JOURNAL OF MATERIALS SCIENCE 31 (1996) 1893–1901

Recrystallization and solubility of 1,3,5-triamino-2,4,6-trinitrobenzene in dimethyl sulfoxide

M. F. FOLTZ, D. L. ORNELLAS, P. F. PAGORIA, A. R. MITCHELL
Lawrence Livermore National Laboratory, P.O. Box 808, L-282, Livermore, CA 94550, USA

The insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) has been recrystallized from dimethylsulfoxide (DMSO) with particle sizes ranging up to 2 mm diameter. Crystal growth was controlled by varying the heating and cooling rates and the solution agitation speed. The role of additives and "green" u.v. radiation-induced impurity in affecting crystal morphology, size, and colour was also studied. To provide the thermal concentration data needed for the crystallization study, the solubility curve of TATB in DMSO was determined gravimetrically. The solubility data spans the range of $0.47 \pm 0.23\,\mathrm{g\,l^{-1}}$ at 21.2 °C to $6.80 \pm 1.13\,\mathrm{g\,l^{-1}}$ at 145.5 °C.

1. Introduction

High explosive (HE) performance and sensitivity studies are routinely done on new crystalline materials prior to scale-up testing. The extent to which these and other experiments addressing fundamental HE properties can be carried out depends on how easily the target material can be grown to the desired particle size. For example, the study of the effect of particle-size on flow properties of paste explosive formulations requires reproducible production of well-characterized particle-size distributions. X-ray studies involving phase transitions also require crystal diameters on the order of several hundred microns. Studies that monitor crystalline thermal expansivity or the shock initiation of single crystals, can require crystals with diameters up to several millimetres in each dimension.

Good-sized crystals are usually easily obtained for such studies because many HE materials are readily soluble and have good crystal growth properties from common solvents. Some compounds, however, are notorious for their insolubility and for their difficulty in growing to large crystal size. An example is the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [1, 2]. In addition to its application as a HE, this compound has also been used to produce the important intermediate benzenehexamine [3–6] which is used in the synthesis of new heteropolycyclic molecules like 1,4,5,8,9,12-hexaazatriphenylene (HAT), a strong electron acceptor ligand for low-valence transition metals [4, 5], and in the preparation of ferromagnetic organic salts [7]. Although some work has been done to produce an analytical standard of TATB by recrystallization, [8] and to produce ultrafine crystalline TATB, [9, 10] attempts in the past to crystallize TATB to dimensions > 200 μm have met with limited success. An exception was a high temperature dry amination process which reported the successful production of large (up to 100 μm) pitted particles [11]. Solvents with the greatest TATB solubility at room temperature (estimated solubility > 20% weight per volume) are the "superacids": chlorosulfonic, fluorosulfonic, trifluoromethanesulfonic, and concentrated sulfuric acid [12]. Yet due to the highly corrosive and hygroscopic nature of the superacids, single TATB crystals have been historically grown from the less reactive and lower TATB solubility solvents, nitrobenzene [13] and diphenyl ether [14, 15]. There appears to be a large gap in TATB solubility between (estimated) ~ 820 p.p.m. for methanesulfonic acid and ≥ 200 000 p.p.m. for superacids [12]. In the lower solubility group of solvents, methyl sulfoxide (dimethyl sulfoxide, DMSO; estimated solubility ~ 70 p.p.m.) [12] has been recognized as suitable for producing extremely high purity TATB crystals, [16] although recrystallization on a large scale has been considered impractical [14, 15].

The degree of solubility is not the only limiting factor in producing clean, relatively defect-free HE crystals from a hot concentrated solution. Thermal decomposition is more rapid for dissolved than for solid-state material and typically increases with elevated temperature. Depending on the solubility curve, a temperature high enough to achieve a production-oriented optimized amount of dissolved material may also be high enough for rapid decomposition on the timescale of recrystallization. Crystal growth by a thermally-driven concentration gradient can then be complicated by the presence of dissolved impurities arising from thermal degradation. These impurities can act not only as morphology modifiers but can also lower sample purity. An additional complication for TATB in particular is the stress- [17] or UV

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light-induced [18] formation of stable radicals. The presence of radicals gives the normally yellow material a characteristic green to green–black coloration. The structure of the free radical when dissolved in DMSO or *N*,*N*-dimethylformamide (DMF) has been tentatively identified by electron spin resonance spectroscopy as a TATB-H adduct (H-atom coupled to the NO_2 group) [18]. Growth of pure crystals will be compromised if solution-phase radical formation is not inhibited, since undesirable solvated radicals can co-crystallize with TATB [17]. With these restrictions in mind, a recrystallization effort was started to determine conditions required to produce pure, relatively defect-free TATB crystals with reproducible size distributions spanning the range of a few hundred micrometres to several millimetres in diameter for use in both basic and applied research. Further work addressing scale-up of crystalline TATB is discussed in a second paper [9].

2. Experimental procedure

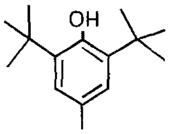
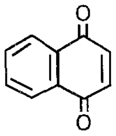
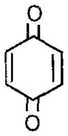
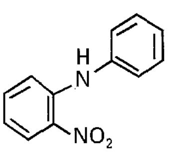
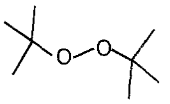
2.1. Crystallization

The experimental schematics used for both parts of this study are given in [20]. Depending on the saturation concentration (based on solubility data) expected for a given experiment, up to 250 mg of TATB was added to 60 ml of DMSO in a 100 ml three- or four-necked Pyrex round-bottomed flask. The solution was heated from below with a heating mantle and the temperature controlled with an Omega (series 2010) programmable controller via a K-type thermocouple inserted into the solution through a rubber septum. The solution was heated for forty-five minutes at a linear heating rate from ambient to the programmed maximum temperature. This temperature was maintained for about fifteen minutes while the solids finished dissolving. The upper half of the round-bottomed flask was wrapped in glass wool to slow heat loss, and to minimize the spontaneous seed formation that occurs during the cooldown cycle at the surface of the hot solution. A glass rod assembly suspended a Teflon stirrer blade above the bottom of the flask to avoid grinding the crystals as they accumulated. The rate of stirring was regulated by a Cole Parmer (model 4555-30) solid state controller with fast agitation ($\sim$60 r.p.m.) for maximum solvation during the heat cycle and slow ($\sim$25 r.p.m) or no stirring during the cooldown cycle. Cooling times varied from 12 h to six days with linear cooling ramps.

