JOURNAL OF MATERIALS SCIENCE 27 (1992) 5101–5107

Crystalline modifications of linear *trans*-quinacridone pigments

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Different crystalline structures of linear *trans*-quinacridone were prepared and analysed by combination of X-ray diffraction, specific surface areas, optical and scanning electron microscopy, infrared spectroscopy, spectrophotometric analysis and differential thermal analysis. The lattice parameters of each crystalline phase were determined by X-ray diffraction. A new crystalline phase of this pigment was obtained and named the ζ-phase. Isothermal crystallization studies indicated that the crystallographic texture induced by pressure has a strong influence on the crystallization behaviour of this dyestuff.

1. Introduction

Linear *trans*-quinacridone is a commercial pigment of high tintorial strength and outstanding light, heat and chemical resistances. It exhibits excellent fastness properties, being comparable with copper phthalocyanine. This stability is required when the pigment is used in automobile finishes and colouring manufactured plastics [1]. This pigment was synthesized early by Liebermann [2], and Labana and Labana [3] gave a detailed study on the quinacridones and their derivatives.

The linear *trans*-quinacridone pigments can exist in six different crystalline phases (α, β, γ, γ′, δ and ε) described by several patents, but the β- and γ-phases are the ones most commonly used as commercial pigments [4, 5]. These phases have been used as nucleating agents for producing the β-modification of isotactic polypropylene, improving its properties such as ductility and impact strength [6].

In this paper the different crystalline phases of linear *trans*-quinacridone are characterized by a combination of different methods.

2. Experimental procedure

The linear *trans*-quinacridone used in this study was the commercial pigment Hosteperm E3B (Hoechst AG). The crystalline phases were prepared by the methods described in [7–12]. X-ray diffraction data were obtained on powder samples and used to distinguish one crystal phase from another. The lattice parameters were determined using X-ray diffractometry (Philips Norelco, nickel-filtered CuK_α radiation). The specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method as usual (specific area analyser CG 2000). The infrared absorption spectra were obtained with KBr pastille using a spectrometer (Perkin–Elmer 467). The powder density was measured by picnometry in isopropanol. The shape and morphological structure of the powder were observed by scanning electron microscopy (SEM) (Cambridge Instruments Stereo Can 250) and optical microscopy (Axioplan Zeiss 20). The visible absorption spectra were obtained from a fine powder dispersion of each crystal phase in nujol oil using a spectrophotometer (Beckman DU-70). Differential thermal analyses (DTA) were recorded using a Regaku Thermotlex analyser in nitrogen atmosphere.

3. Results and discussion

Linear *trans*-quinacridone is insoluble in common organic solvents. This substance is soluble only in the presence of strong acids and bases capable of producing its soluble derivate salts. The different crystalline phases of this pigment were prepared by acid and base milling, vacuum sublimation and heating in the presence of solvents [7–12]. In this work it was observed that the preferential formation of a determined crystalline structure depends on the crystallization conditions, being very commonly the simultaneous formation of two or three crystalline phases during the preparation process. Each crystal phase showed a characteristic colouration: α-phase (bluish red), β-phase (brilliant violet), γ-phase (bright red), γ′-phase (intense red), δ-phase (bluish red) and ε-phase (orange red).

The linear *trans*-quinacridone molecule consists of a planar molecule of five fused rings of dimensions 1.406 nm × 0.52 nm calculated by the bond lengths between its atoms [13]. The X-ray diffraction patterns of each crystalline phase of linear *trans*-quinacridone are shown in Fig. 1. The powder patterns were indexed and the *d*-spacings are listed in Table I. The intensities were measured as peak heights above the background and expressed as percentages of the strongest peak. The unit-cell dimensions for each crystalline phase and its possible space crystalline groups are shown in Table II. The α-phase has a

