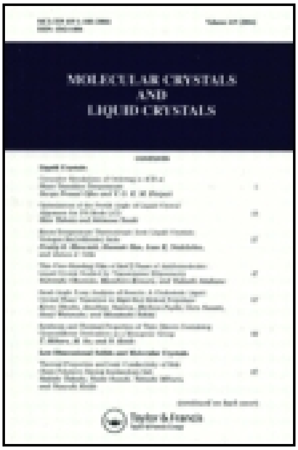

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Time Dependence of the Crystallization of Tetrabenzo [a, cd, j, lm]perylene Evaporated Film as a Function of Purity

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Time Dependence of the Crystallization of Tetrabenzo [a, cd, j, lm]perylene Evaporated Film as a Function of Purity†

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The rate of crystallization from the amorphous state of Tetrabenzo[a, cd, j, lm]perylene(TBP) film under various temperature conditions was examined as a function of the purity of the specimen.

On the basis of the absorption and fluorescence spectra of TBP film, the rate of crystallization of TBP film evaporated at room temperature was found to be decreased with increasing impurity of the specimen. The rate of crystallization of TBP, with an impurity level of 10^{-6} mol/mol, was decreased at temperatures below the glass transition temperature (135–140°C), while the crystalline thin film was immediately obtained at temperatures above the glass transition point. On the other hand, crystalline thin films of the purest TBP (10^{-8} mol/mol impurity contents) prepared by our methods (J. Chem. Soc. Jpn., **1979** (4), 443) could be obtained immediately after sample preparation independent of the substrate temperature.

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† Preparation of High-Purity Organic Compounds XIII. Part XII, S. Iwashima, H. Honda, J. Aoki, and M. Takekawa, *J. Chem. Soc. Jpn.*, **1979** (4), 443.

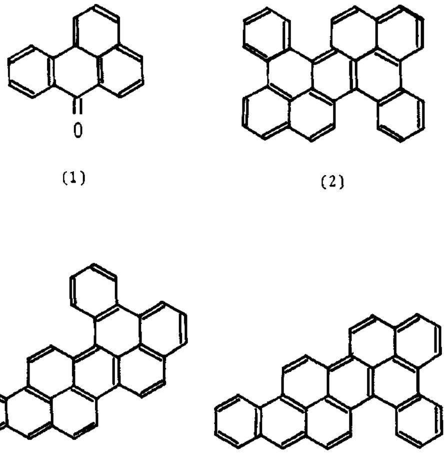
INTRODUCTION

The structures of polycyclic aromatic hydrocarbon thin films depend on various conditions of sample preparation. Especially, the temperature of the substrates for deposition is a critical factor for the transition from the amorphous to the microcrystalline[1] state. Furthermore, the structures also depend on the types of deposited compounds; for example, thin films of perylene and coronene deposited on glass substrates kept at room temperature are easily crystallized but those of naphthacene and pentacene remain amorphous.[2]

In this paper, using absorption and fluorescence spectra, we present the dependence of the crystallization rate of tetrabenzo[a, cd, j, lm]perylene (TBP) film on the substrate temperature and on specimen purity. This procedure is applied to a determination of the purity of polycyclic hydrocarbons up to 10^{-8}mol/mol.

EXPERIMENTAL

TBP (2) was synthesized as follows:[3] a mixture of benzanthrone (**1**) (5.0 g), copper powder (5.0 g), zinc chloride (25.0 g) and sodium chloride (5.0 g) was kept at 220°C for 30 min. After treating the mixture with warm water containing a small amount of hydrochloric acid, the insoluble part was gathered, washed and dried. The crude material is denoted as TBR[R], which was purified as follows: TBP[R] was boiled with maleic anhydride and chloranil,



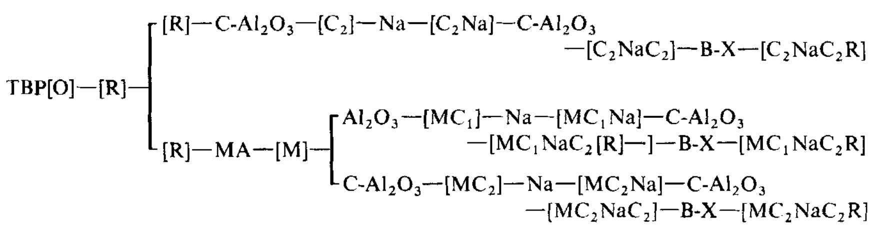
(1) (2)

(3) (4)

FIGURE 1 Structural formulae of Benzanthrone (**1**), Tetrabenzo[a, cd, j, lm]perylene (**2**), Violanthrene-B (**3**) and iso-Violanthrene-B (**4**).