Early attempts in this study to crystallize TATB met with mixed results. Large crystals (0.1 mm to 1.0 mm diameter) produced from a 24 h temperature-controlled heating/cooling cycle in refluxing nitrobenzene, refluxing phenyl ether (diphenyl ether), and tetramethylene sulfone (sulfolane; $T_{\max} \sim 206\,^{\circ}\mathrm{C}$) were opaque and discoloured, turning the normal yellow material a dark amber to brownish-green. Only the aprotic solvents DMSO and DMF produced yellow product. One aprotic solvent that did *not* produce yellow crystals, however, was 1-methyl-2-pyrrolidinone (NMP). When 20 mg of TATB was dissolved in 5 ml of this solvent by heating to $\sim$145 °C, the solution quickly darkened to black. Upon 24 h cooling to room temperature, the solution produced a low yield of dark green micro-crystals, presumably discoloured due to the inclusion of green TATB radicals and/or decomposition products. For cooling periods longer than 24 h, almost no solids were recovered from the dark solution. When the commercial antioxidant/radical scavenger 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene, or BHT) was added to NMP before heating, however, the solution did not discolour and yellow product like that from the other aprotic solvents was produced. It is therefore possible to grow TATB crystals from NMP, but only with the addition of a radical scavenger like BHT.

Of the aprotic solvents tested, DMSO was chosen as the most suitable for recrystallization based on its estimated room temperature TATB solubility (70 p.p.m. versus 27 p.p.m. for DMF) [12] and its resistance to thermal decomposition [21, 22]. However, for experiments involving prolonged heating (e.g. cool-down from 135 °C in six days), some noticeable orange–brown discoloration of the heated solution and final product did occur. An attempt was made to determine the cause of discoloration and whether it could be minimized. For example, if discoloration is the result of thermal decomposition via TATB radical production, the addition of radical scavengers should improve the final product colour. On the other hand, colour degradation could originate with solvent decomposition. Solutions with additives chosen for their radical-scavenging or -initiating ability, or supposed ability to inhibit the thermal decomposition of DMSO, [23] were heated to 145–150 °C for 24 h. The degree of discoloration of the resulting solution and final filtered product were compared and the crystal shape noted (see Table I). The colour of the final solid product varied from slightly off-yellow to yellow–orange for BHT, to red–brown for sodium bicarbonate. Of the additives, BHT showed a pronounced concentration effect. At high concentrations, the discoloration was worse than when nothing was added, yet for low concentrations ($\sim 3.8 \times 10^{-4}$ M) the colour was improved. For example, a 1 : 1 ratio of TATB to BHT produced a product with a colour intensity between that caused by 1,4-naphthaquinone and quinone. In this case, the hot solution was a deep wine-red colour that faded with cooling. The optimum amount of BHT required to suppress discoloration, however, was not determined. The solutions were not stirred in order to remove the effect of agitation on particle morphology. Under these conditions, the crystal habit was predominantly that of irregular needles. Only those additives with *t*-butyl groups (BHT, di-*t*-butyl peroxide) caused a habit modification away from needles to pyramids. It was also noted that the radical initiator di-*t*-butyl peroxide not only strongly discoloured both solution and product crystals, but also caused pitting of the metal thermocouple gauge. Replacing the metal gauge with a Teflon-coated thermocouple gauge greatly reduced the degree of discoloration caused by di-*t*-butyl peroxide in a follow-up experiment. This improvement in product colour suggests that radical production at the metal surface exacerbates TATB

TABLE I. Thermally-induced discoloration of TATB

Additive	Structure	Type	Solution colour	Solids colour and morphology
Butylated hydroxybenzene (BHT)[a]		antioxidant	golden amber	yellow–orange small pyramids
1,4-Naphthaquinone		methyl radical scavenger	orange	golden–orange, fine needles
1,4-Benzoquinone (quinone)		methyl radical scavenger	orange	golden–brown, fine needles
2-Nitrodiphenylamine (2-NDPA)		radical inhibitor	orange	orange–yellow needles
None			amber	orange, needles
Di-*t*-butyl peroxide		radical initiator	intense orange	brown, coarse pyramids
Sodium bicarbonate	$NaHCO_3$	DMSO decomp. inhibitor	black (few hours)	red–brown, dendritic needles
Salt	NaCl	DMSO decomp. inhibitor	black (1 h)	(discarded)

[a] Increasing the concentration of BHT caused greater discoloration (see text).

thermal decomposition. The product colour improvement noted in Table I for radical inhibitors supports this hypothesis. Thus TATB recrystallization should be done in non-metallic (glass and/or Teflon) vessels. A Teflon-coated thermocouple gauge was used thereafter for all crystallization work.

An alternate decomposition pathway accounting for thermal discoloration could arise from intrinsic impurities in the TATB starting material. Extraction of possible impurities [24] by refluxing the starting material in either toluene or DMSO for 8 h prior to crystallization did not improve the degree of product discoloration over that of unwashed material. It was concluded that decomposition of impurities alone is not a major factor contributing to discoloration.

