CHEMISTRY LETTERS, pp. 179-182, 1988.

Direct Synthesis of τ-Form Metal-Free Phthalocyanine from Phthalodinitrile by Seeding Procedure

Toshio ENOKIDA* and Shigeyuki EHASHI
Research and Development Laboratories, Toyo Ink Mfg. Co., Ltd.,
13-1, Kaga 1-chome, Itabashi-ku, Tokyo 173

Direct synthesis of τ-form metal-free phthalocyanine (τ-H_2Pc) was performed from phthalodinitrile by using of 1,8-diaza-bicyclo(5,4,0)undecene-7 (DBU) and crystal nucleus in alcohol. **The** yield of τ-H_2Pc was investigated under various conditions.

Phthalocyanines have been recongnized as important organic materials for its photoconductivity. Well-known examples of phthalocyanines exhibiting polymorphism are metal-free phthalocyanine (H_2Pc) and copper phthalocyanine (CuPc). Both of them have two representative polymorphic form, the β-form is thermally stable and α-form is thermally unstable. In addition, the middle energy stages like as X$^{1)}$-form H_2Pc and δ, ε, R and X-form CuPc have been reported up to this time.

Recently, a new polymorph of metal-free phthalocyanine, designated as τ-H_2Pc, has been reported.$^{2,3)}$ The τ- and X-H_2Pc were obtainable from the α-H_2Pc under appropriate conditions of crystalline conversion in the process of milling, that is, we could not produce the middle energy stages of H_2Pc by direct synthesis from phthalodinitrile. Baumann et al.$^{4)}$ and Borodkin$^{5)}$ studied α- or β-H_2Pc with an alkoxide, and Tomoda et al.$^{6,7)}$ did it with an organic strong bases such as 1,8-diaza-bicyclo(5,4,0)undecene-7 (DBU) or 1,5-diaza-bicyclo(4,3,0)nonene-5 (DBN). So we tried direct synthesis of τ-H_2Pc by using of DBU and crystal nucleus (τ-H_2Pc), consequently, we were able to attain our purpose.

A typical experimental procedure is as follows. The τ-form H_2Pc was prepared by the crystal transformation of α-H_2Pc using wet milling method as previously described.$^{2)}$ Phthalodinitrile (76.8 g, 0.6 mol) was dissolved an alcohol and then DBU (91.2 g, 0.6 mol) was added dropwise to the solution at the refluxing temperature or 100 °C (Table 1). The τ-H_2Pc as seeding crystals (2 g, 3.9×10^{-3} mol : prepared by wet milling) was added by slow degrees (1 g / 5 min), when the temperature reached 60 °C. After 18 h of heating, the products were collected by filteration, washed with water, and purified by extraction technique with acetone.

Crystalline form of the products were checked by X-Ray diffraction patterns using Rotafrex RU-200 (CuKα : Rigaku Denki Ltd.). The UV-Vis spectra were measured in a dispersion in tetrahydrofuran (THF) using Recording Spectrophotometer UV-365 (Shimadzu Seisakusho Ltd.). The X-Ray photoelectron spectra (XPS) were measured using Perkin-Elmer PHI-5400 ESCA system with MgKα X-Ray target. The shape of the particles were observed by scanning electron microscope (SEM). Table

1 shows the yield of H_2Pc from phthalodinitrile under various conditions.

The yield of H_2Pc increased with increasing the length of alkyl radical of alcohol and reaction temperature. In a secondary alcohol, the yield of H_2Pc was low. On the contrary, using methyl alcohol which was more than twice as effective as using ethyl or n-propyl alcohol. The yield was influenced by reaction temperature and the length of alkyl radicals. In the case of secondary or tertiary alcohol, the formation of τ-H_2Pc was little occurred except isopropyl alcohol. This results suggested that the formation of alkoxide ion was difficult. On occasion of methyl alcohol, the electric constant was larger than any other alcohol, consequently, the formation of alkoxide ion was promoted and a large amount of 1-alkoxy-3-iminoisoindolenine was formated. Thus a good yield was attained. In the case of 2-alkoxyethanol, the yield of τ-H_2Pc increased the same tendency, however, there were a little effective. Figure 1 shows the dependence of the yield of τ-H_2Pc using 2-buthoxyethanol on the reaction time and reaction temperature. That value increased with an increase in reaction time and reaction temperature. When reaction temperature was under 100 °C, and added H_2Pc as seeding crystal, we could obtain the pure τ-H_2Pc. And, we could not obtain the τ-H_2Pc without adding seeding crystal in this work. The maximum yield of τ-H_2Pc with 2-buthoxyethanol may therefore presume about 55wt%.

