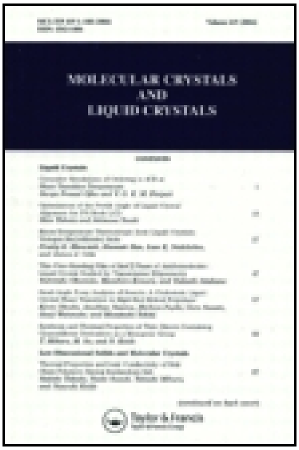

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Morphology and Polymorphism of Terephthalic Acid

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MORPHOLOGY AND POLYMORPHISM OF TEREPHTHALIC ACID.

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Abstract The phase characterisation and morphologies of forms I and II terephthalic acid are presented. The structural nature of the II ↔ I polymorphic phase transition has been explored and form II shown to be more stable at room temperature and pressure. A new mechanism is proposed for the apparent stability of multiply twinned slamples of form I.

INTRODUCTION

Terephthalic acid, is purified and isolated by recrystallisation from water in a multistage process in which the solution temperature and pressure are gradually reduced from values in excess of 250°C and 50 bar to atmospheric. These extreme conditions are dictated by the solubility of terephthalic acid (TA) in water and ultimately yield material of purity greater than 99.9%.

The crystal structure of TA was first determined by Bailey and Brown(1) who found two polymorphic structures both with triclinic unit cells, space group $P\bar{1}$. The unit cell data are given in table 1. In both structures molecules are linked through hydrogen bonded carboxyl dimers into infinite chains which are held in two dimensional sheets by van der Waals and C-H....O interactions. The structures differ in the juxtaposition of these sheets. In form I the chains are directed along [110] with the sheets lying in the (001) plane such that the dimer motifs in one layer lie directly above those of the adjacent ones. In form II the chains lie along [100] with the sheets in the (011) plane such that the carboxyl dimers of one chain lie over the phenyl rings of the adjacent layers. These differences are shown in Fig.1. Bailey and Brown(1) assumed that Form I was the more stable because it had the higher density and because form II 'tended to become rarer on storage'. Saska and Myerson(3) calculated the lattice energies of the two forms and performed powder diffraction on a range of samples but failed to observe form II. Using Raman spectroscopy Gerasimov et al (4) were able to observe the phase transition between forms I and II and to identify that the transition temperature, 349K, was sensitive to sample pressure. They concluded that the transition was reversible and that form I was more stable at atmospheric pressure.

Two aspects of TA crystal chemistry are covered here, firstly its crystal morphology and in particular the morphogenesis of industrially prepared products, and secondly the structural nature of the polymorphic transformation between forms I and II.

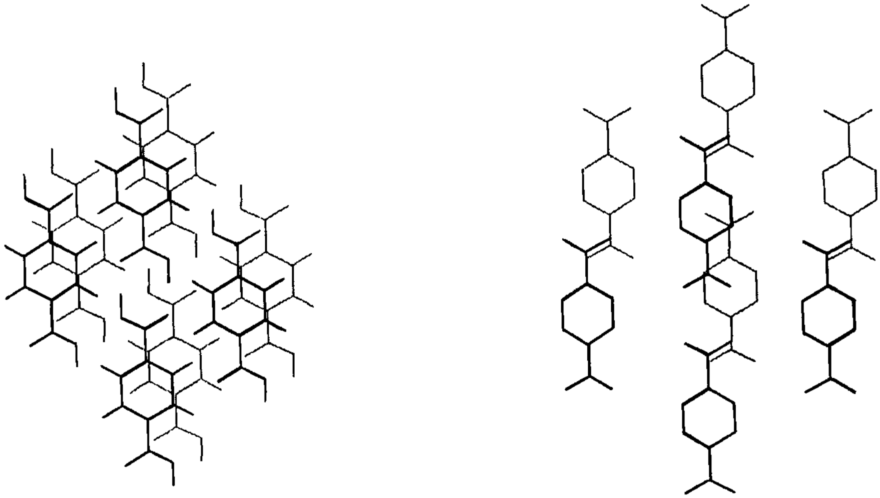


Fig 1 The crystal structure of TA (a) Form I, (b) Form II.