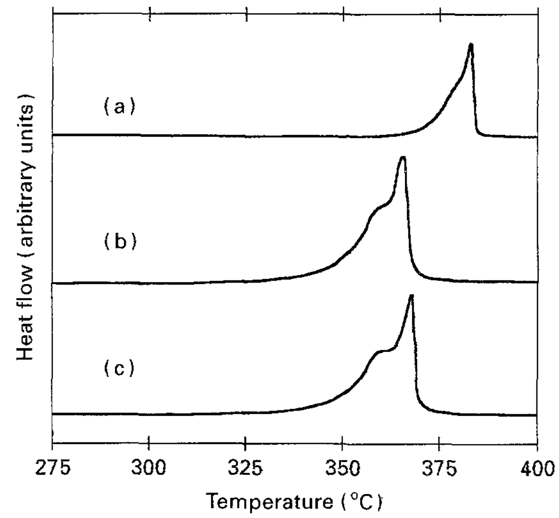


Figure 1 Differential scanning calorimetry (DSC) records (10 °C min^{-1}, perforated aluminium pan) of (a) untreated yellow TATB powder, (b) TATB rendered green by exposure to a u.v. lamp, and (c) TATB discoloured to orange-brown by prolonged heating in DMSO.

Another discoloration problem encountered in crystallizing TATB comes from the presence of "green" TATB impurity. Exposing powdered TATB to fluorescent lights causes some fraction of surface material to turn green. This change is due to u.v. irradiation from line emission of trace mercury in the lamps. Although the u.v. intensity is low, with long enough exposure time (days) enough surface material turns green to make a noticeable colour change. The thermal stability of solid-state green TATB is less than that of pristine yellow TATB, as is shown in the differential scanning calorimetry (DSC) records of Fig. 1(a) (yellow) and (b) (green). The onest of the reaction exotherm is ~10 °C lower for "green" TATB (sample stirred for thorough exposure during irradiation by a u.v. lamp) than for yellow TATB. The DSC record for TATB discoloured to orange during crystallization (Fig. 1(c)) also shows an early onset for exothermic reaction. This early onset indicates that orange discoloured TATB is also less thermally stable than yellow TATB.

If green TATB is less thermally stable than yellow, a question to address is will thermal discoloration of green starting material during recrystallization be worse than for the yellow. To address this problem, a dark green TATB sample, first prepared by exposing it to a fluorescent desk lamp for two months, was then recrystallized from DMSO. Both the final solution and crystallized product were the same orange colour described in Table I. Although minimizing the crystallization temperature and adding small amounts of BHT helped reduce product discoloration of yellow TATB starting material, these options were not explored for the green material.

2.2. Solubility

Ten grams of TATB were placed in 1 l of DMSO (spectrophotometric grade) in a 1 l Erlenmeyer flask equipped with a mercury thermometer and a Teflon-coated magnetic stir bar. The flask was placed in an insulated temperature-controlled oil bath (Red Line Synthetic Oil Corp., Dot 5 Silicone Brake Fluid). The controller (Ace Glass Inc., model 12110-06 proportional temperature controller) can be set at 1 °C increments and will control to approximately ± 0.2 °C. The mixture of solid and liquid was stirred vigorously except during sampling operations. The mixture was taken to about 150 °C and allowed to equilibrate for 30 min. The temperature was lowered to 145 °C, the magnetic stirrer stopped and the solution allowed to equilibrate for 20 min while the solids settled. The 20 min equilibration period was repeated at each successively lower sampling temperature. At each temperature, 50 ml solution samples were taken by pipette and delivered to a beaker. The sample beakers were held at 120 °C for 24 hrs in a thermally controlled oven (National Appliance Co., model 5510-7 oven; Omega model CN 310 controller) to promote larger TATB crystal growth for filtering efficiency. The samples were then cooled to room temperature and filtered through tared 30 ml Gooch crucibles with a fine fritted disc of 5 μm nominal maximum pore size, washed with acetone and dried.

Room temperature samples were distilled down to about a millilitre under $19.9\text{–}26.6 \times 10^2$ Pa vacuum while heated with water at 85–90 °C. The remaining solvent in the flask was evaporated to dryness and constant weight on a high vacuum line, the sample again held at 85–95 °C. Liquid nitrogen cryogenic assistance and diffusion pump backing were used on the vacuum line. The room temperature solubility determined from these samples, an average of three runs, was added to the values at all other temperatures to obtain the final solubility values.

TABLE II Solubility of TATB in DMSO

Temperature (°C)	± error	Solubility (g l^{-1})	± error
145.5	0.2	6.80	1.13
136.0	0.2	5.17	0.803
124.5	0.2	3.78	0.590
117.4	0.2	2.92	0.458
110.2	0.2	2.36	0.342
97.6	0.2	1.63	0.221
84.9	0.2	1.30	0.183
74.6	0.2	0.975	0.142
65.0	0.2	0.810	0.121
55.0	0.2	0.635	0.113
45.1	0.2	0.533	0.109
34.9	0.2	0.510	0.109
21.2	0.2	0.473	0.230

3. Results

The TATB solubility data for DMSO is listed in Table II and plotted in Fig. 2. The fitted curve (Table III) is also plotted in Fig. 2. The data have been corrected for solubility at room temperature, and this correction is reflected in the error bars shown. Solubility values determined in the range of 115–145 °C were used to determine the required weight of TATB needed to saturate solutions at temperature in the crystallization experiments reported here. By varying the ultimate concentration of TATB, the molar ratio of BHT, the speed of solution agitation, and the linear rates of heating and cooling as well as soak time, it was possible to grow crystals up to ~2 mm in diameter. For example, a distribution of crystal sizes ranging up to 500 μm in diameter were grown using a 24 h cool-down period from a maximum temperature of 135 °C. Many crystals exhibit a bipyramidal shape, although

