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Technical report

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Characterisation of Crystallised FOX-7

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Report title

Characterisation of crystallised FOX-7

Abstract (not more than 200 words)

FOX-7, 1,1-Diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$) is a recently developed energetic material with low sensitivity and high performance. FOX-7 was developed by FOI, Swedish Defence Research Agency, it is produced by the Swedish company EURENCO Bofors and can be obtained from there. This report concentrates on characterisation of crystallised FOX-7 and presents data on thermal stability, processes involved during phase transitions and crystal structure. FOX-7 was crystallised from various solvents and the products were characterised. A gold coloured non-transparent product is formed during heating of crystallised FOX-7 at ~220°C. Elemental analysis of the product points towards FOX-7 molecules present in the product. X-ray studies indicate the structure of this material to be amorphous. A long term storage stability study was started. Samples were after 11 months of storage at room temperature, 60°C and 80°C. The result shows that FOX-7 is thermally very stable.

Keywords

FOX-7, thermal stability, thermal analysis, crystallisation, structure, XRD, DSC, TGA

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Karaktärisering av kristalliserad FOX-7

Sammanfattning (högst 200 ord)

FOX-7, 1,1-Diamino-2,2-dinitroetylen ($C_2H_4N_4O_4$) är ett nytt energetiskt material med låg känslighet och hög prestanda utvecklat vid FOI. Det produceras as Eurenco Bofors och kan köpas därifrån. Den här rapporten beskriver karaktärisering av kristalliserad FOX-7 och tyngpunkten har lagts vid de processer som sker vid fasövergångar. FOX-7 har kristalliserats från olika lösningsmedel och har sedan karaktäriseratas med avseende på fasövergångar, viktsförluster, elementarsammansättning samt kristallstruktur. Ett guldfärgat icke-transparent material bildas vid upphettning av kristalliserad FOX-7 till ca 220°C. Elementaranalys tyder på att produkten innehåller FOX-7 molkyler. Röntgenstudier pekar mot en amorf struktur hos produkten. En långtids-stabilitetsstudie har också påbörjats med kristalliserat material. Prover har analyserats med jämna mellanrum och de prov som förvarats längts togs ut från förvaring efter 11 månader. Proven har förvarats vid rumstemperatur, vid 60°C och vid 80°C: Resultaten visar på en mycket god termisk stabilitet hos FOX-7.

Nyckelord

FOX-7, termisk stabilitet, termisk analys, kristallisation, struktur, röntgen diffraktion, DSC, TGA

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1 Sammanfattning

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2 Abstract

FOX-7, 1,1-Diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$) is a recently developed energetic material with low sensitivity and high performance. FOX-7 was developed by FOI, Swedish Defence Research Agency[1], it is produced by the Swedish company EURENCO Bofors and can be obtained from there. This report concentrates on characterisation of crystallised FOX-7 and presents data on thermal stability, processes involved during phase transitions and crystal structure. FOX-7 was crystallised from various solvents and the products were characterised. A gold coloured non-transparent product is formed during heating of crystallised FOX-7 at ~220°C. Elemental analysis of the product points towards FOX-7 molecules present in the product. X-ray studies indicate the structure of this material to be amorphous. A long term storage stability study was started. Samples were after 11 months of storage at room temperature, 60°C and 80°C. The result shows that FOX-7 is thermally very stable.

3 Introduction

A great variety of explosives, propellants and pyrotechnics, i.e. energetic materials, are used for both civilian and military applications. The ongoing research in this area is mainly focused on development of materials that are more powerful, safer and more environmentally friendly. This directs the research towards energetic materials and compositions with lower sensitivity, which improves the ammunition safety. A problem with lower sensitivity energetic materials in munitions has been that insensitivity almost always has meant lower performance. Composition B has been used for over 50 years in a wide range of explosive applications. This well known explosive has very good performance, is readily processed using standard melt cast facilities and utilizes low cost materials. However, it suffers from several problems such as cure shrinkage, which results in cracks and voids, relatively poor impact sensitivity and somewhat violent reaction during cook-off[2]. With new energetic substances, energetic plasticizers and binders it might be possible to manufacture charges with low sensitivity and high performance.

FOX-7 (1,1-Diamino-2,2-dinitroethylene)Figure 1 was first synthesized in 1998 at FOI[1] and is an explosive that has rendered much interest. The interest in the substance lies in its applicability in several areas thanks to its low sensitivity combined with relatively high performance (slightly lower than that for RDX). For safety reasons it is of great importance to understand the processes that surrounds the thermal behaviour and processes affecting the long term storage stability of FOX-7.