TABLE I

Purification process of Tetrabenzo[a, cd, j, lm]perylene



Al_2O_3:	Column chromatography (activated alumina)
C-Al_2O_3:	Column chromatography (activated carbon and activated alumina)
Na:	Treatment with diethylene glycol and metallic sodium
B-X:	Recrystallization from benzene and then from xylene
MA:	Treatment with maleic anhydride
TBP[O]:	Crude Tetrabenzo[a, cd, j, lm]perylene
[R]:	Recrystallization (extraction) from xylene

neutralized by aqueous sodium hydroxide, and extracted with toluene. The extracted material, TBP[M], was chromatographed over activated carbon-activated alumina, treated with metallic sodium in 2,2′-dioxydiethylether (diethylene glycol), and chromatographed again over activated carbon-activated alumina. The eluate was condensed by means of vacuum distillation and the precipitate was collected. The precipitate was recrystallized from benzene and then from xylene.[4] By these purification procedures, impurities including Violanthrene-B (**3**) and iso-Violanthrene-B (**4**) were removed from crude TBP. Table I shows this purification process. (See Figure 1)

The TBP thin films were prepared on quartz plates kept at room temperature (RT-film) or at high temperature (100°C, 130°C, 135°C and 140°C) (HT-film) in a vacuum of 10^{-4} Torr.

The absorption spectra of the RT-film were measured at room temperature by a Shimadzu Double-40 Multiconvertible Spectrophotometer and the fluorescence spectra of the RT-film and the HT-film were measured at room temperature by a Hitachi Type-3 Fluorescence Spectrophotometer.

RESULTS AND DISCUSSION

1) The structure of thin films evaporated on quartz plates kept at room temperature (RT).

The time dependence of the absorption spectra of TBP [C_2NaC_2R] containing 10^{-6} mol/mol impurity is shown in Figure 2. Peaks of the absorption spectra were found at 317, 338, 355, 430 and 460 nm, respectively, when we

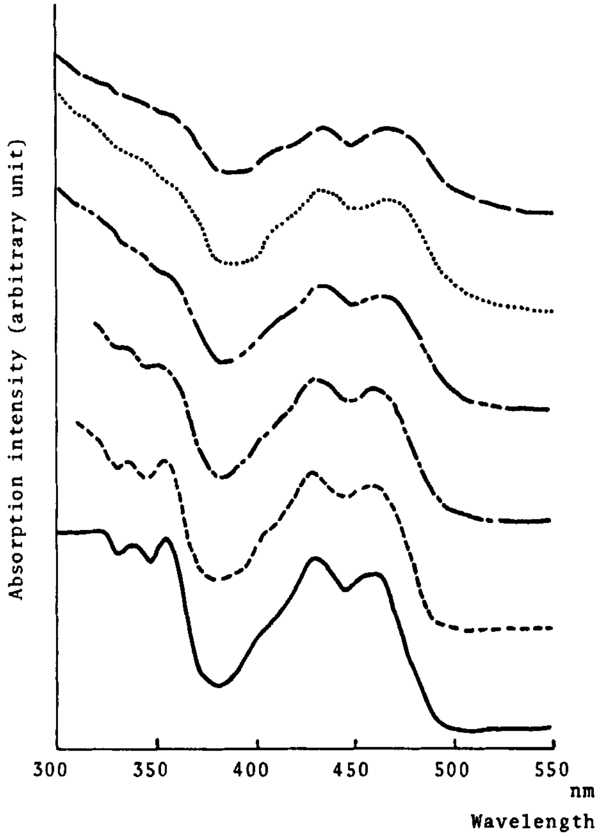


FIGURE 2 Time dependence of the absorption spectra of thin film of TBP[C_2NaC_2R] evaporated at room temperature (RT-film), [C_2NaC_2R] ———: immediately after evaporation ------: after 1 hr, —·—: after 3 hr, —··—: after 5 hr, ······: after 7 hr, — — —: after 1 day, (observed at room temperature).

observed the spectra immediately after the sample preparation; the 430 nm-peak is higher than 460 nm-peak. After one day, the spectral change was as follows:

a) The peaks in the wavelength region shorter than 400 nm were broad.

b) The peak heights at 430 and 460 nm were nearly equal and these two peaks were shifted to longer wavelength up to 433 and 468 nm respectively. No further shift of the peaks was observed.

