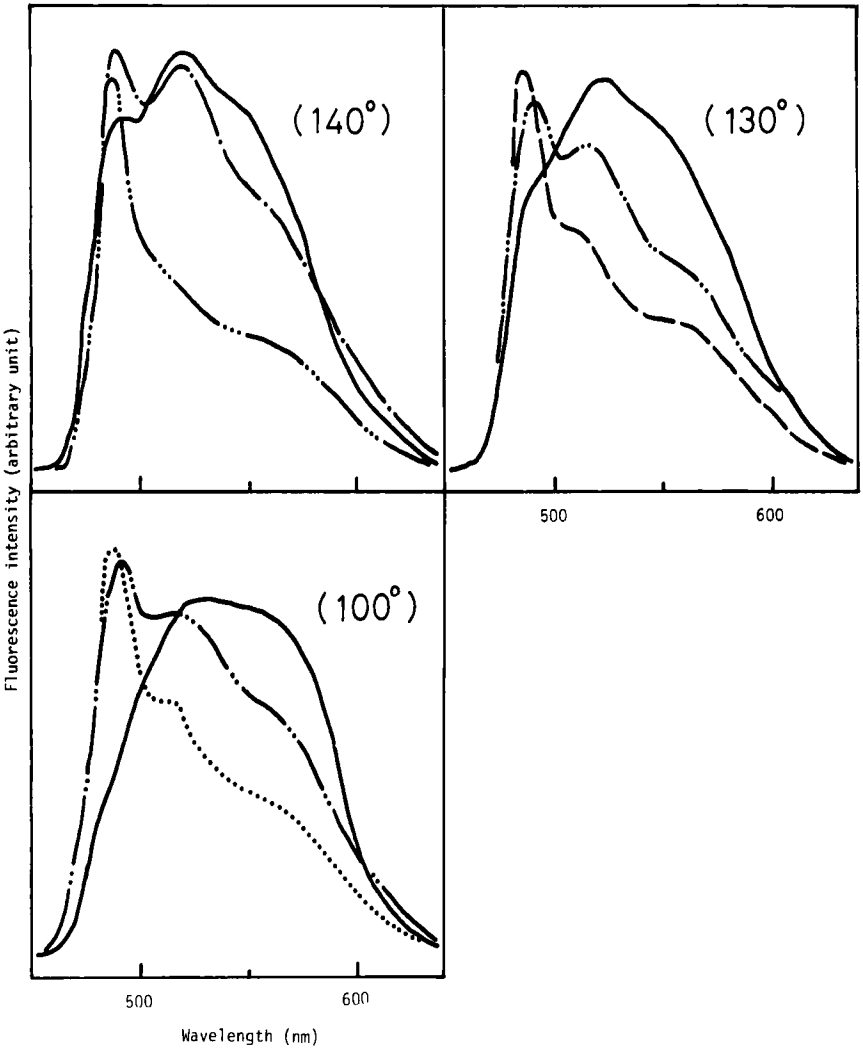

FIGURE 5 Time response of the fluorescence spectra of TBP-VEB (10^{-4} mol/mol) thin films evaporated at 140°C, 130°C and 100°C. ———: immediately after evaporation; —·—: after 1 hr. —··—: after 3 hr. —···—: after 7 hr. – – – –: after 9 hr. ·····: after 24 hr.

CONCLUSION

Table II summarizes the time response of the fluorescence spectra of RT-film and HT-film samples. The crystallization rate was found to depend strongly on the purity of sample and on the substrate temperature. The concentration

TABLE II

Time response of the crystallization of TBP-VEB, TPB-iso-VEB crystals

	Concentration of VEB or iso-VEB in TBP (mol/mol) (observed)	Temperature (°C)	Period (hour)†	
			TBP-VEB	TBP-iso-VEB
RT-film	10^{-3}	Room Temperature	48	48
	10^{-4}		24	24
	10^{-5}		24	9
	10^{-6}		9	7
	10^{-7}		5	3
	10^{-8}		3	1
HT-film	10^{-4}	100	24	
		130	9	
		140	7	

† The time required to form the crystalline film from the amorphous film.

impurity, as described in our previous paper,[1] was in good agreement with that in Table II. The crystallization rate of high-purity TBP [$MC_2NaC_2R_2$] was 0 hour (Table I). On the other hand, the rate of TBP-VEB crystals (10^{-8} mol/mol) was 1 hour (Table II). Therefore, the concentration of impurity in TBP [$MC_2NaC_2R_2$] may be considered to be less than 10^{-8} mol/mol.

We confirmed that the impurity contents reported in the previous paper had been good estimates,[1] and that the crystallization rate could be used as a new monitor of the purity of TBP. This method may be applied to other polycyclic aromatic hydrocarbons as a new monitor of purity.

Acknowledgments

The authors wish to express thanks to Dr. H. Honda for helpful discussion and to Mr. T. Aida, Miss E. Miyahara and Miss I. Fujieda for their assistance.

References

1. S. Iwashima, H. Honda, J. Aoki and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, **59**, 207 (1980).
2. J. Aoki, M. Takekawa, S. Fujisawa and S. Iwashima, *Bull. Chem. Soc. Jpn.*, **50**, 1017 (1977).
3. S. Iwashima, H. Honda, M. Takekawa and J. Aoki, *J. Chem. Soc. Jpn.*, **1979**, 443.