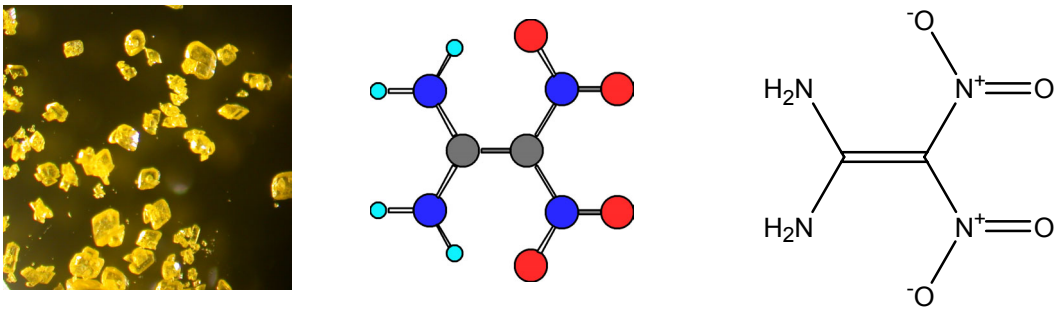

Figure 1 FOX-7.

This report concentrates on characterisation of crystallised FOX-7 and presents data on crystal structures, thermal stability and processes involved during phase transitions.

4 Experimental

4.1 Crystallisation of FOX-7

Crystallised FOX-7 material, lot number 2002-7033, was obtained from Eurenco Bofors (Sweden). The material was crystallised from wet raw FOX-7 material. A mixture of N-methylpyrrolidinone (NMP) and water 50/50 vol-% with the raw material was heated to approximately 95°C and then cooled down slowly to room temperature. The slurry was then filtered and the crystals washed with water.

FOX-7 was also crystallised at FOI from raw material in acetonitrile, γ-butyrolactone (GBL) and a mixture of 75/25 vol-% of dimethylformamide (DMF) and water. Sodiumsulfate (Na_2SO_3) was used to dehydrate GBL before it was used. A mixture of the solvent and FOX-7 raw material was heated. A double walled 200 ml flask was used with water as heating and cooling medium. The acetonitrile mixture was heated to approximately 70°C and the GBL and the DMF/water mixtures to approximately 95°C. The mixtures were brought to room temperature beginning with a cooling rate of ~0.2°C/min and ending with a cooling rate of ~0.02°C/min. The slurries were agitated at 150 rpm during the process. The slurry was filtrated and the crystals washed with a small volume of the same type of solvent as was used for the crystallisation. The filtrate from GBL was left for two months for crystal growth in an open beaker. The solvent was allowed to evaporate in room temperature with a small portion of the crystals obtained from the first crystallisation.

4.2 Thermal analysis

The thermal properties of FOX-7 were determined using a differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and heat flow calorimetry (HFC).

A Mettler DSC 30 was used for DSC analysis working under a nitrogen atmosphere (50 ml/min). The samples were sealed in 40µl aluminium pans with pierced lids. The sample weight was between 1 and 2 mg and calibration was made with indium (Tm = 156.6°C). The TG/DTA used by FOI is a Mettler TGA 850. All tests were performed in a nitrogen atmosphere. The samples were put into 70 µl alumina cups and the flow of nitrogen was approximately 50 ml/minute. The TG/DTA was calibrated by melting indium and aluminium standards. The dynamic DSC and TG analyses were performed between 30°C and 400°C with heating rates of 2, 5 and 10°C/min.

Single differential thermal analysis (SDTA) data has been calculated from the sample temperature and the reference temperature in the dynamically obtained TG data. SDTA was then calculated according to equation in Equation 1, where T_r is the reference temperature and T_s the measured sample temperature.

$$SDTA = T_s \text{ (measured)} - T_r \text{ (calculated)}$$

Equation 1. *Equation for SDTA calculation*

Cyclic DSC and TG analysis were performed between 30°C and 185°C at a rate of 5°C/min and back to 30°C at a rate of -5°C/min. The cycle was repeated four times in the DSC and three times in the TG. The cyclic repeated DSC analysis was also performed between 30°C to 135°C and back to 30°C at the rates of 5 and -5°C/min.

