BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1259—1261 (1970)

Molecular Orientation and Absorption Spectra of Quaterrylene Evaporated Film

Yusei MARUYAMA, Tohru IWAKI,*1 Takashi KAJIWARA, Ichimin SHIROTANI and Hiroo INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Tokyo

(Received October 4, 1969)

When, in 1963, experimental studies of the electrical and optical properties of quaterrylene evaporated films were carried out, interesting results were obtained.[1] In the optical absorption spectrum of the evaporated film, the large absorption peak in about the 540 mμ region, as is shown in Fig. 1, seems to be an anomalous one with respect to its position and absorbance in comparison with the spectrum of the crystalline state and also with the solution spectrum. It seems to be true that this peak appears only in the spectrum of the evaporated film, but not in that of the single crystal.

Therefore, the relation between the molecular orientation and the absorption spectra must be persued in order to analyze the structure of thin organic film.[2] The orientation of the molecules in the film was observed by the X-ray diffraction method, and its change was examined as a function of the deposited temperature, which was controlled by heating a glass plate substrate during the evaporation. The temperature dependence and pressure dependence of this absorption spectral peak were also measured.

Experimental

Quaterrylene evaporated films were prepared by the following method.[3] During the evaporation, the substrate was heated by a proper heater and a temperature gradient was set up along the substrate surface; the substrate temperature thus changed from 90°C to 300°C. The X-ray diffraction patterns and the optical absorption spectra of each part were observed. The structure of the highest-temperature part of the film was rather crystallized, and microcrystallites were deposited on the film. The absorption spectra produced by polarized light to the proper axis of the single crystal were measured by microscope-spectroscopy employing the micro-crystal thus obtained.

In order to ascertain the origin of the optical absorption bands, especially that of the 540 mμ band, of the evaporated film, the temperature dependence and pressure dependence of the optical absorption bands were observed. The former, the temperature dependence of the absorption bands, was observed down to 4.2°K using a liquid helium cryostat, while the latter, the pressure dependence, was measured up to 6.6 kbar using a high-pressure optical cell.[4]

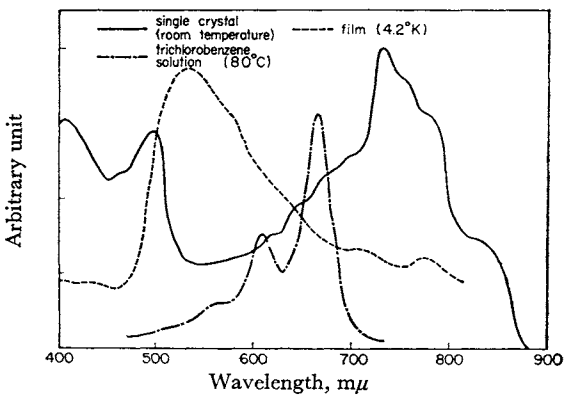

Fig. 1. The spectral response curve of absorption of quaterrylene.

*1 Department of Chemistry, Faculty of Science, Hiroshima University.

1) Y. Maruyama, H. Inokuchi and Y. Harada, This Bulletin, **36**, 1193 (1963).

2) H. Inokuchi, Y. Maruyama and H. Akamatu, *ibid.*, **34**, 1093 (1961).

3) Y. Maruyama and H. Inokuchi, *ibid.*, **39**, 1418 (1966).

4) T. Kajiwara, H. Inokuchi and S. Minomura, *ibid.*, **40**, 1055 (1967).

Results and Discussion

Figure 1 shows the absorption spectra of quaterrylene evaporated film, of its trichlorobenzene solution, and of the single crystal. The last is a polarized spectrum of a typical crystal axis. The absorption peaks in the 550—700 mμ region observed in the trichlorobenzene solution spectrum may be due to the lowest singlet excitation of the quaterrylene molecule. The 710 mμ and 780 mμ peaks in the film spectrum may correspond to an exciton band arising from this lowest molecular excitation. They are shifted in the direction of wavelengths longer than those of the solution spectrum because of intermolecular interaction in the solid state. These peaks also appear in the single crystal spectrum.

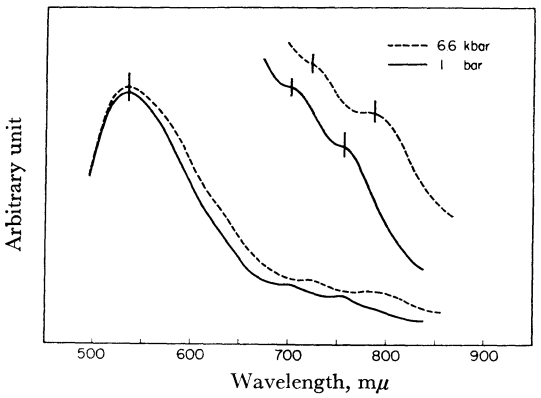

Fig. 2. The pressure induced red-shift of absorption spectral bands of quaterrylene.