X-Ray diffraction patterns are shown in Fig.2. The pattern of direct synthesis (a) was quite alike as that of wet milling (b). UV-Vis absorption spectra are shown in Fig. 3. The spectra of (a) and (b) showed quite alike peaks due to scattering. The wavelength of absorption peaks were almost same. The absorbance of (b) was weaker than (a), however, the Q-band transition at ca. 655 and 690 nm were very sensitive. The Q-band transition is a $\pi - \pi^*$ transition of lower energy. Consequently, τ-$H2Pc$ of direct synthesis is more sensitive and oriented of nearest neighbor Pc molecule in THF. The split of absorption peaks in the Q-

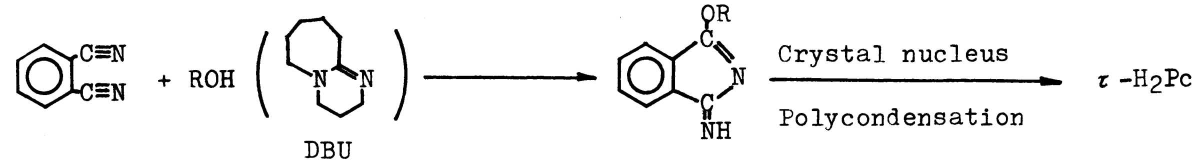

Table 1. Yield of τ-H_2Pc from phthalodinitrile under various conditions

Alcohol	Temp °C	Time h	Yield wt%
CH_3OH	bp (64.5)	18	50
C_2H_5OH	bp (78.3)	18	24
$(CH_3)_2CHOH$	bp (82.4)	18	15
n-C_3H_7OH	bp (97.0)	18	26
n-$C_6H_{13}OH$	100	18	48
$CH_3O(CH_2)_2OH$	100	18	36
$C_2H_5O(CH_2)_2OH$	100	18	35
$C_4H_9O(CH_2)_2OH$	100	18	55
$C_6H_{13}O(CH_2)_2OH$	100	18	60

band are because the reduction of symmetry in τ-H_2Pc molecule from D_{4h} to D_{2h} by removal of the molecule center. The XPS of N1s for τ-H_2Pc are shown in Fig. 4. There are two kinds of peaks which indicates at least two chemically different nitrogen atoms.8) The spectrum of (b) has two peaks with almost equal intensity. The higher energy peak of (a) is smaller than the lower energy peak. Namely, the spectra of (a) and (b) suggested the bonded structure with hydrogen of central nitrogen for D_{4h} and bridged structure for D_{2h},

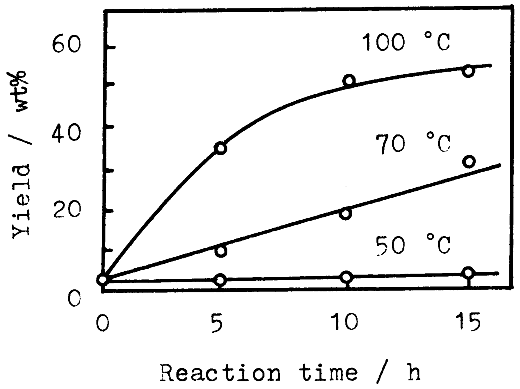

Fig. 1. Dependence of the yield of τ-H_2Pc on the reaction time and reaction temperature.

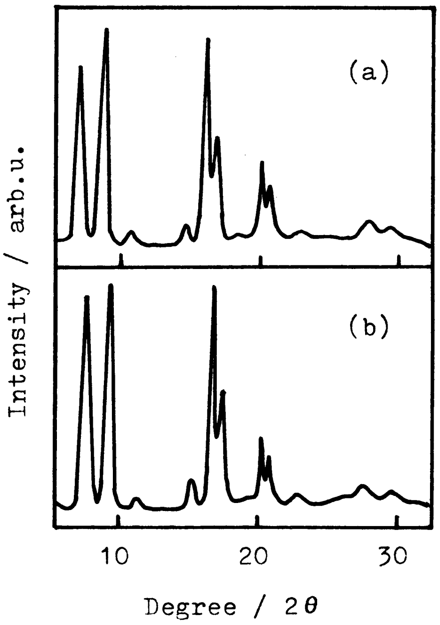

Fig. 2. X-Ray diffraction patterns of τ-H_2Pc. (a) wet milling
(b) direct synthesis
cf. Table 1 100 °C x 18 h
Solvent : buthoxyethanol

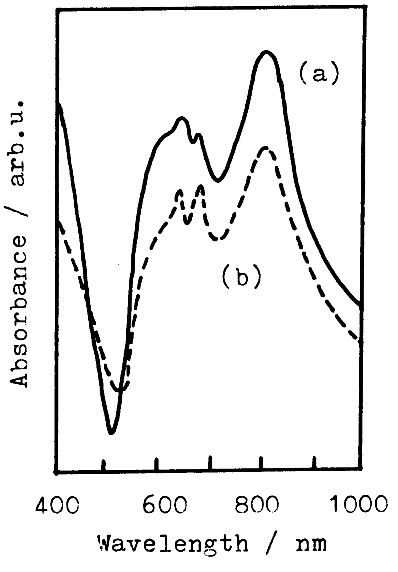

Fig. 3. UV-Vis absorption spectra of τ-H_2Pc. (a) wet milling
(b) direct synthesis
cf. Table 1 100 °C x 18 h
Solvent : buthoxyethanol

