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Fluorescence Spectra of Aromatic Hydrocarbons in Polystyrene under High Pressure

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The effect of pressure on the fluorescence spectra of aromatic compounds in the solid phase has been studied. Under pure hydrostatic pressures up to 8 kbar, ordinary fluorescence spectra of crystalline anthracene were observed.⁽¹⁾ However, when a quasi-hydrostatic pressure*1 of 7—10 kbar was applied to an anthracene crystal placed in the optical cell, a new broad emission band located in the 600 mμ wavelength region appeared.⁽²⁻⁴⁾

Between the new fluorescence band and the absorption spectra, no mirror image symmetry was found⁽⁵⁾; this new anomalous emission can be explained as an excimer fluorescence produced at high pressure. Similar phenomena were found on the fluorescence spectra of naphthalene, chrysene, 1,2-benzanthracene, 9,10-diphenylanthracene, and 2-methylanthracene. The increase in the fluorescence intensity of naphthacene doped in the anthracene host crystal with an increase in the pressure may be produced predominantly by the increment in the probability of energy transfer from the host to the guest.⁽⁶⁾

In this note, the fluorescence spectra of aromatic hydrocarbons dissolving in polystyrene under high pressure will be presented.

The high-pressure apparatus and the optical measurement attachment have already been reported.⁽⁶⁾ A pressure up to 52 kbar was applied to the optical cell. A polystyrene sample containing aromatic hydrocarbons of about 0.05 wt% was prepared by the thermal polymerization of the monomer styrene containing dissolved hydrocarbons. The hydrocarbons used in this experiment were anthracene, perylene, benzo[*g,h,i*]perylene, and violanthrene B.

Figures 1 and 2 illustrate the fluorescence spectra of benzo[*g,h,i*]perylene and violanthrene B in polystyrene at several isobars. The fluorescence intensity of anthracene increased remarkably in the pressure range of 0—30 kbar,⁽⁶⁾ but the intensity for perylene and violanthrene B decreased with an increase in the pressure. The peak shifts were smaller than that of the crystalline states, and a similar pressure effect has been found on their absorption spectra.⁽⁷⁾ As is shown in Figs. 1 and 2, diffuse bands were observed at 52 kbar, but

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*1 As a pressure transmitting medium, sodium chloride was used.

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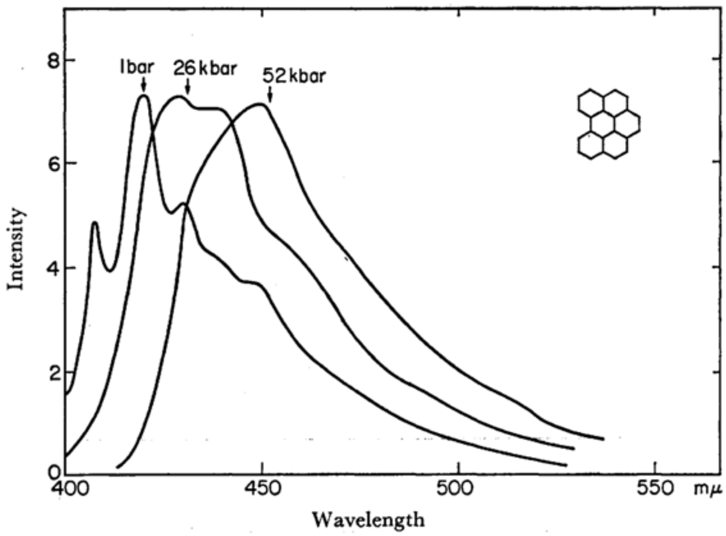

Fig. 1. The fluorescnce spectra of benzo[*g,h,i*] perylene in polystyrene matrix as a function of applied pressure.