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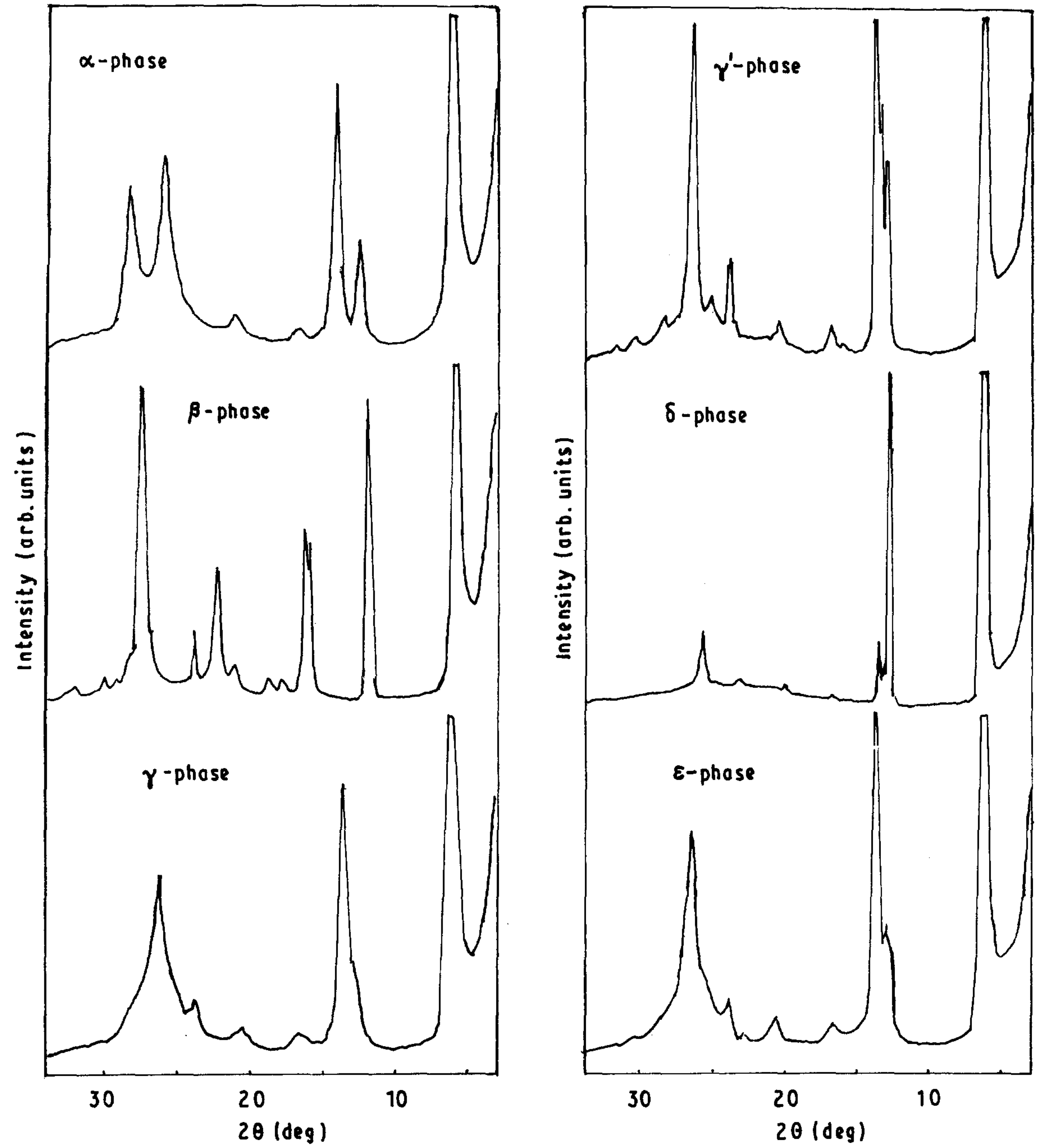

Figure 1 X-ray diffraction patterns of the crystalline phases of linear *trans*-quinacridone.

tetragonal structure, the β-, γ-, γ'- and ε-phases have orthorhombic structures and the δ-phase has a monoclinic structure. The γ- and γ'-phases show a very slight difference in their X-ray patterns with a spacing between 0.68 and 0.65 nm (Fig. 2). While the γ-phase shows a little-resolved doublet, in the γ'-phase this is replaced by well-resolved triplet. The results suggest that the crystallinity of γ'-phase is improved, giving a better-resolved X-ray pattern than the γ-phase.

