Thermochimica Acta, 134 (1988) 107–113
Elsevier Science Publishers B.V., Amsterdam

THERMAL ANALYSIS OF AGFA (10)

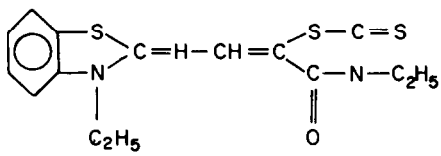
CHANG YOUMING, LIU TONGMING, NIANG MANAND ZHANG ZHONGLIANG
Institute Of Chemistry, Academia Sinica
Beijing China

ABSTRACT

The thermal behaviour of crystal phases of 3-ethyl-5-(2-(3-ethyl-2-benzothiazolinylidene)-ethylidene)-rhodanine (commercial name AGFA 10) has been studied. The transition temperatures and transition heats for its crystals were determined by DSC. The entrophy changes for those crystals were calculated. Few previously unknown crystalline phases of this compound, have been identified from the DSC study. One of the new crystals found by DSC has been identified with X-ray diffraction.

INTRODUCTION

The compound 3-ethyl-5-(2-(3-ethyl-2-benzothiazoliny-lidene)-ethylidene)-rhodanine (BTER), known under its commercial name AGFA(10), has the following molecular structure [1].



Different solid forms of this compound were found to have good photoconductivity. For instance, we have studied the photoconductivity of its film casting by vapourization [2]. We have also succeeded in growing two kinds of its crystals, one is a red needle shaped single crystal, and another is a green plate single crystal. They have been denoted to be α- and β-modifications. They were crystallized from the same crysallizing bath. As X-ray structure

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

analysis showed that they had the same molecular structure but of different molecular packing in the crystal [3], we concluded that the compound BTER should exhibit polymorphic crystalline forms. The purpose of this investigation is to study the polymorphism and the phase transition behaviors of BTER, particularly, the thermodynamical stability of the compound and its crystals.

EXPERIMENTAL

The preparation of the α- and β- modifications of BTER crystals was previously described [3]. . The calorimetric experiments were performed on Perkin-Elmer DSC-4 and DSC-2C and on DuPont 1090 thermal analyser. DSC curves were recorded between 350 and 600K in a flow of nitrogen at a scanning rate of 10 K/min. The temperature scale has been calibrated with pure reference substances (indium, tin and aluminium). About 1mg was accurately weighed for each run. Each sample was covered with an aluminium pan (about 10mg). DTA and TG curves were recorded on the chinese made LCT-1 Thermal Analyzer.

Changes in the molecular structure of BTER between the heated and unheated sample were studied by IR spectroscopy, recorded on a Bruker IFS113V in the form of KBr disks. Crystalline transitions of BTER were monitored by X-ray powder diffraction which was carried out on an X-ray polymorphic diffractometer DMAX-3B. The α-modification of BTER was heated at a temperature which is higher than the transition temperature found from the thermal analysis study. This treatment has been performed in a furnace which was controlled at 220±2°C.

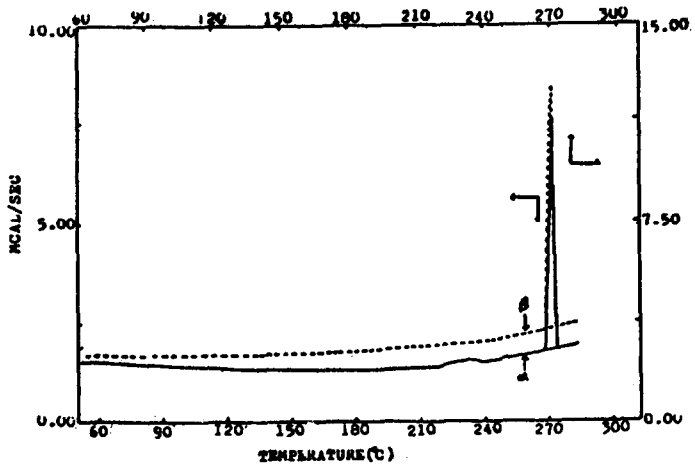


Fig 1. DSC of BTER at a heating rate of 10K/min, recorded on a Perkin-Elmer DSC-4.

RESULTS AND DISCUSSIONS

DSC, DTA and TG traces for the two, α- and β-modifications of BTER recorded on different instruments are shown in figs.2. and 3.