The time dependence of the absorption spectra of TBP [MC_1] and TBP[MC_2] agreed with that of TBP[C_2NaC_2R] mentioned above. And the absorption spectrum of TBP[R] agreed with that of TBP[C_2NaC_2R] which

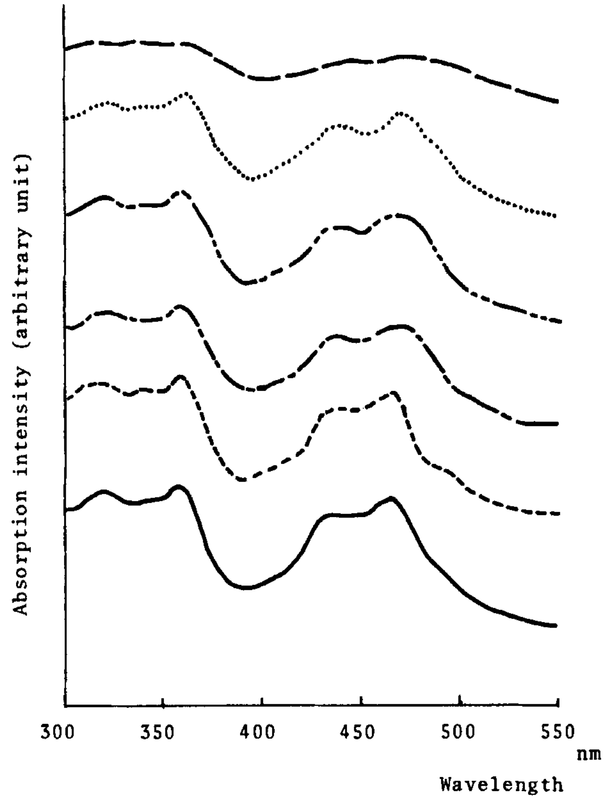


FIGURE 3 Time dependence of the absorption spectra of thin film of TBP[MC_1NaC_2R] evaporated at room temperature (RT-film), [MC_1NaC_2R] ——— : immediately after evaporation ------ : after 1 hr, —·— : after 3 hr, —··— : after 5 hr, ······ : after 7 hr, — — — : after 1 day, (observed at room temperature).

was measured immediately after the sample preparation, and the shoulder was observed at 560 nm. No change of the absorption spectrum of TBP[R] was found as a function of time. The time dependence of the absorption spectrum of TBP[MC_1NaC_2R] is shown in Figure 3 with the changes very similar to that of TBP[C_2NaC_2R]. The absorption spectrum of TBP[MC_2 NaC_2R] (the purest TBP) immediately after sample preparation was nearly the same as that of TBP[MC_1NaC_2R] measured one day after preparation. The spectral peaks of the purest TBP were observed at 440 nm and 472 nm; the 472 nm-peak was higher than that at 440 nm.

The fluorescence spectra of various kinds of TBP are shown in Figures 4 and 5, which showed very characteristic time dependence. The fluorescence maximum peak of TBP[R] was observed at 568 nm immediately after sample preparation, and the peak did not shift with time. As shown in Figure 4, the