The infrared spectra of crystalline phases of linear *trans*-quinacridone are shown in Fig. 3. In all spectra the C=O stretching band is shifted to lower wave number (1660–1640 cm^{-1}) due to conjugation with C=C bonds of aromatic fused rings. It is possible to observe significant differences in the spectra of crystalline phases by the N–H stretching band (Fig. 4) in the range 3300–3100 cm^{-1} due to the existence of different intermolecular hydrogen bonds in each crystalline structure.

The specific surface areas of the crystalline phases of linear *trans*-quinacridone are shown in Table III. The specific surface area determines the tintorial strength of a pigment, and the γ-phase showed a higher value than the other crystalline phases.

Spectrophotometry was used to study the absorption spectrum for each crystalline phase of linear *trans*-quinacridone (Fig. 5). From the characteristic, visible absorption spectra for each crystalline phase were determined the absorption maximum wavelengths, λ_{max} (Table IV). The results suggest that the spectrophotometric method can be useful for the characterization of the different crystalline phases of the dyestuff.

Linear *trans*-quinacridone is an infusible substance and sublimation was observed near the temperature of 425 °C. The thermal stability was studied early for the β- and γ-phases [4]. Fig. 6 illustrates the DTA thermograms obtained from the crystalline phases of

TABLE I X-ray powder diffraction data for the crystalline phases of linear *trans*-quinacridone

α-phase

d (nm)	I/I_0 (%)	*h k l*
1.424	100	100
0.713	27.8	200
0.632	61.9	120, 112
0.533	4.8	202
0.446	7.5	222
0.345	41.7	140
0.318	30.5	240

β-phase

d (nm)	I/I_0 (%)	*h k l*
1.522	100	100
0.755	56.5	200
0.553	32.1	202
0.502	4.0	220
0.479	4.8	301
0.423	6.5	222
0.401	24.5	004
0.375	11.6	231
0.327	89.7	140
0.300	4.0	501
0.281	3.5	423
0.251	2.5	440
0.232	2.5	054

γ-phase

d (nm)	I/I_0 (%)	*h k l*
1.358	100	100
0.680	27.4	200, 120
0.646	62.7	202, 121
0.524	5.5	030, 212
0.469	4.5	204
0.433	6.7	310
0.374	15.4	140
0.347	13.0	234
0.337	46.0	240
0.320	5.0	402, 242
0.304	3.0	206, 105
0.226	2.0	243

γ′-phase

d (nm)	I/I_0 (%)	*h k l*
1.358	100	100
0.680	36.8	200, 120
0.665	45.6	201, 121
0.646	73.3	202
0.524	4.8	030, 210
0.435	5.8	310
0.391	2.5	040, 320
0.373	16.8	141
0.354	10.1	142, 223
0.338	61.3	304
0.313	5.2	420
0.294	3.0	341, 152
0.282	2.0	404, 431

δ-phase

d (nm)	I/I_0 (%)	*h k l*
1.510	10.0	010
1.360	100	100
0.675	82.0	200
0.641	6.2	012
0.523	8.5	022, $22\bar{1}$
0.436	3.3	310
0.411	3.0	230
0.400	3.0	130
0.374	4.0	041, $31\bar{3}$
0.364	2.5	321
0.353	2.5	123, $33\bar{1}$
0.337	9.2	240
0.334	2.5	312
0.328	2.0	$40\bar{3}$
0.324	2.0	$42\bar{2}$
0.318	2.0	142
0.312	3.0	420, 233
0.295	2.0	340
0.281	2.5	043
0.241	2.5	$10\bar{5}$

ε-phase

d (nm)	I/I_0 (%)	*h k l*
1.402	100	100
0.691	22.7	200
0.650	86.8	020
0.527	6.0	121
0.433	6.3	002, 301
0.390	2.0	131
0.373	9.6	103
0.352	8.0	231, 312
0.338	41.1	410, 132
0.293	4.0	240, 004
0.283	2.5	042, 133
0.219	2.0	025

ζ-phase

d (nm)	I/I_0 (%)	*h k l*
1.496	11	010
1.447	100	100
0.749	6.6	020
0.713	28.6	200
0.675	3.6	201
0.594	4.8	202
0.373	3.3	040
0.354	6.1	304
0.342	6.4	404

linear *trans*-quinacridone. The occurrence of solid–solid phase transitions inside the crystalline structure during heating can be observed. The DTA scan for the γ′-phase shows an exothermic transition in the range 320–360 °C. During the heating process both exothermic and endothermic transitions occur simultaneously due to reorganization in the crystalline structure of each phase.