TABLE III Fourth-order polynomial fit to solubility data of TATB in DMSO

Temperature (°C)	Solubility (g l^{-1})
145	6.65
140	5.82
135	5.07
130	4.40
125	3.80
120	3.27
115	2.81
110	2.41
105	2.06
100	1.77
95	1.52
90	1.31
85	1.15
80	1.01
75	0.908
70	0.828
65	0.767
60	0.722
55	0.687
50	0.660
45	0.634
40	0.605
35	0.569
30	0.522
25	0.458

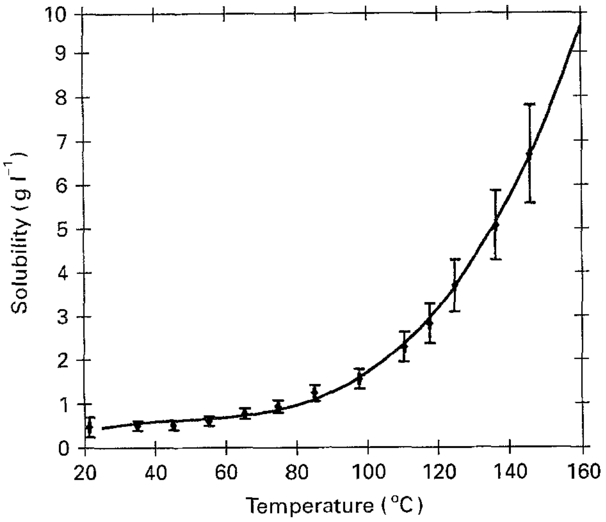


Figure 2 The TATB solubility data for DMSO (Table II) superimposed with a fitted curve (Table III) as a guide to the eye.

inefficient stirring could result in a morphological change to thin hexagonal platelets and no stirring resulted in needles. Faster cooling rates produced not only smaller crystals but also more defects per crystal, a greater concentration making an otherwise transparent crystal an opaque yellow.

Fig. 3(a–c) show scanning electron micrographs (SEMs) of TATB crystals grown early in the study from nitrobenzene (50 × magnification), diphenyl ether (50 × magnification), and sulfolane (100 × magnification). Of these solvents, only nitrobenzene produced crystals with a somewhat regular shape. Those crystals grown from diphenyl ether fragmented easily due to their layered morphology, while those from sulfolane formed clumps of irregular platelets. All three sets of crystals were a dark amber to brownish-green compared to the original bright yellow colour. Fig. 4(a–c) show SEMs of crystals (50 × magnification) grown from a 1 : 2 TATB/BHT molar ratio mixture in DMSO heated to a maximum temperature of 135 °C and cooled for periods of one, three, and six days. This concentration of BHT was much higher than required to reduce product discoloration (see Table I). The faster the cooling rate, the thinner and poorer the quality of crystal as demonstrated by how easily they were damaged during gold-coating preparation for the micrographs. Crystals grown more slowly were larger and sturdier, but still had surface irregularities indicating some defects. The crystals of Fig. 5(a–d) seen at 20 × magnification, were grown from DMSO solutions heated at 135 °C without BHT and cooled for periods of 12, 18, 24 and 72 h. Again as cooling time increased, the crystals grown were larger in size and more regular in shape. Although there was no apparent difference in particle size between crystals grown over a 24 h period from solutions with or without BHT, those grown with BHT tended to have a more regular shape. This difference, more pronounced without stirring (Table I) may be due to BHT acting as a morphology modifier. Alternatively, its addition may affect the solubility curve, decreasing the slope to allow a slower and more uniform crystal growth over a given temperature drop.

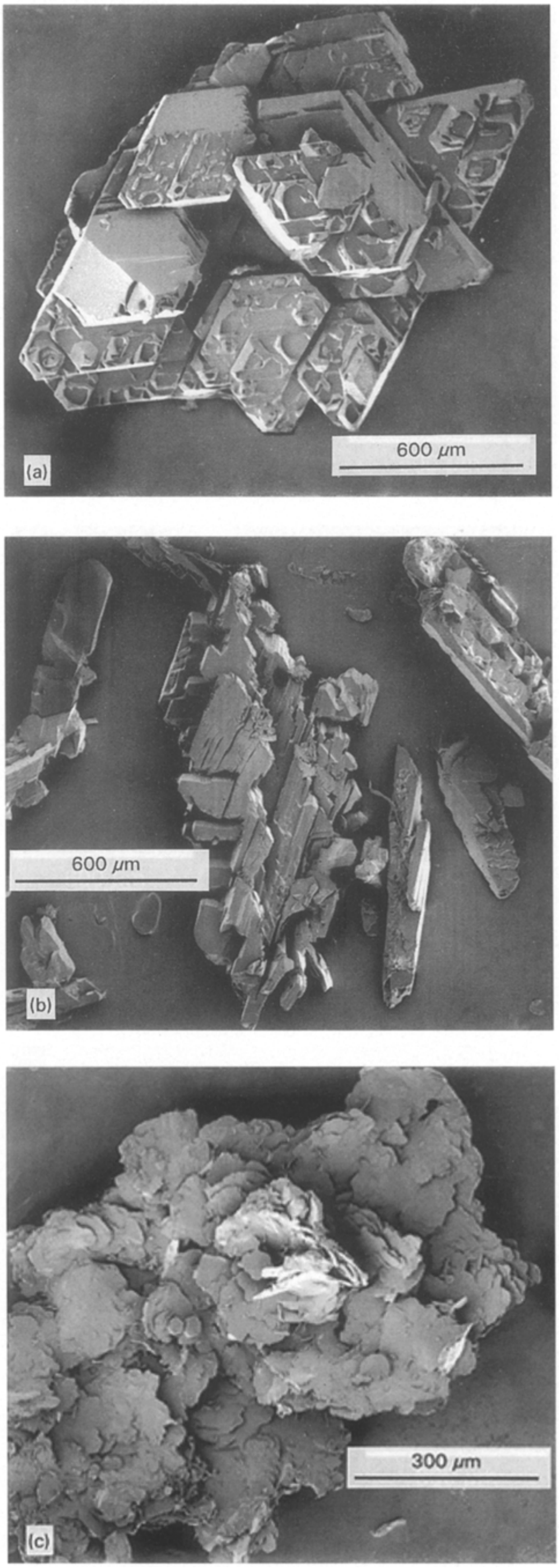


Figure 3 TATB crystals grown from (a) nitrobenzene (50 × magnification), (b) diphenyl ether (50 × magnification), and (c) sulfolane (100 × magnification).