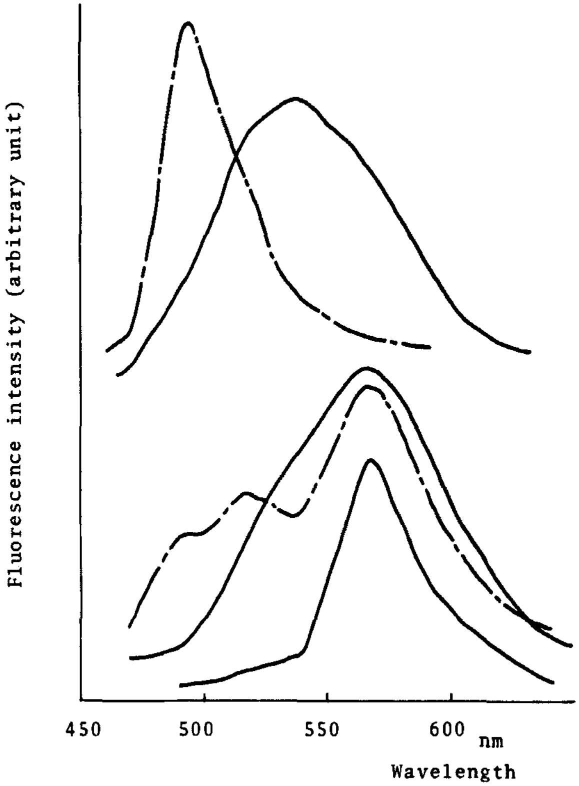


FIGURE 4 Time dependence of the fluorescence spectra of thin films of TBP evaporated at room temperature, $[MC_2]$ (above) ———: immediately after evaporation —·—: after 1 day, $[MC_1]$ (middle) ———: immediately after evaporation —·—: after 2 days, [R] (below) ———: no change with time (observed at room temperature).

broad maximum peak of $TBP[MC_1]$ was observed at 566 nm immediately after sample preparation, and after two days, two new weak peaks were observed at 490 and 516 nm. For $TBP[MC_2]$, the broad fluorescence maximum peak appeared at 538 nm immediately after sample preparation, and after one day, the peak shifted to 492 nm as shown in Figure 4. The activated carbon-activated alumina column (C_2) adsorbs impurities more strongly than TBP. On the other hand, the activated alumina column (C_1) adsorbs both TBP and impurities very weakly. Therefore, column (C_2) is more effective for the removal of impurities than alumina column (C_1), so that $TBP[MC_2]$ is purer than $TBP[MC_1]$. The fluorescence maximum peak of $TBP[C_2NaC_2R]$ was detected at 520 nm and also at 486 nm immediately after sample preparation, and the 520 nm-peak was shifted to 486 nm after 9 hours, but the 486 nm-peak did not change after that.

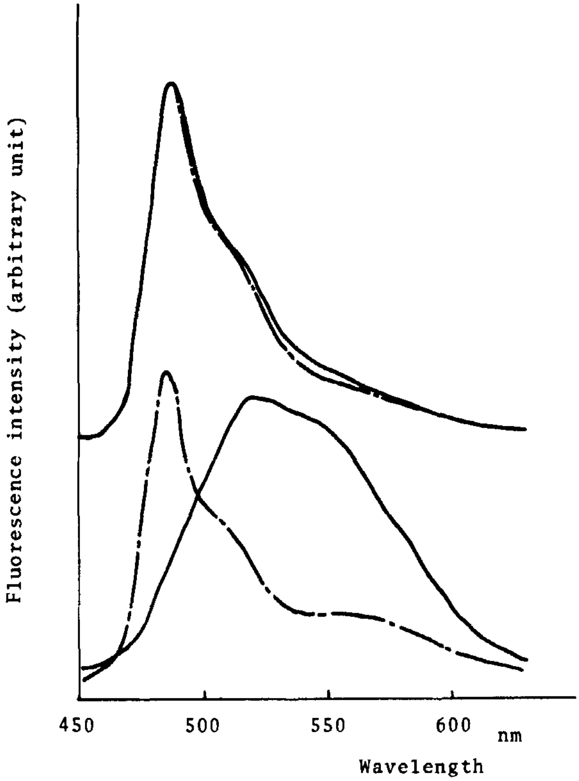


FIGURE 5 Time dependence of the fluorescence spectra of thin films of TBP evaporated at room temperature, [MC_2NaC_2R] (above) ——— : immediately after evaporation —·— : after 5 min.-1 day, [C_2NaC_2R] (below), ——— : immediately after evaporation, —·— : after 9 hr.-1 day, (observed at room temperature).

The time dependence of the absorption and fluorescence spectra was in good agreement with the results reported by Maruyama[1] and Kamura.[2] The broad fluorescence maximum peaks of TBP[MC_2] and TBP[C_2NaC_2R] were observed in the region of 520–540 nm immediately after sample preparation and were shifted to the shorter wavelength region with time. These shifts are understood as the crystallization process: the rearrangement from amorphous to microcrystalline thin film. However, TBP[R] film is not rearranged to the microcrystalline state at all. With increase of purity of TBP from [MC_1] to TBP[C_2NaC_2R], the rate of crystallization was increased.

2) The structure of evaporated thin films on quartz plates at high temperature (HT).