EXPERIMENTAL

99% pure TA was supplied by ICI Chemicals and Polymers Ltd. Recrystallisations from water and aqueous acetic acid were carried out in an autoclave at 250°C and 650psi. Crystals were recovered at room temperature and pressure. Both commercial and recrystallised materials were characterised by a number of techniques. Morphologies were studied using optical microscopy, SEM,and optical goniometry. For industrial samples this included embedding in resin and sectioning with a microtome knife in order to examine the internal microstructure. Phase characterisation was carried out by a combination of X-ray powder diffraction, Weissenberg and synchrotron radiation Laue single crystal X-ray diffraction, and low frequency Raman Spectroscopy. A combination of single crystal XRD and Raman spectroscopy of both powders and single crystals provided the most reliable combination of characterisation techniques. Phase transitions were studied by hot stage optical microscopy, Raman spectroscopy and single crystal Laue diffraction. The latter employed station 9.7 of the synchrotron radiation source at Daresbury, UK, together with a special temperature controlled furnace(5). Diffraction patterns were recorded on film every 5C in the range 80 to 150C and interpreted using the programs SPOTIN, NEWLAUE, and GENLAUE(6). Lattice energy and morphological calculations were performed using the program HABIT together with potential constants from Lifson et al (7).

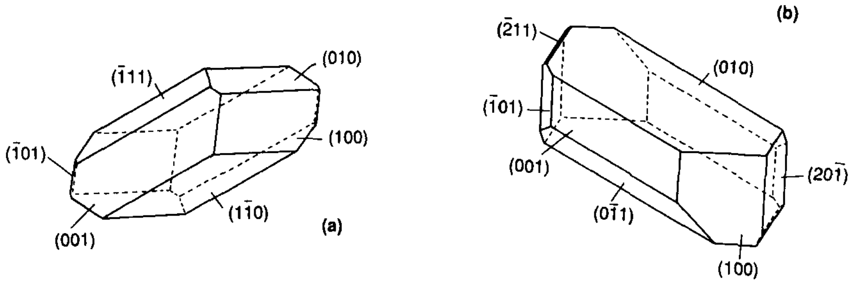


Fig 2 Predicted morphologies of TA (a) Form I, (b) Form II.

RESULTS AND DISCUSSION

Morphological Predictions

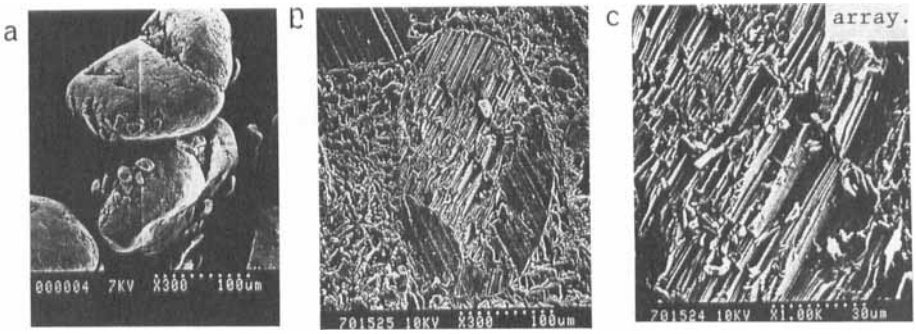
The predicted morphologies of forms I and II are shown in Fig 2. Elongated prisms are predicted for both forms with the fastest growth direction that of the H-bonded chains. Lattice energies of -33.04kcal/mol and -31.19kcal/mol were obtained for forms I and II respectively. These values compare well with the measured heat of sublimation, 33.3kcal/mol (8) and suggest that form I will be more stable. This is in contradiction to calculations of Berkovitch-Yellin and Leiserowitz(2) who calculated the reverse order of stability with lattice energies of -37.2 and -36.8kcal/mol for forms II and I respectively.