Temperatures other than 135 °C were also used to study how the rate of change in solubility affects crystal growth. Growing crystals from temperatures lower than 135 °C uses a flatter, less steep part of the

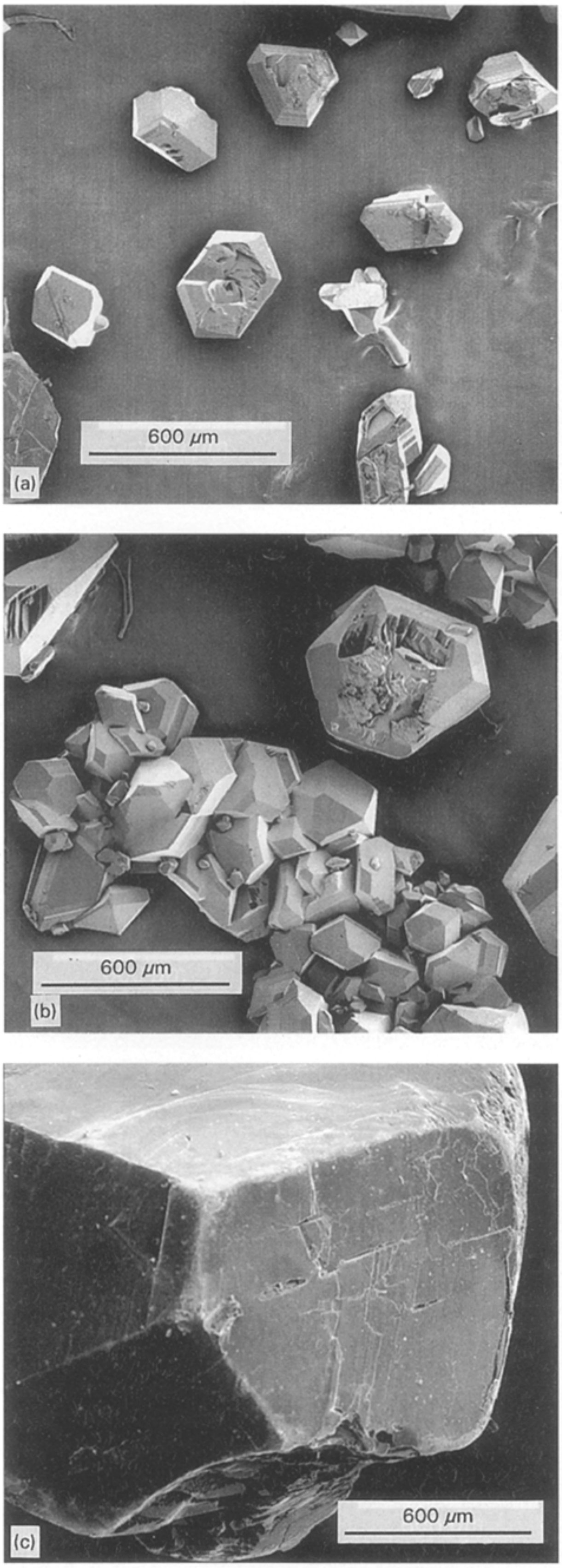


Figure 4 TATB crystals (50 × magnification) grown from a 1 : 2 TATB/BHT molar ratio in DMSO heated to a maximum temperature of 135 °C and cooled for periods of (a) one, (b) three, and (c) six days.

solubility curve than exists above 135 °C. One would expect more defect-free crystals grown at the shallow end of the curve because of the slower and more uniform rate of precipitation and growth throughout the total cooling period. Crystals grown from solutions cooled from higher temperature would experience a rapid initial change in solubility during seed formation and early growth. Defects would be more likely to form and propagate under these conditions than in lower temperature growing conditions involving the shallower part of the solubility curve, the rate of desolvation being closer to constant. Fig. 6(a, b) show TATB crystals (3000 × magnification) grown from 100 °C for cooling periods of 16 and 32 h. These crystals were smaller than those crystallized from 135 °C; the solubility is lower at 100 °C so less material is available for crystal seed growth. Overall, crystals grown from 100 °C had a slightly more uniform shape than those grown from higher temperature. This small improvement in morphology is probably due to the shape of the solubility curve, and not to the degree of agitation which was kept constant for all runs. The role of agitation in controlling crystal growth will be discussed in more detail in a second paper [19].

It was possible to grow very uniform TATB crystals by adjusting the rate of cooling and agitation. Sampling problems in the solubility study yielded qualitative observations relating crystal morphology and size with cooling rate. Fig. 7(a, b) show two magnifications (1000 × and 20 000 ×) of the ultrafine TATB starting material used in the solubility study (LLNL batch number C-122, sub-micrometre particle size). For the first solubility measurement attempt, this powdery material stayed suspended in solution at 145 °C, even after agitation had been stopped for half an hour. It was therefore not possible to sample the solution without inadvertantly siphoning undissolved particles. Larger particle size material was needed so settling could occur. It was decided to allow the solution to cool by simply turning the heater off to promote crystal growth of this very fine undissolved "seed" material. The crystal size distribution would thus be shifted to larger, heavier particles. A second attempt to measure solubility resulted in fewer suspended particles at temperature due to some crystal growth, although this attempt did not produce a solution clear enough of particulate matter to be sampled. A sample of these uniformly shaped crystals is shown in Fig. 8(a, b) (magnification 50 × and 1000 ×). These crystals indicate a hundred-fold increase in particle size from the original ultrafine material. For comparison, the TATB crystals of Fig. 9(a, b) (magnification 20 × and 50 ×) grown over six days of cooling from 135 °C show a thousand-fold increase in size over the ultrafine starting material. Crystals retrieved from the third successful solubility run, which involved a stepwise cooling curve with equilibration at the sampling temperatures, had many defects and were irregularly shaped. It would appear that the smoothness of the cooling curve is one important factor in obtaining defect-free crystals. In a later experiment, the rate of cooling was slowed by wrapping the oil bath with insulating fibreglass wool. The crystals produced were larger than those made with the faster cooling initially uninsulated oil bath.