Thermogravimetric analysis has also been applied under isothermal conditions for 120 min at 175° to 230°C with a 5°C interval. A heating rate of 5°C min^{-1} was used from 30°C to the temperature set for isothermal measurements. The set temperature was then held for 120 min before a decrease of -30°C min^{-1} to 30°C was applied.

The HFC analyses of FOX-7 were performed isothermally at 75°C in a Thermal Activity Monitor, TAM 2277, microcalorimeter for 19 days. The accuracy of the microcalorimeter is better than ±0.5 J/g, during one week. The samples where put in 3 ml glass ampoules and then hermetically sealed. The sample weights were approximately 0.5 grams.

4.3 X-ray analysis

All single crystal data come from a STOE IPDS diffractometer on a rotating anode X-ray diffraction instrument[3]. A Guinier X-ray diffraction pattern of the preheated FOX-7, gold coloured non-transparent product, was taken with a HUBER G670 camera.

4.4 Particle shape analysis

The particle size, shape and surfaces have been analysed using a JEOL 6400 scanning electron microscope (SEM). The photos of Ox-7 crystals were taken using a Nikon SMZ-U-DIA STAND (Japan) optical microscope.

4.5 Moisture determination

The water determination was performed at Analyscentrum AB (Nacka, Sweden) according to the Analyscentrum Karl Fischer titration method 98 AM 005-02 with some minor modifications. The method is shortly described here.

2 ml sample vials with screw caps were dried at 120°C and allowed to cool in a desiccator. The vials were weighed and moved to a glove box with a controlled environment with constant humidity (30-40 ±2 %RH), where they were filled with a sample (approximately 40mg) and capped. They were weighed again and the exact sample amount calculated. The Karl Fisher titration equipment was kept inside a glove box. 100 ml of titration solution was added to the titration vessel and titrated until a low drift value was obtained. 1ml of the reagent was transferred to the sample vial via a syringe and needle, and the sample was dissolved. The dissolved sample solution was returned to the titration vessel via the syringe and the titration was performed. Sometimes, if the sample is difficult to dissolve, the dissolution procedure is repeated before titration.

A blank titration value, which was subtracted from the sample, was obtained by treating empty sample vials in exactly the same way. Table 1 shows the equipment and parameters used.

Table 1 Equipment and parameters used for Karl Fischer titration of crystallised FOX-7.

Titration apparatus:	Metrohm 737 KF, series 1
Titration vessel:	Vessel with stirrer 728. Cell without diaphragm
Reagent:	Riedel de Haën Hydranal Coulomat AG (34836) mixed with DMF (54:46)
Syringe:	1 ml Hamilton 81301 with a 0,80 x 100 mm needle
Drift correction:	Auto
Stop drift:	Auto
Delay time:	3 s
Extr.	10 s

4.6 Elemental and trace inorganic elemental analysis

Trace analysis of the crystallized FOX-7 was done by Analytica AB (Luleå, Sweden). 0.48 g of FOX-7 was dissolved in 17,6 ml HCl (PA grade). The anaysis was performed by ICP-AES and HP-ICP-MS. Elemental analysis was performed by H. Kolbe Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

4.7 Long term stability study

FOX-7 crystallised in NMP/water from Eurenco Bofors (2002-7033) was used for the long term storage stability study. The samples were stored in 2 ml vials closed with screw caps holding teflon septas. A steel needle was placed in the septa in each vial for pressure release. Approximately 0.5 g of FOX-7 were placed in each vial. A total of 42 vials were put in three desiccators, i.e. 14 vials in each desiccator. The desiccators were stored at room temperature, 60°C and 80°C. The sample weights were registered once a month. One sample per desiccator were taken from the storage every second month until eight months. After eight months samples one sample from each desicctor were taken out every third month. The samples were analysed using DSC and TGA between 30°C and 400°C at a heating rate of 10°C/min. The samples were also analysed using HFC (see chapter 4.2 in this report) besides weighing.

5 Results

5.1 Crystallisation of FOX-7 in various solvents

FOX-7 was crystallised in acetonitrile, GBL and a mixture of DMF/water from raw material, Figure 2, produced at FOI. Crystals crystallised in NMP/water, Figure 2, obtained from Eurenco Bofors were in a range of 250 µm to 400 µm. The crystallisation of FOX-7 in acetonitrile produced relatively small crystals, Figure 3. Crystals of < ~50 µm were obtained. The mixture of DMF and water produced crystals of approx. 55µm to 110 µm, shown in Figure 3. In GBL a broader range of crystal sizes were obtained, measuring approx. 50µm to 185 µm. After growing in the GBL filtrate crystals up to a size of ~500µm were obtained, Figure 4. Table 2 shows the crystal sizes obtained from the various solvents.