The morphology of the plate form of the δ-phase is shown in Fig. 7. The (1 0 0) face is the most desenvolved face and the (0 0 1) plane is the crystal cleavage plane. No other end-face was observed. The intermolecular hydrogen bonding has an important influence on the crystallization of linear *trans*-quinacridone. The (1 0 0) face well desenvolved suggests fast crystalline growth in the direction of this plane. In the

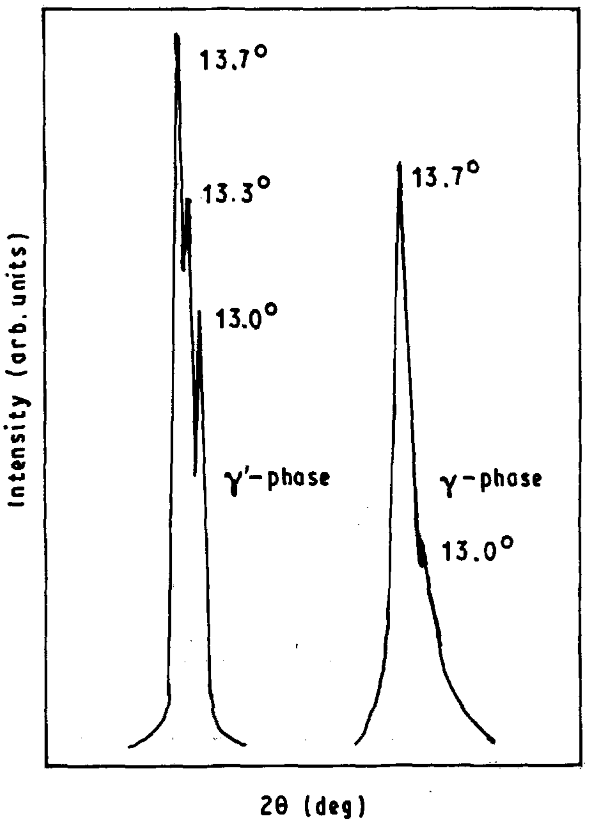

Figure 2 X-ray diffraction patterns of γ- and γ'-phases of linear *trans*-quinacridone in the 2θ range 13–14°.

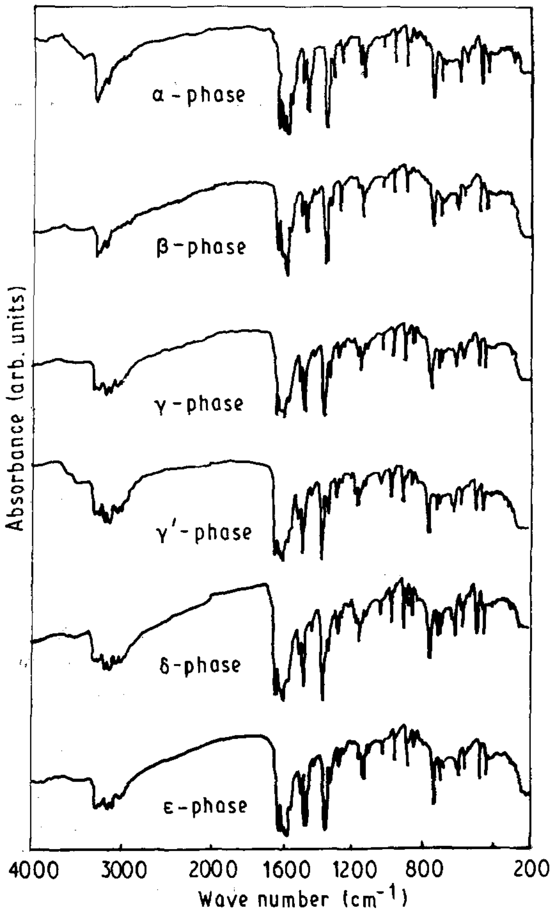

Figure 3 Infrared spectra of the crystalline phases of linear *trans*-quinacridone.

