Note

PHASE BEHAVIOUR OF COPPER AND ZINC PHTHALOCYANINES

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The properties of phthalocyanines (Pc) have assumed especial importance recently with regard to their device applications, particularly in the field of gas sensors [1–5]. The relevant electrical properties of these organic semiconductors are particularly dependent upon the crystal modifications relating to the various dimorphic forms and there is much current interest in how these are affected by material preparation methods and subsequent thermal treatment [6,7]. In the present work CuPc and ZnPc have been studied using differential scanning calorimetry and infrared absorption spectroscopy in order to characterize the phase transition behaviour.

EXPERIMENTAL

The copper phthalocyanine was supplied in powder form by Fluoro-chem U.K. and the zinc phthalocyanine by Thorn-EMI Central Research Laboratories. These materials were then entrainer sublimed in a three-zone electrically heated tube furnace using a steady 0.5 l min^{-1} flow of zero grade argon.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to study phase behaviour and was calibrated using AnalaR tin and high purity indium. Phases were characterized using infrared absorption spectroscopy [8].

RESULTS AND DISCUSSION

Zinc phthalocyanine

In order to characterize the phases observed in the DSC studies, infrared absorption spectra of the α and β forms were determined. The α-ZnPc was prepared by precipitation from concentrated sulphuric acid by addition of water using, for comparative purposes, the method of Robinson and Klein [9] in which the α-form is prepared from the raw β-ZnPc and the method of
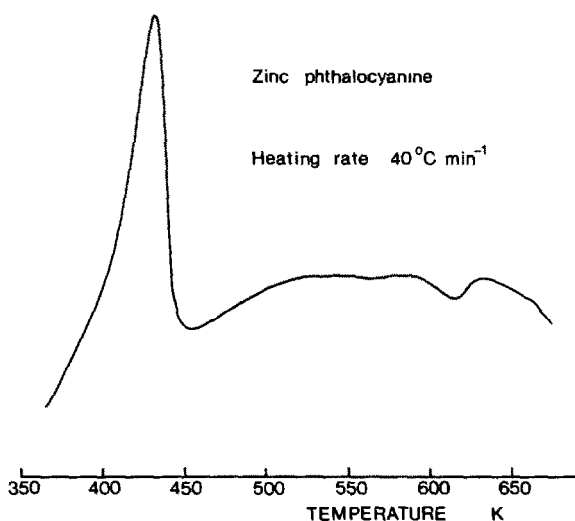
Fig. 1. DSC thermogram of an α-ZnPc sample heated at 40°C min^{-1}.

Iwatsu et al. [10] in which the α-form is prepared from the sublimed β-form. The spectra obtained for the α-form were in agreement with the results of Sidorov and Kotlyar [8] and Iwatsu et al. [10]. Our β-form spectra were also in agreement, apart from two peaks at 678 and 694 cm^{-1} which were not observed by Sidorov and Kotlyar. The α-spectra for samples prepared by the two different methods were identical. The α–β polymorphic phase transition has been studied from 350–670 K at different heating rates. Figure 1 shows a typical DSC thermogram for an α-ZnPc sample heated at 40°C min^{-1} (sensitivity range 10 mcal s^{-1}) from 350 to 670 K. It is clear that there is a large exothermic peak at 435 K and a small endothermic peak at 615 K. The peak temperatures were found to be dependent upon the sample heating rate, varying from 393–585 K at 5°C min^{-1} to 435 K and 615 K at 40°C min^{-1}. Infrared spectra of samples heated to 520 K or below were indicative of the α-form. However, samples heated through the first exothermic peak showed an additional IR peak at 706 cm^{-1}. Samples heated to above the endothermic peak were found to be in the β-form. It would appear that the exothermic peak is associated with the transition to a metastable form of ZnPc. Whilst the IR spectra for this type are very similar to the α-form, the size of the peak indicates that a significant transition has occurred. The activation energy and heat of transition for this process were determined as follows.

The activation energy E is given by [11,12]

$$-E = R\frac{\ln d_1 - \ln d_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

TABLE 1

Heating parameters for ZnPc

Mass of sample (mg)	Heating rate (°C min^{-1})	Activation energy (kcal mol^{-1})	Heat of transition (cal g^{-1})
8.4	10	–	0.834
7.6	10	19.7	0.885
14.1	20	14.9	1.2035
–	40	13.3	–

where, d_1 and d_2 are any two distances from the thermogram base line at associated absolute temperature T_1 and T_2. This equation assumes that the Arrhenius plot over the appropriate temperature range is linear, as proved to be the case with the present data.