A sample of TATB crystals grown from DMSO was submitted for X-ray analysis [25]. The unit cell is

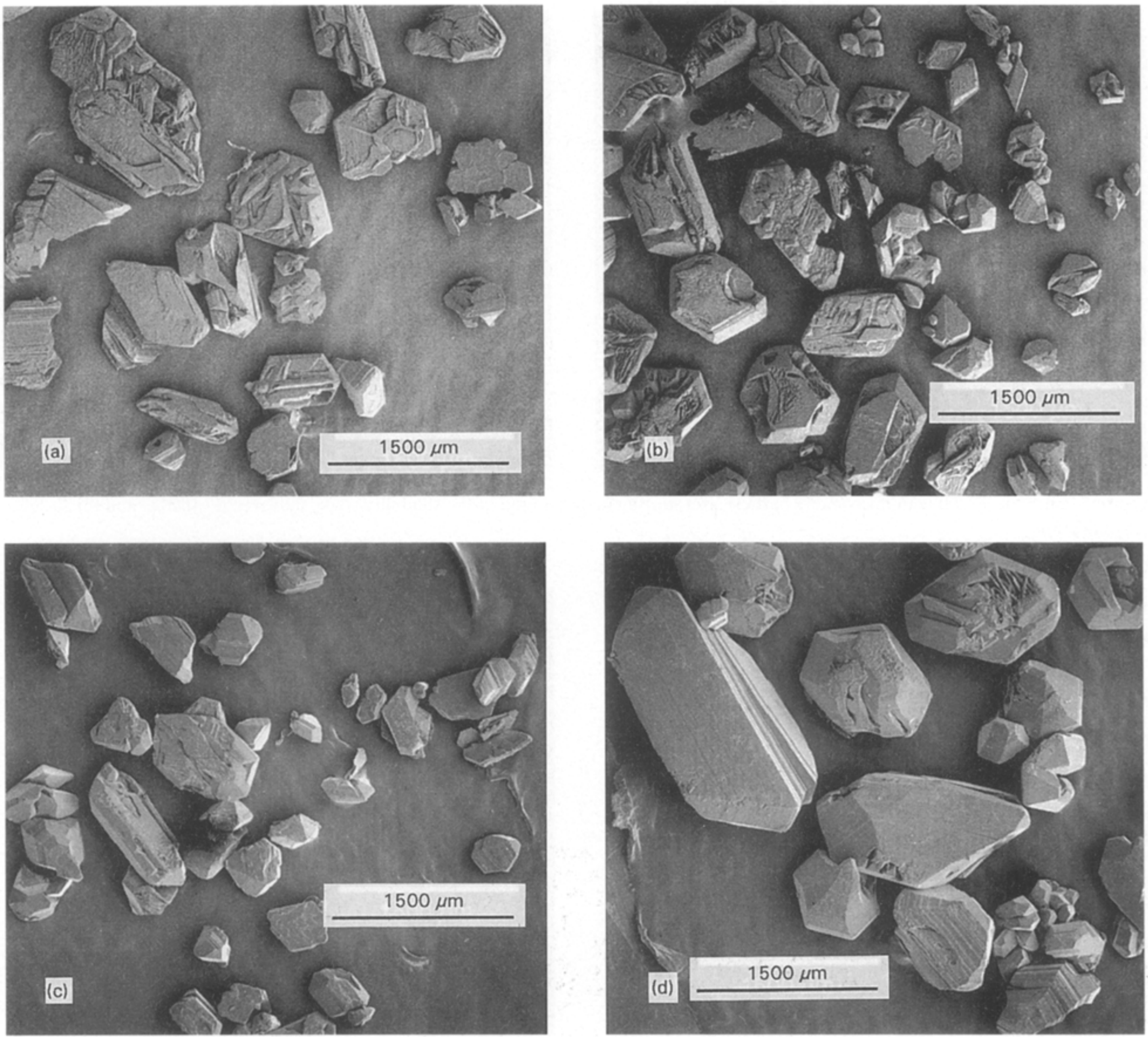


Figure 5 TATB crystals (20 × magnification) grown from DMSO solutions heated to 135 °C without BHT, and cooled for periods of (a) 12 h, (b) 18 h, (c) 24 h and (d) 72 h.