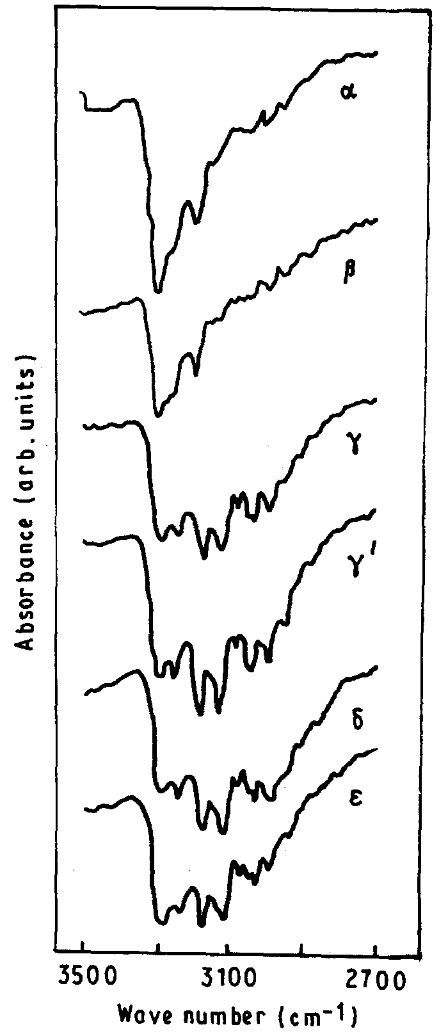

Figure 4 Infrared spectra of the crystalline phases of linear *trans*-quinacridone in the range 3500–2700 cm^{-1}.

pentacene crystallization the (0 0 1) face is more desenvolved than the (1 0 0) face due to weak van der Waals forces that act effectively in this direction [14]. SEM of the other crystalline phases of linear *trans*-quinacridone (Fig. 8) show a random disposition of leaflet crystals on the dye particle.

The influence of the thermomechanical history on the isothermic crystallization process of linear *trans*-quinacridone was studied in the present work. X-ray diffraction revealed that the commercial pigment is the γ-phase. This pigment was pressed at 300 kg cm^{-2} for 20 min and the pastilles obtained were heated at 350 °C for different times in nitrogen atmosphere. The X-ray diffraction patterns showed the preferential crystallization of γ-phase. Commercial pigment samples not submitted to initial pressing were heated under the same conditions. X-ray diffraction analysis showed the crystallization of both β- and γ-phases (Fig. 9). This result demonstrates that the isothermic crystallization process depends strongly on the influence of crystallographic texture.

A new orthorhombic crystalline phase of linear *trans*-quinacridone was obtained and was named the ζ-phase. This phase was prepared by vacuum sublimation under conditions appropriate to avoid the simultaneous formation of the δ-phase. This new crystalline

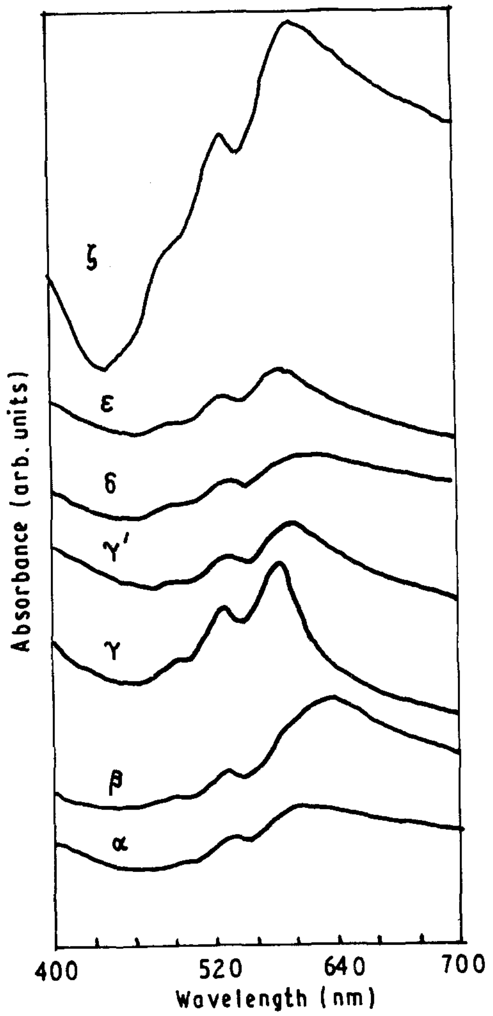

Figure 5 Visible spectra of the crystalline phases of linear *trans*-quinacridone.