In order to investigate the temperature dependence of the crystallization of evaporated films, the TBP thin films were evaporated on quartz plates at 100°,

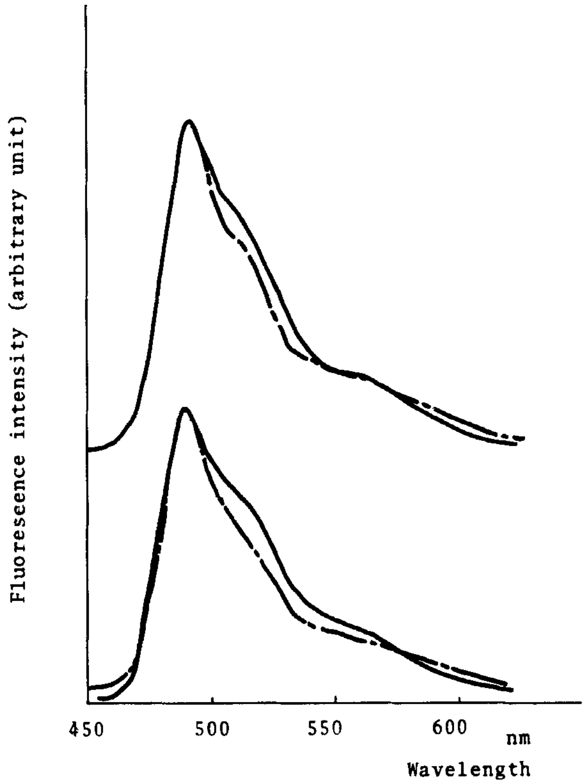


FIGURE 6 Time dependence of the fluorescence spectra of thin films of TBP[MC_2NaC_2R] evaporated at 130°C (above) and 140°C (below) (HT-film), [MC_2NaC_2R] ——— : immediately after evaporation —·— : after 5 min.-1 day (25 days), (observed at room temperature).

130°, 135° and 140°C, respectively, and their fluorescence spectra observed. As shown in Figures 5 and 6, the maximum peak of the purest TBP was observed at 490 nm immediately after sample preparation, when the quartz plates were kept both at 135° and at 140°C, and no further peak-shift with time was observed. The peak at 490 nm was also observed when the plate was kept at room temperature. These results indicate that the purest TBP was in the microcrystalline state independent of the quartz plates temperature when TBP was evaporated on the substrate.

The fluorescence maximum peak of TBP[C_2NaC_2R], with an impurity level of 10^{-6} mol/mol, was observed at 492 nm immediately after sample preparation as shown in Figure 8, when the quartz plates were kept both at 135° and 140°, and the 492 nm-peak did not change with time. These results show that the microcrystalline state was reached immediately after sample preparation when the temperature of the substrate was high.

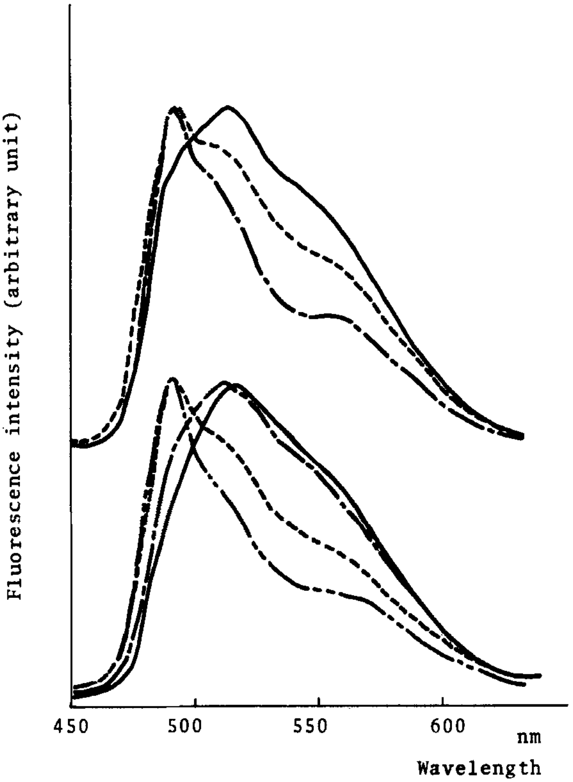


FIGURE 7 Time dependence of the fluorescence spectra of thin films of TBP[C_2NaC_2R] evaporated at 130°C (above) (HT-film), ———: immediately after evaporation, ------: after 2 hr, —·—: after 3 hr.-1 day, at 100°C (below) (HT-film), ———: immediately after evaporation, ------: after 3 hr, —·—: after 4 hr, —··—: after 9 hr, (observed at room temperature).