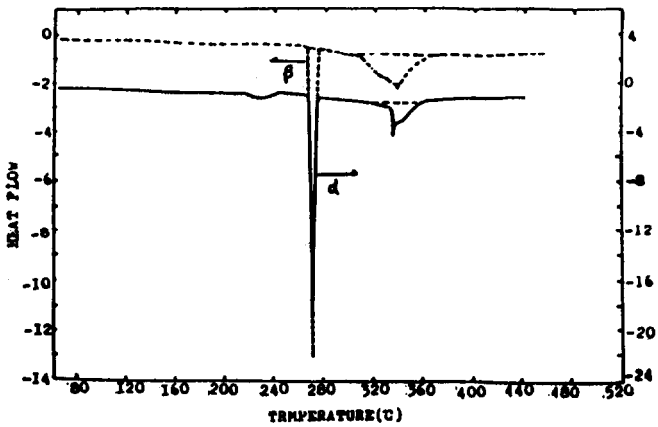


Fig 2. DSC of BTER at a heating rate of 10K/min, recorded on a Dupont 1090.

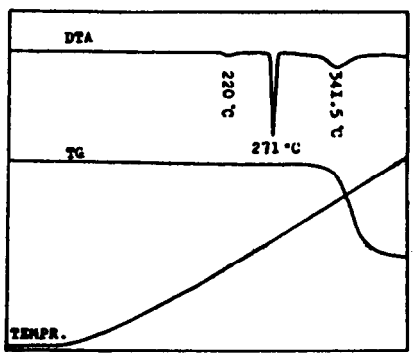


Fig 3. DTA and TG curves of BTER at a heating rate of 10K/min, recorded on LCT-1 Thermal Analyzer (made in China).

The enthalpies, entropies and temperatures of the transitions from the different apparatuses are given in Table 1.

Prior to the discussion of the thermal transition of the individual crystal modifications, certain terms and notations used in the literature for each transition stage must be defined. The notations are α, β, β_1, β_2 and they refer to the different crystal modifications of BTER and of liquid BTER, respectively. The schematic diagram for the entropy-transition temperature curves of BTER is shown in Fig.4. This figure is based on results obtained from Perkin Elmer DSC-4 only.

Table 1: Thermal parameters for transitions of BTER, as determined with different DSC instruments

Crystal form		α-modification				β-modification
T/K	DSC-4	491.2vw	496.6vw	526.5vw	542.2	542.5
	DSC-2C					542.5
	Dupont	493.6	500.8	526.3	542.0	542.6
$H/J.mol^{-1}$	DSC-4	1185	1150	102	44433	45857
	DSC-2C					46090
	Dupont	2446		146	42865	38683
$S/J.K.^{-1}$ mol^{-1}	DSC-4	2.4	2.3	0.2	81.9	84.5
	DSC-2C					85.0
	Dupont	4.9		0.3	79.1	71.3

vw = very weak.

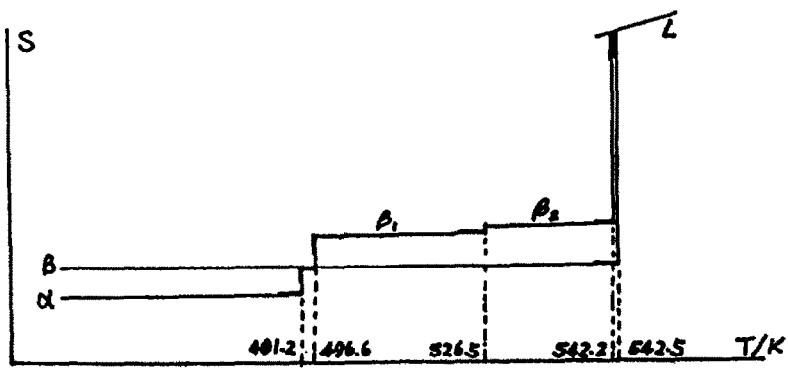


Fig.4. Schematic diagram for the entropy-temperature relationship of BTER.

Table 2. X-ray diffraction data of α-modification, α-modification heated to 493K and β-modification of BTER

α-form			α-form heated			β-form		
2-Theta	D	1/10	2-Theta	D	1/10	2-Theta	D	1/10
8.49	10.406	34				8.56	10.321	26
10.91	8.103	31				11.03	8.015	25
			11.30	7.824	21	11.23	7.872	32
			12.39	7.138	28	12.37	7.149	35
13.03	6.789	56	13.40	6.602	47	13.33	6.636	76
			13.82	6.403	37	13.72	6.449	21
			14.97	5.913	32	14.84	5.964	28
16.50	5.368	31				16.58	5.342	24
			17.07	5.190	26	16.86	5.254	27
17.33	5.113	34				17.44	5.081	28
			19.62	4.521	32	19.44	4.562	23
20.39	4.352	24				20.43	4.343	22
			21.96	4.044	22	21.73	4.086	20
23.98	3.708	70	24.12	3.687	100	24.04	3.699	100
			24.97	3.563	72	24.91	3.571	41
25.90	3.437	100	25.69	3.465	76	25.68	3.466	36
						26.00	3.424	57
27.15	3.282	26	27.02	3.297	24			
			27.41	3.251	46	27.34	3.259	22
29.58	3.018	26						
			30.93	2.889	21			
			31.39	2.848	25			
			32.86	2.723	23			
			34.00	2.635	21			