Experimental morphologies

Form I:

Form I crystals were only observed in this study when paratoluic acid was included as an additive and, in agreement with Bailey and Brown, these crystals were always found to be twinned parallel to their needle, c, axes. Commercial material was also always found to be form I and is shown in Fig 3. Fig 3a is an SEM view of the exterior of a typical ovoid with Figs 3b and c showing sections at increasing magnification. These data demonstrate the polycrystalline nature of these particles and show how the c-axis fibres of TA are highly oriented within domains. This is consistent with Ozaki and

Fig 3 Commercially produced TA. (a) exterior view, (b) internal section, (c) internal section showing details of crystalline array.



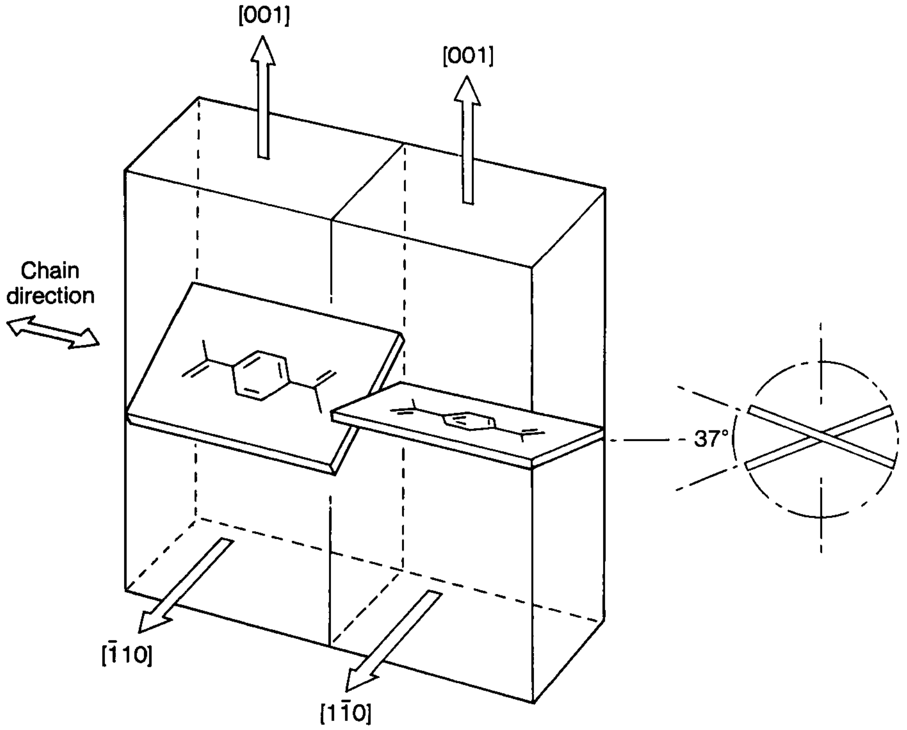


Fig 4 Diagramatic representation showing the relative orientation of form I twinned crystals.

Fig 5 Hydrothermally grown form II crystals.

Shigeyasu's conclusion (9,10) that these particles comprise ordered arrays of form I crystals. Overall these data lead to the conclusion that the observed microstructure of commercial products is a direct result of the tendency of form I to twin during growth. Weissenberg photographs demonstrated that within a twinned crystal the common directions are $[1\bar{1}0]$ and $[001]$, (i.e. one of these is the same in both twins and the other exactly reversed). This is consistent with the observed microstructure of industrial products and results in the preservation of the chain direction across the twin boundary together with a twist of 37.06° in the molecular planes as indicated in Fig 4. The observation that twinning is promoted by paratoluic acid is consistent with this structural understanding since this molecule could act as a chain terminator at the growing surfaces and hence allow the necessary change in molecular orientation to occur.

Form II:

Fig 5 shows a typical selection of form II crystals. Morphologically they exist both as hexagonal, c axis needles and rhombs, bounded by (100),(010) and $(1\bar{1}0)$ forms.

It is interesting to note that for form II as for form I preferred growth does not take place along the H-bonded chains as predicted, but rather in the direction normal to these. This may be the result of the solvent,water,binding strongly to these surfaces and suppressing growth. Similar effects have been found in both succinic (11) and adipic acid(12).