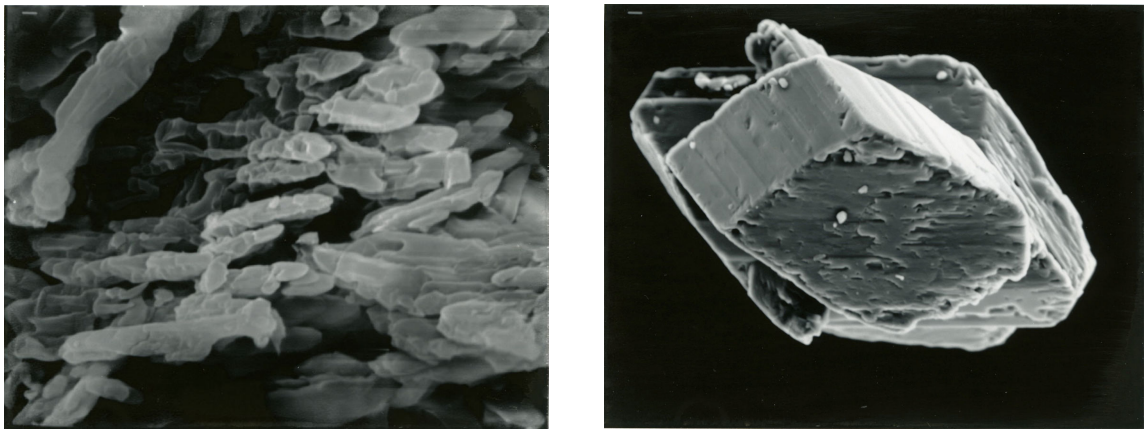

Figure 2 To the left SEM photo of FOX-7 raw material (FOI batch 991116:31) (x 2000 magnification) and to the right FOX-7 crystallised in NMP/water (x 400 magnification).

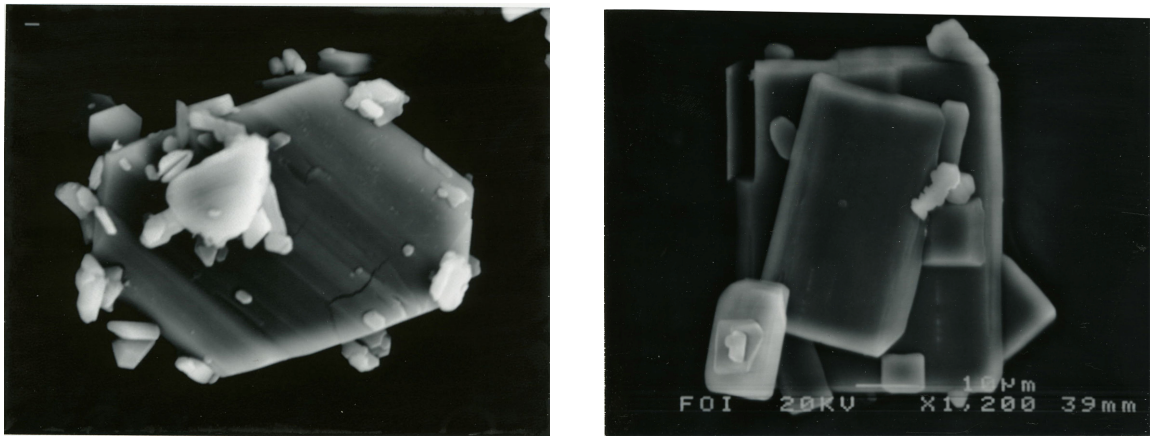

Figure 3 To the left SEM photo of FOX-7 crystallised in acetonitrile (x 1500 magnification) and to the right FOX-7 crystallised in DMF/water (x 1200 magnification).