The heat of transition (enthalpy change) was determined using the method described by Barrall and Johnson [13], using high purity tin as the calibration standard. The magnitude of the endothermic peak was felt to be too small to realistically determine these quantities.

For the exothermic peak both the activation energy and the heat of transition were found to be dependent upon the heating rate, as shown in Table 1.
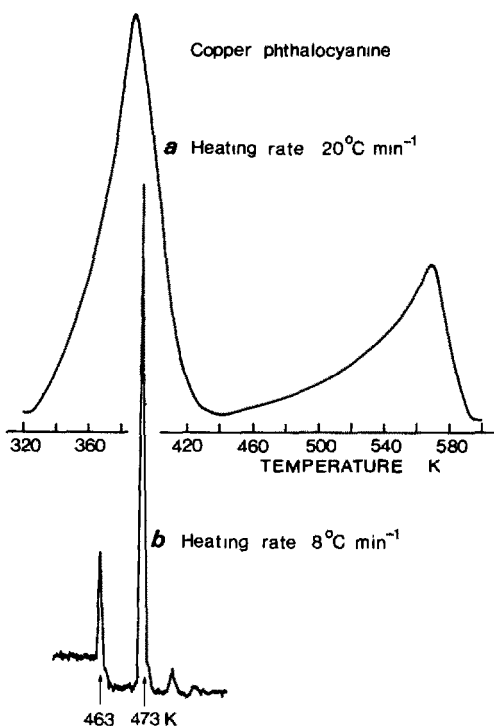

Fig. 2. DSC thermograms of samples of α-CuPc heated at: (a) 20°C min^{-1}; (b) 8°C min^{-1}.

TABLE 2

Heating parameters for CuPc

Mass of sample (mg)	Heating rate (°C min^{-1})	Activation energy (kcal mol^{-1})		Heat of transition (cal g^{-1})
		1st peak	2nd peak	
15.6	5	–	50.2	0.211
19.4	10	22.2	33.6	1.09
9.7	20	7.8	13.3	1.48
4.2	40	–	12.6	–

Copper phthalocyanine

Figure 2a shows a typical DSC thermogram of a vacuum deposited α-CuPc sample heated at 20°C min^{-1}. Two large peaks can be observed. It is assumed that the first peak represents a slow first order transition $\alpha \rightarrow \beta$ and that the second peak represents complete conversion to the β-form. The infrared spectra show this to be the case. The peak widths and temperatures were found to be strongly dependent upon the heating rate. Figure 2b shows that for a heating rate of 8°C min^{-1} the first exothermic peak is both shifted on the temperature scale and can be resolved into two individual peaks. Evidence for a number of much smaller subsidiary peaks is also apparent.

Following the procedure used for ZnPc the activation energies and heats of transition were determined for samples heated at different rates, the results being shown in Table 2.

CONCLUSIONS

The calorimetric and infrared data indicate that for both ZnPc and CuPc, the α–β polymorphic phase transition occurs in two stages. In the case of ZnPc an exothermic peak occurs in the 393–433 K temperature range followed by a second endothermic peak in the range 585–615 K. For CuPc, exothermic peaks occur at 390–463 K and 473–570 K respectively. It may be noted that Fustoss-Wegner [14] also found two peaks in the thermograms for the H_2Pc $\alpha \rightarrow \beta$ transition. This complex transition behaviour is also reflected in the fact that the activation energies, calculated from simple Arrhenius plots based on the individual peaks show a dependence on sample heating rate. The activation energy values obtained are rather higher for these metal-substituted phthalocyanines than for H_2Pc. This is also true for the values obtained for the heats of transition (0.8–1.2 cal g^{-1} for ZnPc and 0.24–1.47 cal g^{-1} for CuPc).

With regard to the application of these materials in thin film gas sensors, for which thermal stability and consistency of electrical behaviour is of importance, it is clear that conversion to the β-form (which is of higher conductivity than the α-form) is desirable. However, the temperatures required for $\alpha-\beta$ conversion (i.e., above the second peak) may be precluded for sensors integrated with other microcircuit components unless the phthalocyanine can be processed separately. Additional problems may arise for α-Pc device materials in situations where local temperature variations may cause partial $\alpha-\beta$ conversion into a metastable form. The electrical behaviour in such situations is to be reported elsewhere.

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