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Photoreaction between Carbazole and *trans*-Stilbene Occurring at the Interface of Their Crystallites

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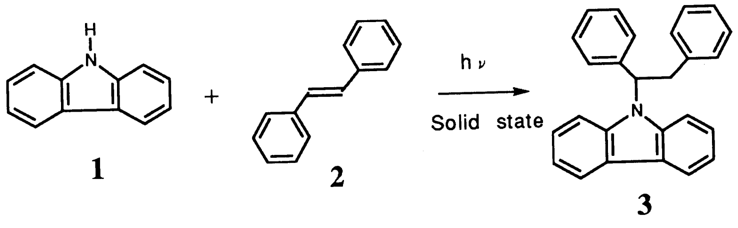
Irradiation of the mixed crystal which is a simple mixture of carbazole and *trans*-stilbene gave a photoadduct. The photochemical reaction proceeds at the interface of the crystallites of carbazole and *trans*-stilbene in the mixed crystal.

Mixed crystals between different organic compounds prepared by a melting-resolidifying process are classified into two main groups; a simple mixture of component crystallites[1)] and a molecular compound. Photoreactions of such polycrystalline mixtures have been already reported.[2,3)] The interpretation that solid-state intermolecular reactions of the mixtures proceed at the interface of each crystallite seemed to be reasonable. We report here the evidence by correlating the crystallite size to the photoreaction rate for the mixed crystal of carbazole **1** and *trans*-stilbene **2**.



The mixed crystal was prepared by melting a 1:1 molar mixture of **1** and **2** followed by resolidifying at room temperature and pulverizing in a mortar. The powder sample placed between two Pyrex glass plates was irradiated with a 400 W high-pressure mercury lamp for 20 h under argon at 20 °C. HPLC determination showed the formation of a photoadduct **3** in 25% yield[4)] at 30% and 92% conversions of **1** and **2**, respectively. In addition, cis-stilbene in 1% yield, phenanthrene in 5% yield, some stilbene dimers and polymers were also produced.

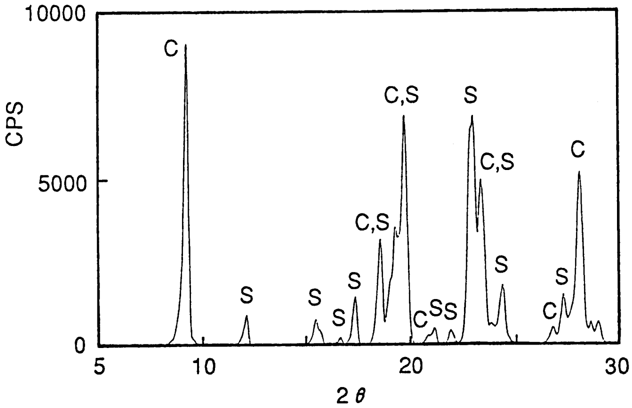


Fig. 1. Powder X-ray diffraction spectrum of the mixed crystal. C and S denote the peaks due to carbazole and *trans*-stilbene, respectively. Copper-target X-ray tube.

The mixed crystal is polycrystalline and consists of a simple mixture of the crystallites of **1** and **2** because the powder X-ray diffraction spectrum is the sum of the spectrum of each component (Fig. 1). The crystallite size was determined by the Scherrer method using a powder X-ray diffraction profile.$^{5)}$ The independent peaks of 9.16° and 12.06° 2θ for **1** and **2**, respectively in Fig. 1 were taken to determine each crystallite size by using RAD-C system coupled with Rigaku Geigerflex X-ray diffraction spectrometer. The 1:1 melt solidifies completely under 120 °C which is probably the eutectic point by the DSC curve. We investigated the effect of cooling rate of the 1:1 melt of **1** and **2** on each crystallite size by using a cooling bath with different temperatures (Table 1). The faster cooling of the melt gave the smaller sizes of crystallites of **1** and **2** as was expected. Next, the photoreaction rate at the early stage of the mixed crystals prepared by cooling at -78 °C, 20 °C and 100 °C was measured under the following controlled conditions. A 500 W super-high-pressure mercury lamp, which gave a constant light strength within a 5-cm diameter circle, was used. Twenty mg of the mixed crystal spread between two Pyrex glass plates in a 5-cm diameter circle as possible as homogenously was irradiated for up to 3 h. Figure 2 shows the result. The ordinate is the yield of **3** per hour, i.e., the formation rate of **3**. Assuming that the crystallite form is a cubic, the specific surface area is ininverse proportion to second power of the crystallite size; the abscissa corresponds to the crystallite specific surface area. At the early reaction stage (<5% in yield), the crystallite surfaces were not so disturbed because *cis*-stilbene and phenanthrene were not produced. In conclusion, this result indicates the solid-state photoreaction of the simple crystallite mixture of **1** and **2** occurred at the interface of each crystallite.

Table 1. Crystallite size in the 1:1 mixed crystal prepared at different temperatures

Cooling temperature	Crystallite size/Å	
°C	Carbazole	*trans*-Stilbene
-78	294	342
20	364	381
100	412	415

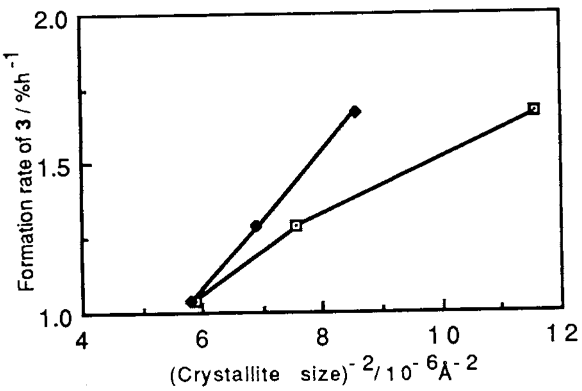


Fig. 2. Effect of the specific surface area of the crystallite in the mixed crystal on the solid-state photoreaction. ( ) and ( ) are carbazole and *trans*-stilbene, respectively.

References

1) "Crystallite" is defined as a single grain in a polycrystalline substance and "polycrystalline" as consisting of crystals variously oriented.

2) J.-B. Meng, W.-G. Wang, H.-G. Wang, T. Matsuura, H. Koshima, I. Sugimoto, and Y. Ito, *Photochem. Photobiol.*, **57**, 597 (1993).

3) J.-B. Meng, W.-G. Wang, G.-X. Xiong, Y.-M. Wang, D.-C. Fu. D.-M. Du, R.-J. Wang, H.-G. Wang, H. Koshima, and T. Matsuura, *J. Photochem. Photobiol., A: Chem.*, **74**, 43 (1993).

4) Spectral data of photoadduct **3**: 18% in isolated yield by preparative TLC; Colorless crystal, mp 129-131 °C; ^{1}H-NMR (60 MHz, $CDCl_3$) δ = 3.79 (2H, d, J=8.0 Hz, CH-$\underline{C}H_2$), 6.07 (1H, t, J=8.0 Hz, $\underline{C}H$-CH_2), 6.73-8.07 (18H, m, aromatics). IR (KBr) No NH band, 3030, 1595, 1485, 1455, 1330, 750 cm^{-1}; UV (ethanol) λ_{max} =237 nm (log ε =4.69), 261 (4.31), 294 (4.26), 328 (3.65), 343 (3.72); Found: C, 89.94; H, 6.29; N, 3.91%. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03%.

5) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," 2nd ed, Wiley-Interscience, New York (1974), Chap. 9.

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