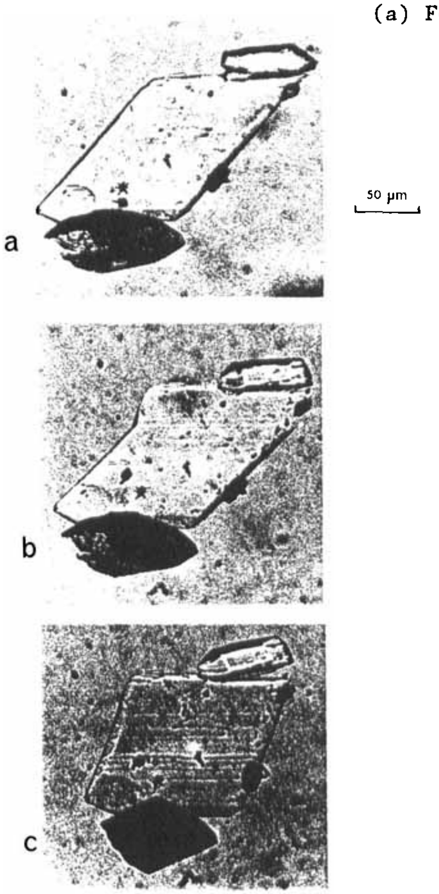
POLYMORPHIC TRANSFORMATION

Having investigated the conditions under which the two forms of TA may be prepared further studies were made in order to examine the interconversion between the forms.

Hot Stage Microscopy

Crystals of both forms were heated and any gross changes in their opacity or morphology observed. Crystals and ovoids of form I showed no changes on heating to 200°C, while form II crystals on the other hand behaved in a dramatic way. In the temperature range 75 to 100°C these crystals underwent a spontaneous shape change from rhombic to rectangular. This is shown in Fig 6 at various stages in during heating. *Fig.6a shows a form II crystal at room temperature.* Fig 6b was taken at 90C and Fig 6c at 95C. The morphological change is seen to proceed in two steps, with half the crystal transformed in b and the transformation complete in c. For many crystals this change was associated with the release of sufficient mechanical energy to cause the crystals to 'jump' off the microscope stage. The morphological change was found to be reversible on cooling to about 30°C although it was observed that many crystals were able to retain the high temperature morphology, only reverting to rhombs upon the application of slight stress using a metal point.

Fig 6 Morphological changes occurring during phase transformation; (a) Form II crystal at room temperature, (b) at 90C, (c) at 95C.



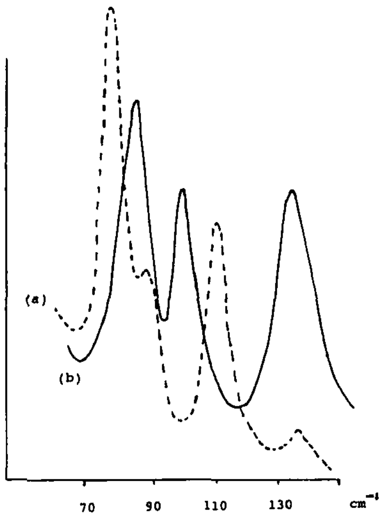


Fig 7 Raman spectra of TA

(a) Form I and (b) Form II.

Raman Spectroscopy

Fig 7 shows the Raman spectra measured on single crystals and powders of Forms I and II. They are consistent with those observed previously by Gerasimov et.al.(4) who assigned the three lowest bands to librational vibrations and the 132-133 cm^{-1} band to intramolecular vibrations of the carboxyl group relative to the phenyl ring. It is important to note, that our phase assignment is the reverse of theirs but based on crystals that have been independently characterised by single crystal XRD. Using a thermostated stage it was possible to heat single crystals of form II and simultaneously record their morphologies and Raman spectra. Fig 8 shows a typical example of a crystal heated to 95°C. The morphological change is accompanied by a change in the Raman spectrum from that of form II to that of form I. On cooling the form II spectrum reappeared. It is thus clear that form II is the stable phase at atmospheric pressure and room temperature, converting to form I on heating.