phase shows a chestnut red colouration and its X-ray diffraction pattern (Fig. 10) indicates a crystal structure with the lattice parameters $a = 1.447$ nm, $b = 0.748$ nm and $c = 0.524$ nm and space group Pma2. The visible absorption maximum wavelengths are 580, 528 and 488 nm.

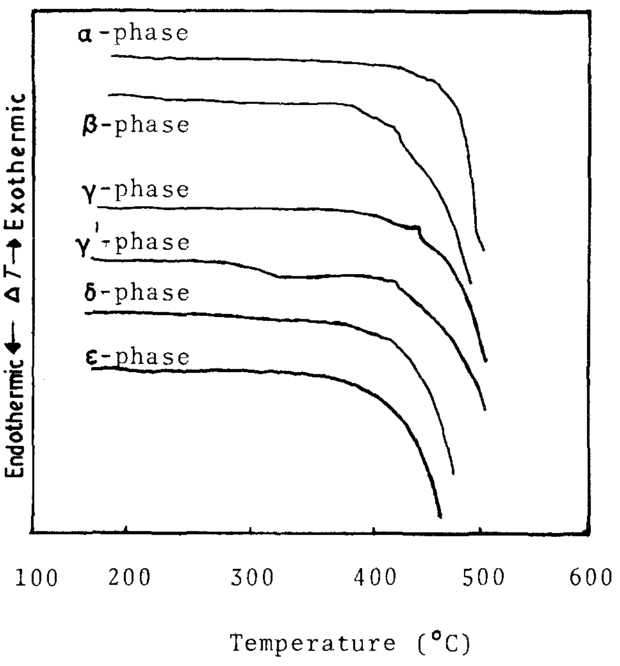

Figure 6 DTA scans of the crystalline phases of linear *trans*-quinacridone.

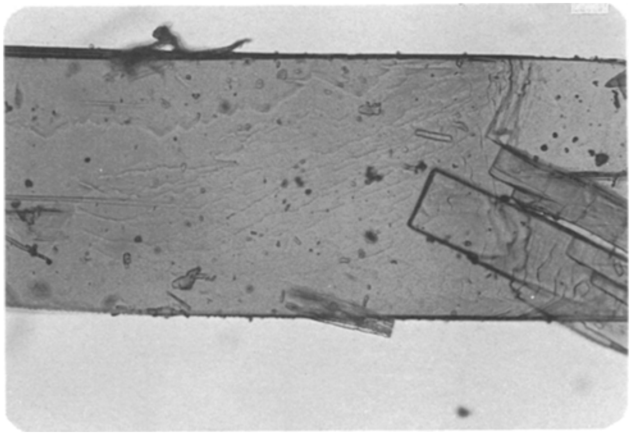

Figure 7 Optical micrograph of the δ-phase of linear *trans*-quinacridone.

TABLE II Crystal dimensions data of crystalline phases of linear *trans*-quinacridone

α-phase	β-phase	γ-phase	γ'-phase
$a = 1.424$ nm	$a' = 0.764$ nm	$a = 1.359$ nm	$a = 1.358$ nm
$b = 1.424$ nm	$b' = 1.336$ nm	$b' = 0.785$ nm	$b = 0.784$ nm
$c' = 0.402$ nm	$c' = 0.804$ nm	$c' = 0.508$ nm	$c' = 0.508$ nm
$v = 0.815\,16$ nm^3	$v = 0.820\,64$ nm^3	$v = 0.541\,94$ nm^3	$v = 0.540\,85$ nm^3
$Z' = 2$	$Z' = 2$	$Z' = 2$	$Z' = 2$
$D_m = 1.35$ g cm^{-3}	$D_m = 1.26$ g cm^{-3}	$D_m = 1.89$ g cm^{-3}	$D_m = 1.88$ g cm^{-3}
Space group I4cm	Space group Pmn2$_1$	Space group Pmc2$_1$	Space group Pmc2$_1$