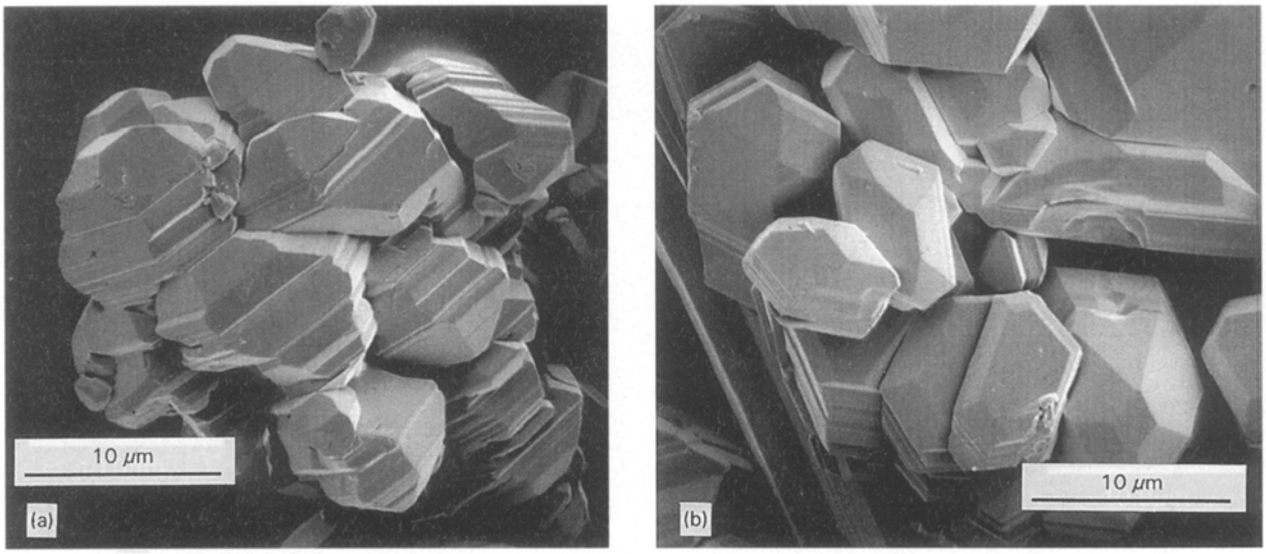


Figure 6 TATB crystals (3000 × magnification) grown from 100 °C over cooling periods of (a) 16 h and (b) 32 h.

triclinic with two molecules per cell, the space group $P\bar{1}$, and the density 1.935 g cm^{-3} (compared with 1.937 g cm^{-3} of [8]). The unit cell parameters are compared in Table IV with those previously reported in the literature for crystals grown from nitrobenzene, [13] and are seen to be in very good agreement. The

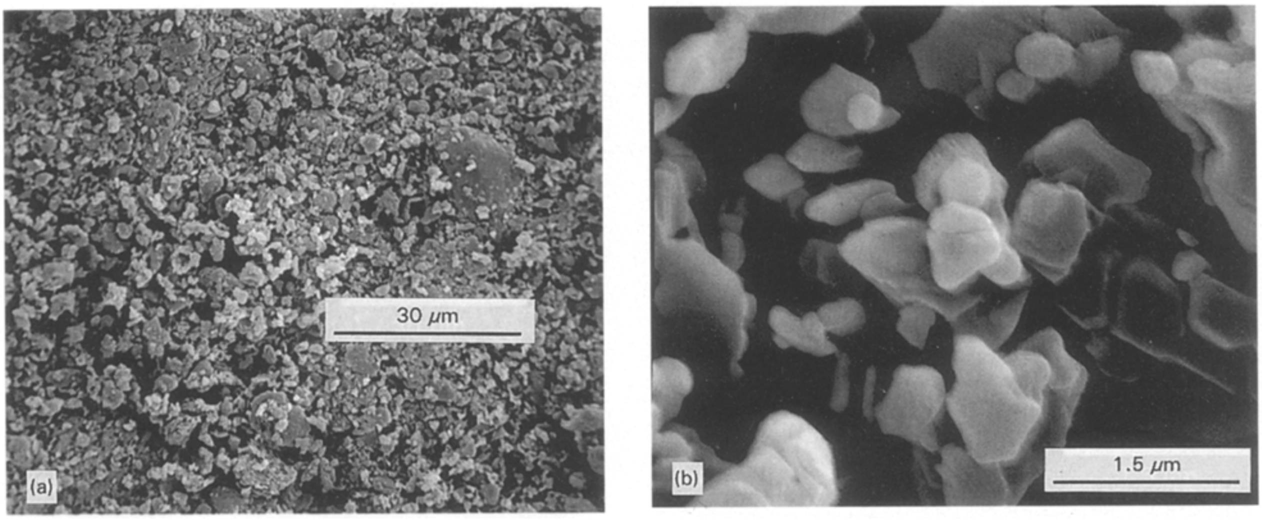


Figure 7 Ultrafine TATB (sub-micrometre particle size) starting material used in the solubility study shown at (a) 1000 × and (b) 20 000 × magnification.

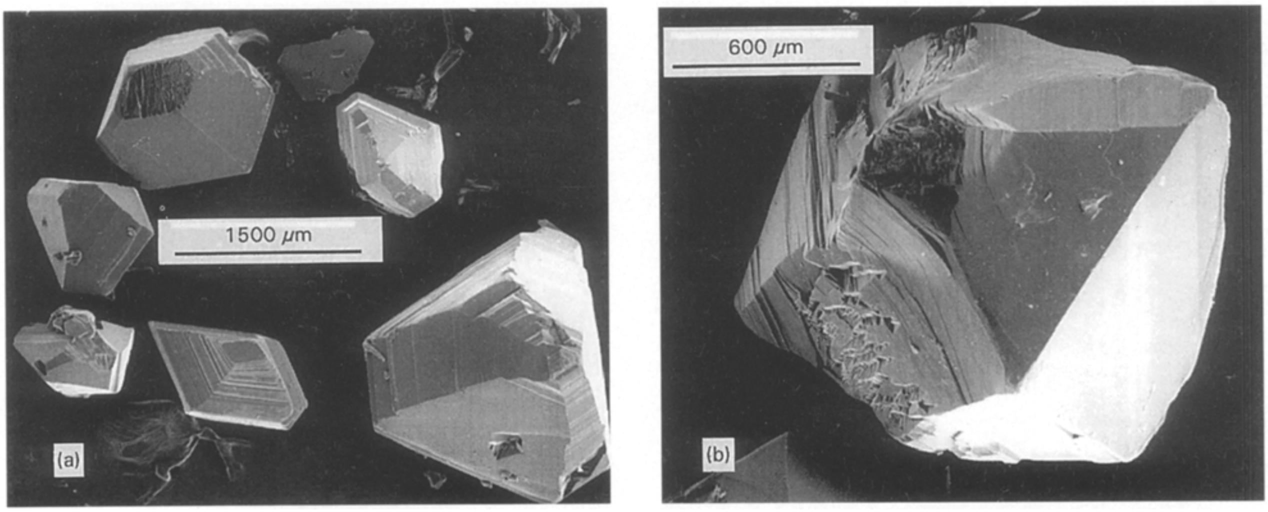


Figure 8 TATB crystals grown in the uninsulated solubility set-up, shown at (a) 50 × and (b) 1000 × magnification, which is a hundred-fold increase in size compared to ultrafine starting material.