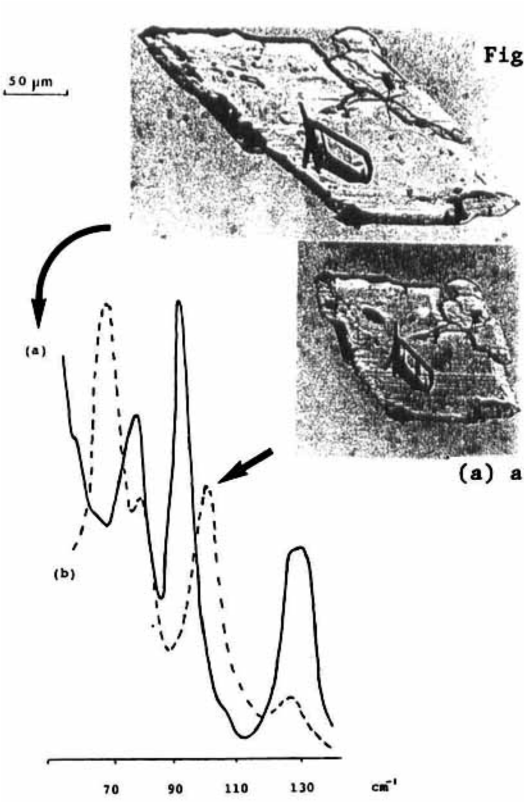


Fig 8 Change in Raman spectra and morphology observed on heating a Form II crystal to 95C, (a) at room temp and (b) at 95C.

Single crystal Laue diffraction

All the crystals examined exhibited highly streaked patterns due to large mosaic spreads. Fig 9 shows the low(30°C) and high(150°C) temperature patterns from one of these crystal. The methodology of data interpretation is given elsewhere (6) but Fig 10 shows the predicted patterns that best match the Fig 9 photographs. These

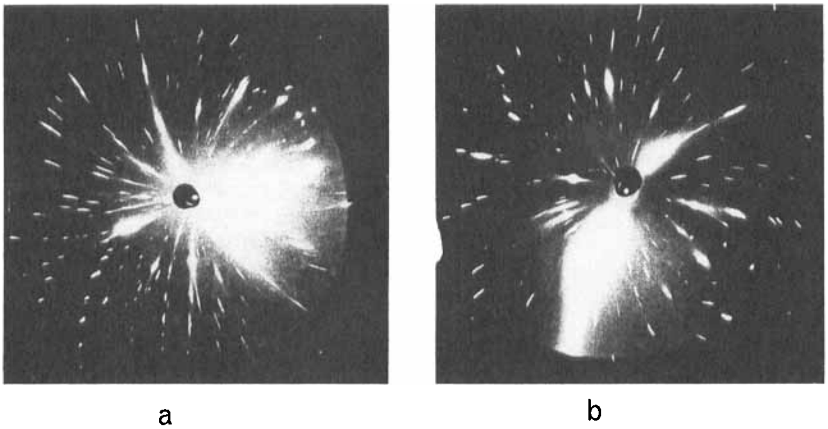


Fig 9 Single Crystal Laue diffractograms of (a) Form II at 30°C, (b) at 150°C.