δ-phase	ε-phase	ζ-phase
$a = 1.36$ nm	$a = 1.401$ nm	$a = 1.447$ nm
$b' = 0.387$ nm	$b = 0.650$ nm	$b' = 0.748$ nm
$c = 1.412$ nm	$c = 0.581$ nm	$c = 0.524$ nm
$v = 0.744\,12$ nm^3	$v = 0.529\,54$ nm^3	$v = 0.567\,15$ nm^3
$Z' = 2$	$Z' = 2$	$Z' = 2$
$D_m = 1.33$ g cm^{-3}	$D_m = 1.29$ g cm^{-3}	$D_m = 1.83$ g cm^{-3}
Space group P2$_1$/c	Space group Pmna	Space group Pma2

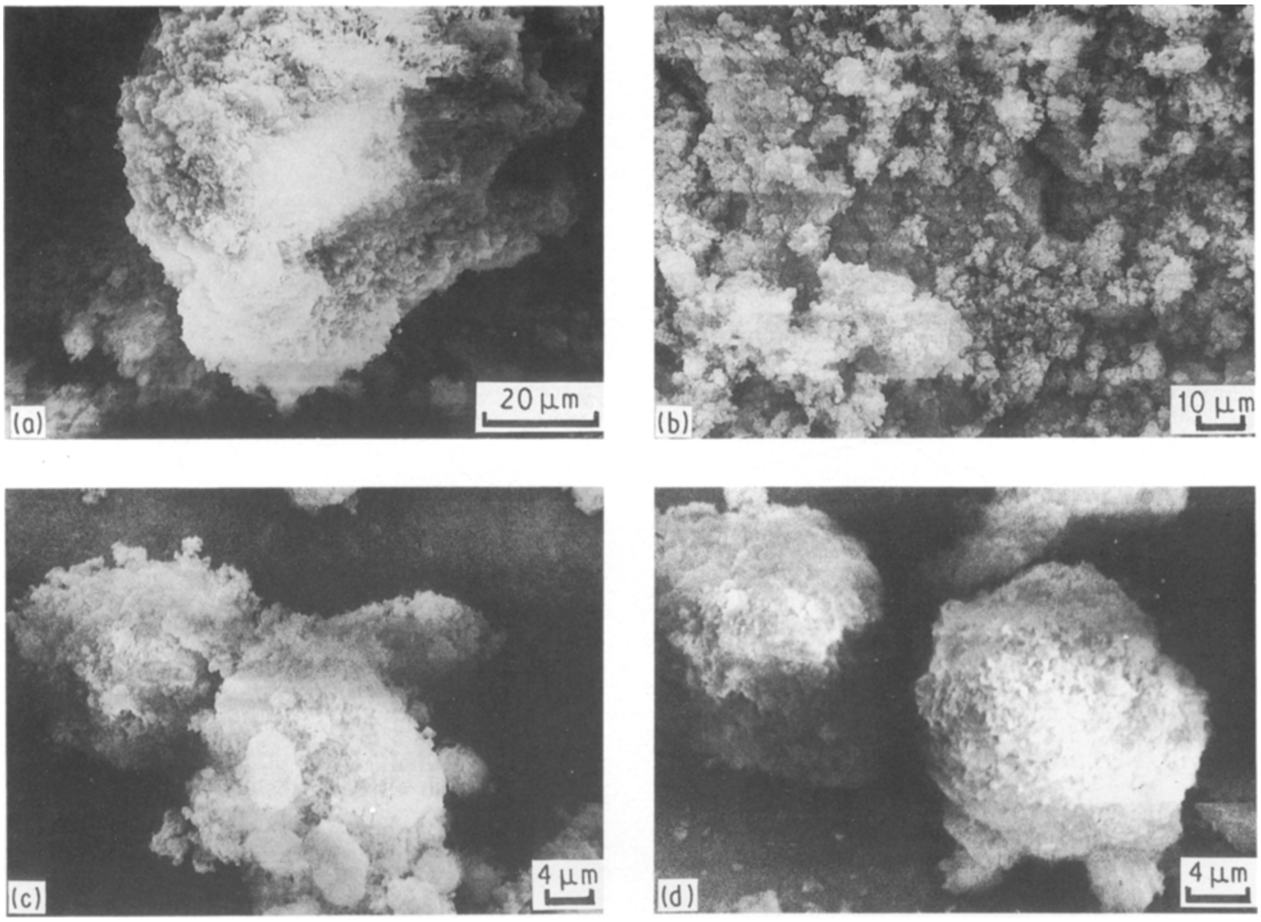

Figure 8 SEM micrographs of the crystalline phases of linear *trans*-quinacridone: (a) α-phase, (b) β-phase, (c) γ-phase and (d) ε-phase.

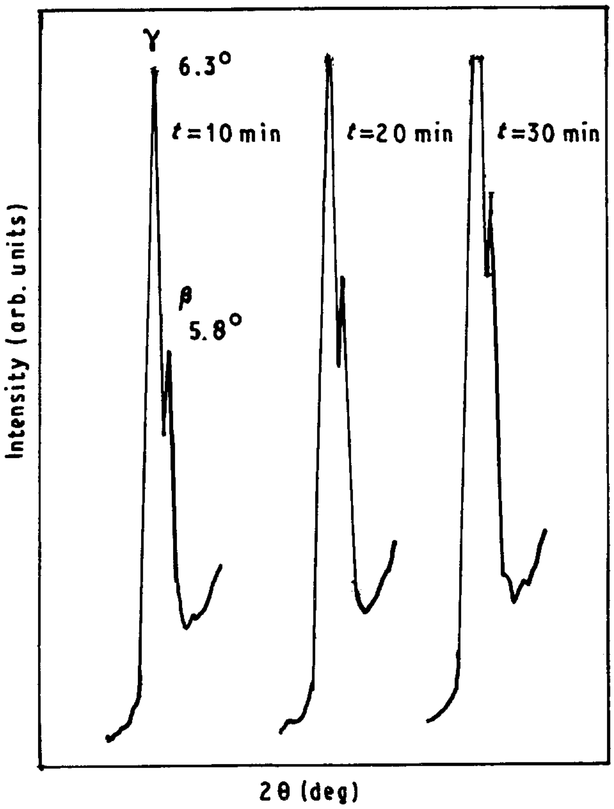

Figure 9 X-ray diffraction patterns in the 2θ range 4–7° of linear *trans*-quinacridone heated at 350 °C for 10, 20 and 30 min.