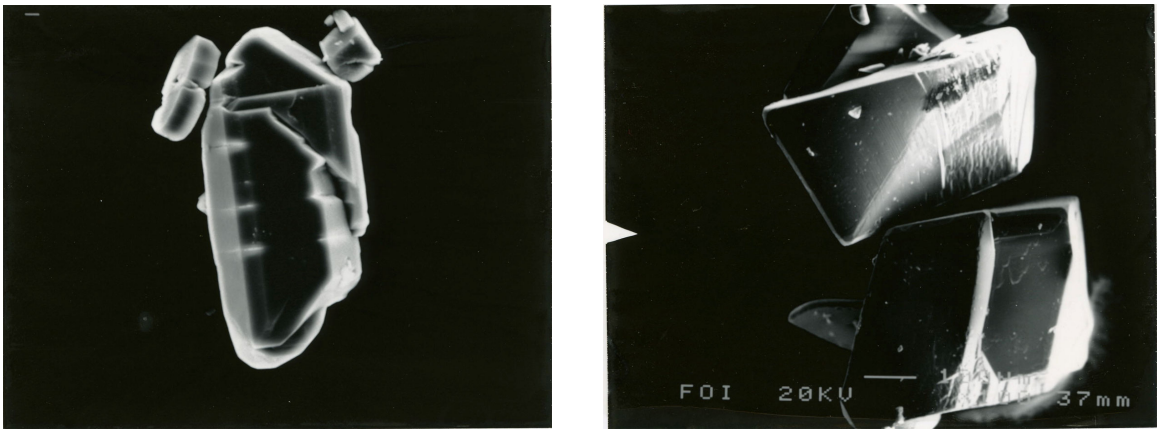

Figure 4 To the left SEM photo of FOX-7 crystallised in GBL (x 650 magnification) and to the right FOX-7 crystallised in GBL and grown in the GBL filtrate(x 100 magnification).

Table 2 Approximate crystal sizes of crystallised FOX-7.

FOX-7 crystallisation solvent	Approximate crystal size (µm)
NMP/water	250 - 400
GBL (large crystals)	<500
DMF/water	55 - 110
GBL (small crystals)	50 - 185
Acetonitrile	<50

A comparison of the shape and surface of the larger crystals were made. Rhombic shapes in two dimensions are observed with crystals obtained from acetonitrile, the smaller fraction of GBL and NMP/water. The larger fraction obtained from GBL has a rhombic shape built in three dimensions. The crystals from DMF/water have a flat rectangular shape. The surfaces of the larger crystals obtained from GBL and crystals obtained from DMF/water, Figure 5, appears to be smoother than the surfaces observed at the crystals obtained from NMP/water, Figure 6.

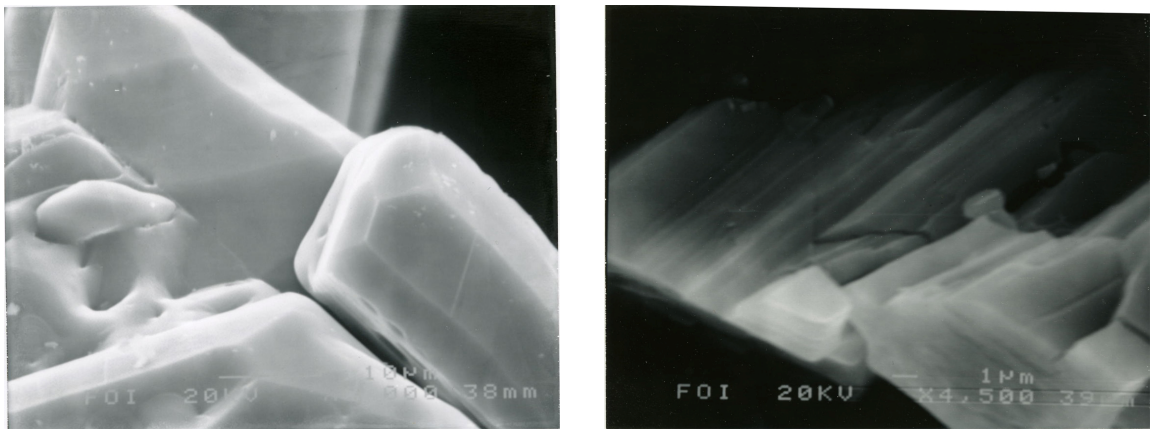

Figure 5 The left picture shows the surface of the larger fraction of FOX-7 crystals grown in the GBL filtrate (x 2000 magnification) and the right picture shows the surface of FOX-7 crystals crystallised in DMF/water (x 4500 magnification).