The thermal transitions due to crystal modifications of BTER have been examined by different instruments, as shown in Figs. 1, 2, and 3. Very weak peaks in the DSC and DTA curves of α-BTER but not in those of the β modification may be due to thermal solid state transitions of the α modification into mesophases.

It is reasonable to believe that the transition temperatures of the crystals of BTER are correct, because the determinations on the different instruments (DSC-4, DSC-2C and DuPont) agree with each other very well, and consequently the enthalpies of the crystals of BTER should be correct. The TG and DTA curves obtained on the LCT-1 show that the α modification of BTER exhibits few crystal transitions and fusion without weight loss until the temperature is about 593 K, when BTER boils and weight is lost. The IR spectra of samples of α BTER heated at 493±2K and unheated were shown in Fig. 5. The spectra do not show any significant change due to heating. It is obvious that the sample does not change and does not decompose during heating.

The X-ray diffraction for the heated α-modification of BTER is the same as for the β-modification. The results of both samples are shown in table 2.

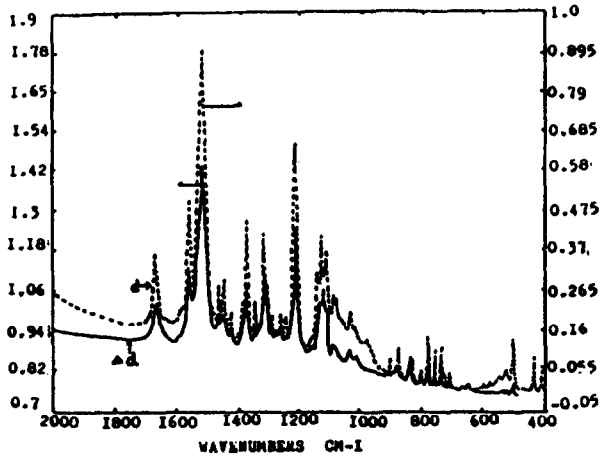


Fig 5. IR spectra of the α-modificataion of crystals of BTER unheated and heated at 493±K.

In conclusion, the mesophases β1- and β2- BTER were found only during the heating of the α-modification, but were not observed on heating the β-modification. The thermal transitions of the crystals of BTER observed in this work are as follows.

When the α-form is heated, three endothermal effects caused by three transitions (α --> β, β --> β1, and β1 --> β2) appear at 491.2, 496.6 and 526.5K, and then another endothermal effect caused by fusion (β2-melts) appears at 542.2K. We assume that there is a transition of the α-modification of BTER into the β-modification. To prove this suggestion we studied the thermal analysis of the α-modification of BTER, after it had been heated at 493K for at least 2 hours. Indeed the DSC, DTA and TG curves of this sample were the same as those of the β-modification.

The α-form heated at 493K and the β-form of BTER have almost the same transition temperatures (541.3K for the heated α-form and 542.5K for the β-form) and heats of transition (45667J/mol for the heated α-form and 45857J/mol for the β-form).

CONCLUSIONS

The α-modification of BTER shows at least three thermal transitions before it melts at 542K. In one of these transitions the β-modification is obtained. The β-modification on the other hand, does not show any thermal transition below its melting point at 542K.

There should be at least two additional modifications, β_1- and β_2-forms, of BTER.

The compound BTER is very stable until it is heated to temperatures of fifty degrees above its melting point when it starts to decompose.

As was previously mentioned [4], the DSC method is unable to fully resolve the transitions but it gives information on T (trans.), ΔH (trans.), and ΔS (trans.) for this compound.

ACKNOWLEDGMENTS

The authors would like to thank the Chinese National Foundation of Natural Sciences for Supporting this research by Fund No.2860098

REFERENCES

(1) Bai Chuli, Chang Youming and Xu Xiaojie "Kexue Tongbao' 28 (1983) 1060

(2) Chang Youming, Liu Tongming, Jiang Man and Zhang Zhongliang, Acta Chimica Sinica 40 (1982) 657.

(3) Chang Youming, Lu Shengoing and Qian Renyuan Phys. Stat. Sol.(A) 98 (1986) 37.

(4) M.A. White. Thermochim. Acta 74 (1984) 55