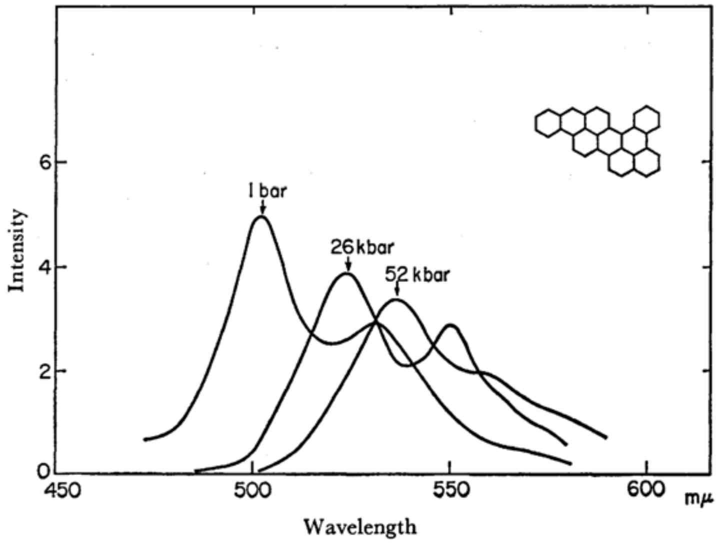

Fig. 2. The fluorescence spectra of violanthrene B in polystyrene under high pressure.

these broad emissions cannot be identified as the fluorescence of an excimer formed under high pressure. When benzo[*g,h,i*]perylene of 10^{-3}mol/*l* dissolved in polystyrene, the average intermolecular distance is not less than 30 Å, which is too large to form an "excimer." From the relation between the pressure and the volume given by Samara and Drickamer,[8] the average intermolecular distance at 52 kbar was estimated to be 94% of that at atmospheric pressure. Therefore, since the decrease in the molecular distance of the aromatic hydrocarbon-polystyrene system with the pressure is very small compared with the distance among the molecules in the polystyrene matrix, the formation of an excimer is difficult even at high pressure.

Figure 3 shows the fluorescence spectra at several isobars when two components—anthracene (5×10^{-2} mol/*l*) and perylene (10^{-4} mol/*l*)—were dissolved in polystyrene. The emission from anthracene was quenched with an increase in the pressure. On the contrary, the fluorescence intensity of perylene increased as the applied pressure increased. This behavior may arise from the energy transfer from anthracene to perylene. However, as has

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[8] G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 474 (1962).

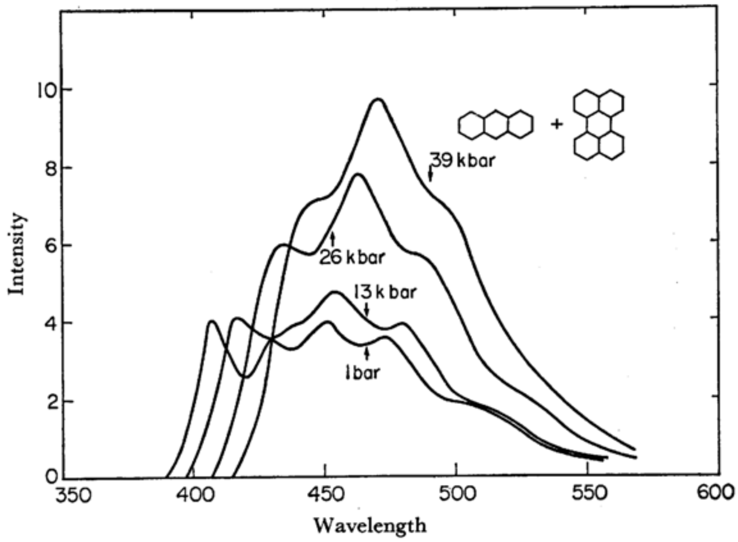

Fig. 3. The fluorescence spectra of anthracene-perylene mixture (guest)-polystyrene-(host)system under high pressure.

been mentioned previously, the discrepancy between the experimental and theoretical results for the anthracene-naphthacene mixed crystal system is very large.[6] For the anthracene-perylene mixture (guest) in polystyrene (host), a large discrepancy was also found. Therefore, the increase in energy transfer from anthracene to perylene may partly contribute to the effect of the pressure on these fluorescence phenomena.

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