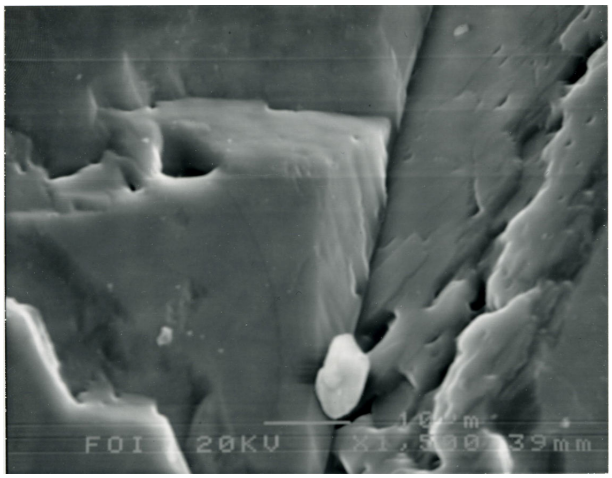

Figure 6 Surface of FOX-7 crystals crystallised in NMP/water (x 1500 magnification).

5.2 Thermal analysis of crystallised FOX-7

Thermogravimetric and differential scanning calorimetry analysis between 30 and 400°C at a heating rate of 10°C/min were done on FOX-7 raw and crystallised material. The DSC measurements between 30°C and 400°C of the raw FOX-7 material show one broad endothermal peak at ~110°C and two exothermal peaks at ~245°C and ~275°C respectively. The DSC thermogram obtained at a heating rate of 10°C/min from 30°C to 400°C is shown in Figure 7.

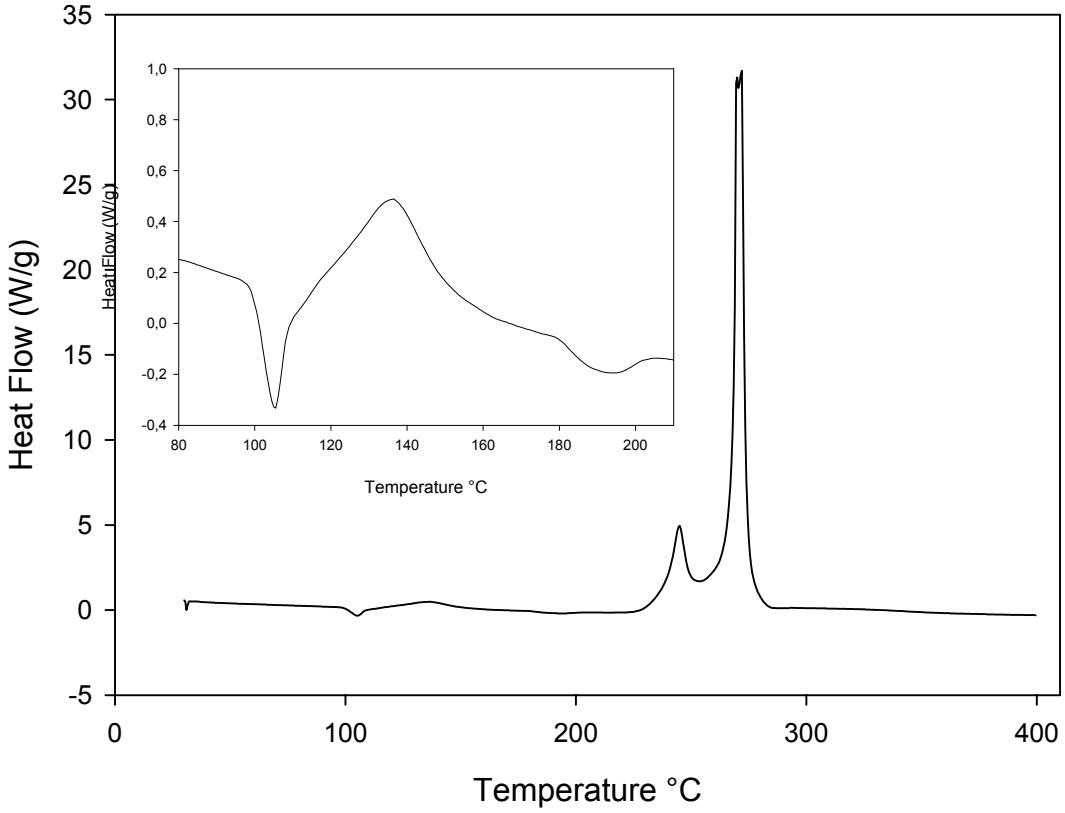

Figure 7 DSC of FOX-7 raw material (FOI batch 991116:31) between 30°C and 400°C at a heating rate of 10°C/min.