This assignment is also supported by the fact that the pressure-induced red shift of these bands is about $-69\ cm^{-1}/kb$, as is illustrated in Fig. 2; this is a reasonable value for an exciton band.[5] These bands became rather sharper when the film was cooled to 4.2°K. This fact also suggests their exciton nature.

However, the 540-mμ band, found in the film spectrum, showed almost no change in its position and sharpness when it was cooled to 4.2°K or pressed to 6.6 kbar. This behavior is the most peculiar aspect of the band.

The relation between the spectra of the film and of the crystal was also strange, as is shown in Fig. 1. The effect of the molecular orientation on the absorption spectrum was studied next. The high temperature (~300°C)*2 part (1) appeared to be crystallized and micro-crystallites were deposited on the thin film. Part (2) (~150°C)*2 was bluish grey, Part (3) (~100°C)*2 was green, and the part (4) (room temperature),*2 violet.

Figure 3 shows the absorption spectra for the film specimens prepared at different substrate temperatures. The 540 mμ band in the spectrum deposited at room temperature seems to split to ~490 and ~630—680 mμ bands in the high-temperature specimens. The spectra of the (1)—(2)*3 and (2)—(3)*3 parts described above are rather similar to that of the single crystal (see Fig. 1).

The X-ray diffraction patterns of these different specimens deposited at various temperatures are shown in Fig. 4. The main diffraction lines of the high-temperature-part specimen (1) correspond to those from the (00n) planes, that is, the ab plane: The quaterrylene molecules are well oriented in

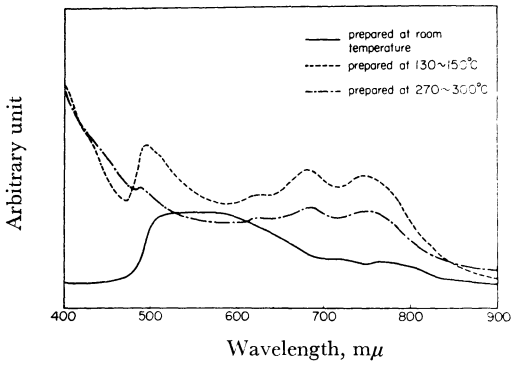

Fig. 3. The absorption spectral response curve of quaterrylene as a function of deposited temperature.

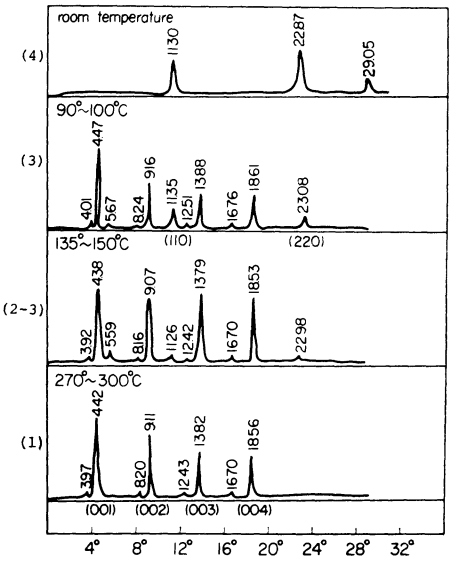

Fig. 4. The X-ray diffraction patterns of quaterrylene films deposited at various temperature: (1) is 270—300°C, (2—3) 135—150°C, (3) 90—100°C and (4) is room temperature.

5) I. Shirotani, H. Inokuchi and S. Akimoto, *ibid.*, **40**, 2277 (1967).

*2 The temperatures given in parentheses illustrate the substrate temperature.

*3 The (1)—(2) spectrum corresponds to the —·— line in Fig. 3, and (2)—(3), to the ------ line of Fig. 3.

this region.[2] In the patterns of (2)—(3) and (3), several diffraction lines other than (00n) appear. Among them, 11.30°, 22.87°, and 29.05° lines survive and grow in the region (4), as is the case with the substrate at room temperature.

The last three lines in (4) are not so sharp and large as the (00n) lines of (1) or (2)—(3), and no reasonable assignment of the crystal plane indices seems feasible. The possibility of crystal polymorphy cannot be perfectly denied, but the three lines in (4) may be, rather, due to an amorphous state judging from the appearance of these lines; that is, there is less sharpness and more weakness. Therefore, we assume that the existence of the 540 mμ band of the quaterrylene film is due to the plane ordering which is observable in the case of amorphous carbon.