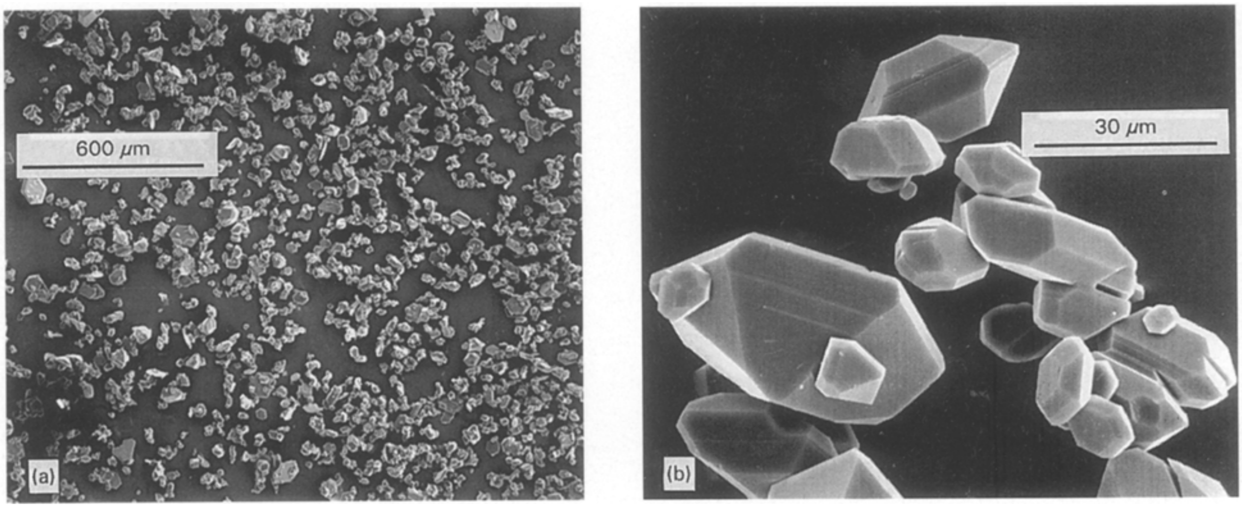


Figure 9 TATB crystals grown from a maximum temperature of 135 °C over six days of cooling, (a) 20 × and (b) 50 × magnification, which is a thousand-fold increase in size compared to ultrafine starting material.

scattering intensity of the crystal studied ($\sim 100\ \mu$m diameter) indicated that the crystal structure was relatively defect-free.

4. Summary

It has been shown that 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) crystals up to 2 mm diameter,

TABLE IV Unit cell dimensions TATB grown in DMSO

Cell dimensions[a]	Cell dimensions[b]
$a = 9.010$	$a = 9.019$
$b = 9.028$	$b = 9.037$
$c = 6.812$	$c = 6.812$
$\alpha = 108.59°$	$\alpha = 108.65°$
$\beta = 91.82°$	$\beta = 91.83°$
$\gamma = 119.97°$	$\gamma = 119.98°$

[a] Reference 13.
[b] This work (Reference 25).

larger than previously reported in the literature, can be grown from DMSO under temperature-controlled growing conditions. To define the high temperature saturation concentrations for this recrystallization study, the solubility of TATB in DMSO as a function of temperature was also determined. The solubility was found to range from $0.47 \pm 0.23\,\mathrm{g\,l^{-1}}$ at 21.2 °C to $6.80 \pm 1.13\,\mathrm{g\,l^{-1}}$ at 145.5 °C. It was necessary to promote particle growth before making the solubility measurements to prevent sampling a suspension of fine particles. The effects of varying the linear heating and cooling rates and agitation speed, and the role of additives in affecting crystal morphology, size, and colour were studied. Rapid cooling not surprisingly produced poorer quality crystals than did slow cooling, with defects and irregular shapes observed in scanning electron micrographs. Cooling the solution from a lower temperature resulted in better formed crystals, attributed to the flatness of the solubility curve at lower temperatures. Pitfalls encountered in growing the crystals revolved around thermal decomposition of both pristine TATB and u.v.-irradiated "green" TATB. It was concluded that the presence or formation of radicals is important in accelerating thermal decomposition of TATB dissolved in DMSO. The preventive addition of the radical scavenger BHT and removal of metallic surfaces in contact with the hot solution were measures that proved useful in retarding thermal decomposition. The optimum concentration of BHT was not determined, nor was an effective way found to prevent decomposition of "green" TATB. The additive BHT did prove to be a morphology modifier, allowing TATB to crystallize as pyramids instead of as needles favoured in the absence of stirring. Continued optimization of crystal growth by changing the rate of cooling and type of agitation in a scale-up of crystallized TATB is reported in a second paper [19].

Acknowledgements

The authors wish to gratefully acknowledge James M. Yoshiyama (Lawrence Livermore National Laboratory) for the scanning electron micrographs, Dr Richard Gilardi (Naval Research Laboratory) for X-ray analysis of TATB crystals, and Frank Garcia for the DSC analysis. This work was performed under the auspices of the US Dept. of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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Received 12 October 1994
and accepted 8 September 1995