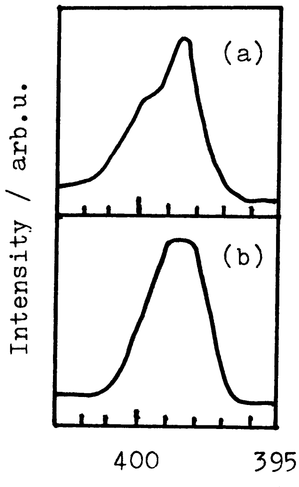

Fig. 4. The nitrogen 1s spectra of τ-H_2Pc. (a) wet milling
(b) direct synthesis
cf. Table 1 100 °C x 18 h
Solvent : buthoxyethanol

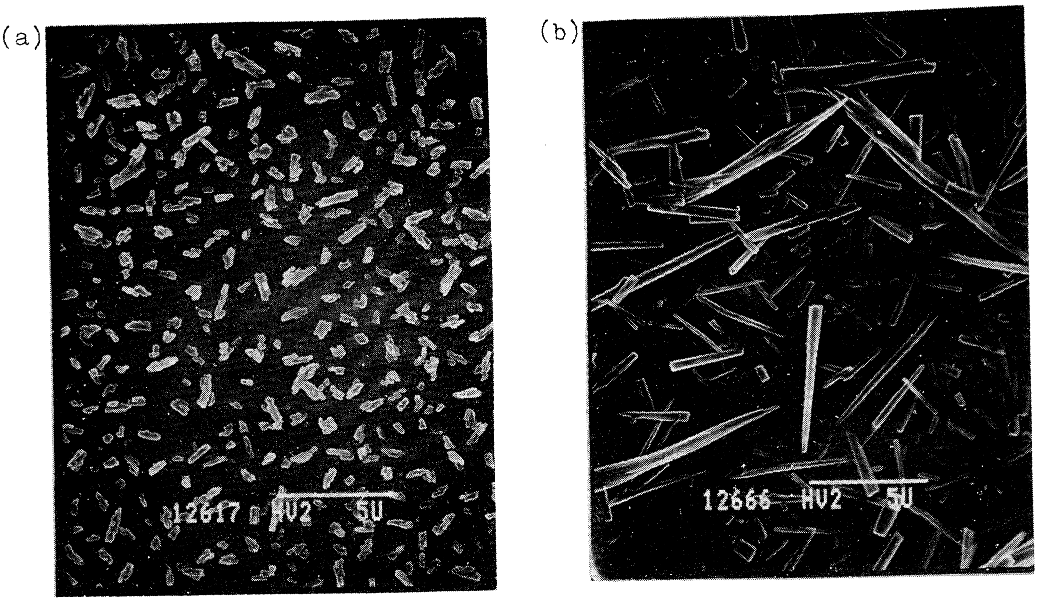

Fig. 5. Scanning electron microscope photographs of τ-H_2Pc.
(a) wet milling (b) direct synthesis
The bars in the photographs represent 5 μm.

respectively. These results were supported the results of UV-Vis spectra. SEM photographs are shown in Fig. 5. The particle size by wet milling (a) are uniform, however, the particles by direct synthesis are rod-like and various size. Therefore, the crystallinity of τ-H_2Pc by direct synthesis may be relatively high because of its mild synthetic conditions. Further investigation of the relationship between synthetic conditions and crystallinity containing in the process of crystal growth in τ-H_2Pc and now in progress.

The authors are grateful to Mr. Kakuta (Hitachi Ltd.) for valuable suggestions, and to Mr. Ito, Mr. Morohashi, Miss Hotta and Mr. Sano for their assistance of these experiments.

References

1) J. H. Sharp and M. Lardon, J. Phys. Chem., 72, 3230(1968).
2) S. Takano, T. Enokida, A. Kakuta, and Y. Mori, Chem. Lett., 1984, 2037.
3) A. Kakuta, Y. Mori, S. Takano, M. Sawada, and I. Shibuya, J. Imag. Technol., 11, 7(1985).
4) F. Baumann, B. Bienert, G. Rösch, H. Vollmann, and W. Wolf, Angew. Chem., 68, 133(1956).
5) V. F. Borodkin, Zh. Prikl. Khim. (Leningrad), 31, 813(1958).
6) H. Tomoda, S. Saito , S. Ogawa, and S. Shiraishi, Chem. Lett., 1980, 1277.
7) H. Tomoda, S. Saito , and S. Shiraishi, Chem. Lett., 1983, 313.
8) Y. Niwa, H. Kobayashi, and T. Tsuchiya, J. Chem. Phys., 60, 799(1974).

(Received September 29, 1987)