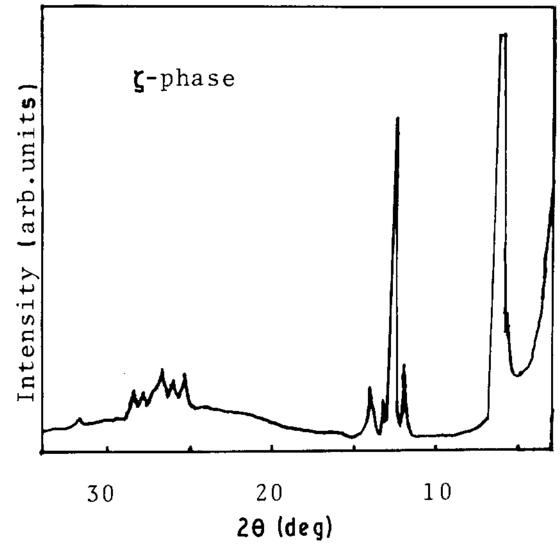

Figure 10 X-ray diffraction pattern of the ζ-phase of linear *trans*-quinacridone.

TABLE III Specific surface area data of the crystalline phases of linear *trans*-quinacridone

Crystal phase	Specific surface area ($m^2 g^{-1}$)
α	19.5
β	18.5
γ	68.5
γ′	26.4
δ	5.2
ε	38.7

TABLE IV Maximum wavelengths of the absorption spectra of crystalline phases of linear *trans*-quinacridone

Crystal phase	Maximum wavelength (nm)		
α	580	530	490
β	608	580	528, 488
γ	565	526	490
γ′	577	530	480
δ	550	550	492
ε	570	526	490

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Received 28 May
and accepted 10 September 1991