As shown in Figure 7, when the quartz plate was kept at 135°C, the broad maximum peak of the same sample, TBP [C_2NaC_2R], was occasionally observed at 513 nm immediately after sample preparation. After the peak-shift to 492 nm occurred in two hours further change could not be seen. However, the intensity above 500 nm still decreased. The maximum peak of the TBP[C_2NaC_2R] was not fixed, when the quartz plate was kept at 100°C: the peak was observed at 516 nm immediately after sample preparation, and the peak-shift to 492 nm occurred in three hours, and after that the 492 nm-peak shifted again to 512 nm in four hours. Finally, the peak-shift to 492 nm occurred in nine hours. These peculiar findings suggested that the alternate rearrangement from the amorphous to the crystalline state and from the crystalline to the amorphous state occurred on the same specimen and finally the thin film became crystalline.

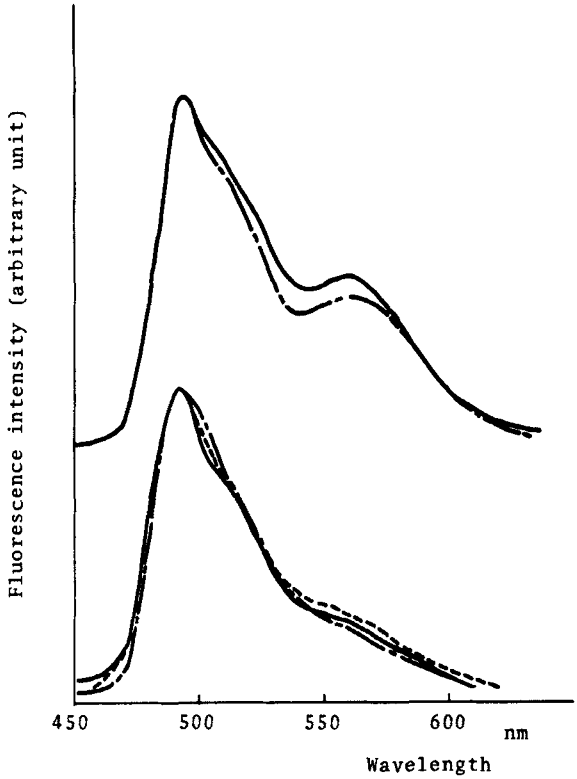


FIGURE 8 Time dependence of the fluorescence spectra of thin films of TBP[C_2NaC_2R] evaporated at 140°C (above) (HT-film), ———: immediately after evaporation, —·—: after 1 day at 135°C (below) (HT-film), ———: immediately after evaporation, —·—: after 1 hr, – – – –; after 14 hr, (observed at room temperature).

The results in this study revealed that the microcrystalline thin film of TBP was prepared easily when the quartz plate was kept at temperatures of 135° to 140°C. The thin film of the purest TBP was microcrystalline independent of the temperature of the substrate.

In Table II the relation between the purity of TBP and the crystallization time is summarized.

The crystallization rates of specimens of various purities can be used to determine the purity of aromatic hydrocarbons.

CONCLUSION

From the investigation of the absorption and fluorescence spectra of TBP thin films the rate of crystallization was found to depend strongly on the purity of the specimen. The spectra of TBP containing 10^{-6} mol/mol impurity

TABLE II

Time dependence of the crystallization of TBP films as a function of purity.

	TBP sample	Temperature (°C)	Period[a] (hour)	Concentration[b] of impurity (mol/mol)
RT-film	[R]	Room temperature	∞	10^{-1}
	[MC_1]		24	10^{-4}
	[MC_2]		24	10^{-5}
	[C_2NaC_2R]		9	10^{-6}
	[MC_2NaC_2R]		0	10^{-8}
HT-film	[C_2NaC_2R]	100	9	10^{-6}
		130	3	
		135	0	
		140	0	
	[MC_2NaC_2R]	130	0	10^{-8}
		140	0	

[a] The time required to form the crystalline film from the amorphous film.
[b] Impurity concentration estimated in papers.[5–9]

showed those characteristic of the crystalline state when the substrate was kept at a temperature higher than the glass transition temperature, 135–140°C, but showed the amorphous characteristics immediately after sample preparation and then changed to those of the crystalline state even when the substrate was kept at a temperature lower than the glass transition point. On the other hand, crystalline thin films of the purest TBP, 10^{-8} mol/mol impurity content, could be prepared immediately after sample preparation independent of the substrate temperature.

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