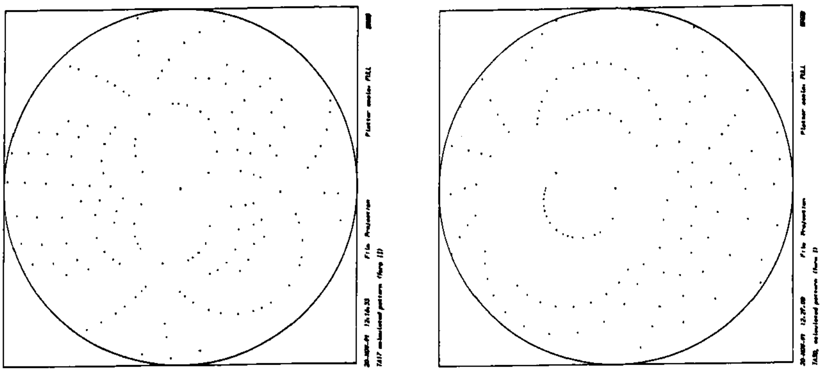


Fig 10 Predicted Laue diffractograms

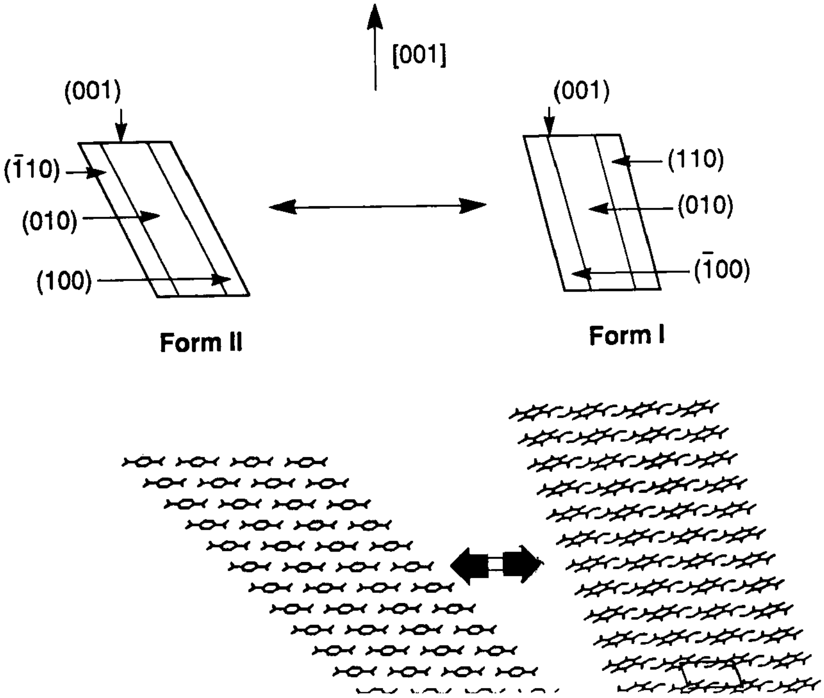


Fig 11 The relationship between morphological and structural changes during the II → I transformation in TA.

TABLE 1 Crystallographic Data for TA Forms I and II (after [1])

	Form I	Form II
a (Å)	7.73	9.54
b (Å)	6.443	5.34
c (Å)	3.749	5.02
α (°)	92.75	86.95
β (°)	109.15	134.65
γ (°)	95.95	104.90

confirm the Raman data that the room temperature form II converts to form I on heating, and indicates that form I crystals generated in this way are untwinned. The data fit shows that both before and after heating the position of the c-axis is virtually unchanged, implying that during the transformations the c-axis is preserved. From the known morphology of form II crystals (see above) Fig 11 has thus been drawn illustrating the relationship between the observed morphological change and the crystal structures of the polymorphs. The change is such that, the H-bonded chains are preserved but the molecular sheets are not. Taken together the data suggest that this transformation is Martensitic in nature; no phase boundaries are present in transforming crystals and its extent is a function only of temperature.

CONCLUSIONS

This study represents a considerabe advance in the understanding of TA crystal chemistry. Form II is now understood to be the more stable polymorph at ambient temperatures and pressures. Transformation to form I occurs over the temperature range 75 to 100°C and is driven by the contribution of proton disorder to the free energy change. The tendency of form I crystals to grow as twins parallel to their c axes explains the observed microstructure of commercial products. In contrast to single crystal samples, these ordered arrays of microcrystals are able, unexpectedly, to remain in the form I structure indefinately under conditions where transformation to form II would be expected. This is presumably a form of collective stabilisation which is possible since the morphological change and release of stress observed as an inevitable consequence of phase transformation in single crystals is impossible in these twinned arrays since it would require a concerted inter-crystal process. The probability of this is extremely low and hence form I is stabilised.

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