The corresponding TG analysis of FOX-7 raw material shows a continuous weight loss starting at ~100°C. A slow weight loss of ~15 wt-% between ~100°C and 230°C proceeds to a rapid weight loss between ~230°C and ~270°C. Overall the sample has lost more than 80 wt-% reaching ~270°C and continue to slowly loose weight during the rest of the analysis, see Figure 8.

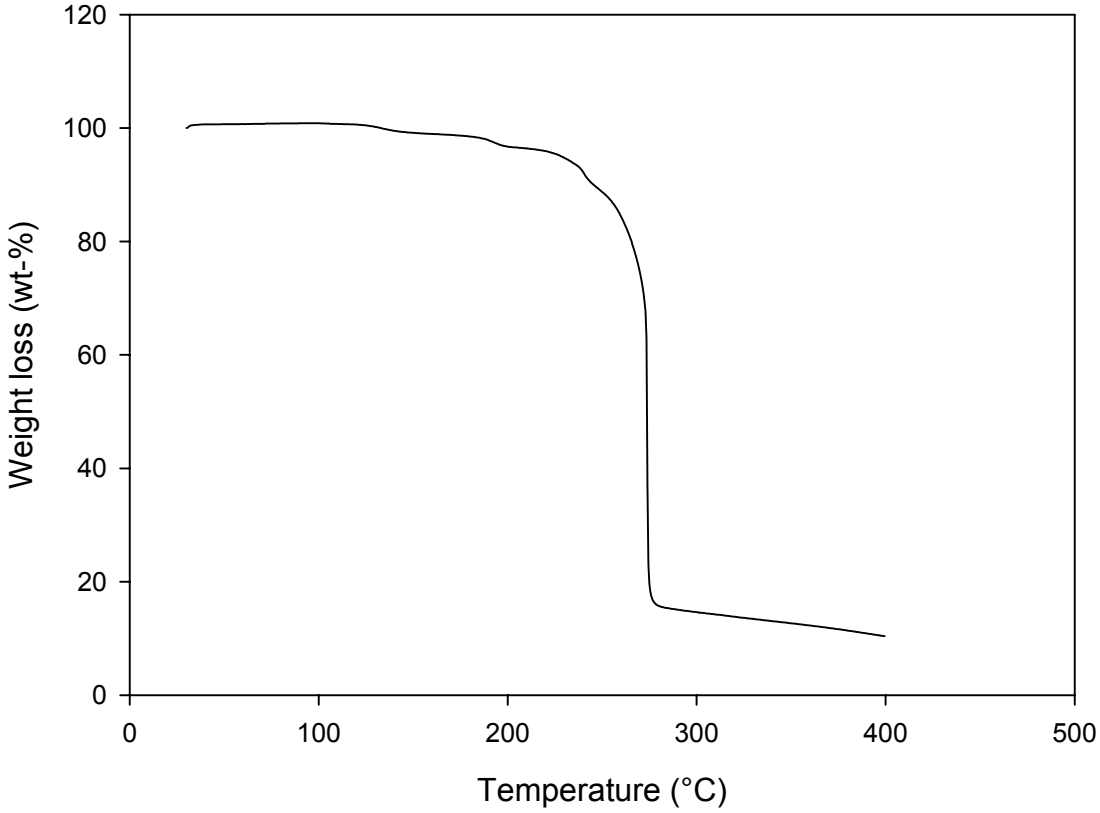

Figure 8 TG analysis of FOX-7 raw material (FOI batch 991116:31) between 30°C and 400°C at a heating rate of 10°C/min.

The DSC measurements between 30°C and 400°C of crystallised FOX-7 show one or two endothermal and two exothermal peaks. In the analysis of FOX-7 crystallised in NMP/water (Figure 9), DMF/water (Figure 14) and the GBL filtrate (Figure 12) the second endothermal peak at approximately 160°C is split. The DSC analysis of FOX-7 crystallised in NMP/water (2002-7033) obtained at a heating rate of 10°C/min from 30°C to 400°C is shown in Figure 9. The endothermal peak temperatures are 117°C and ~160°C, and the exothermal peak temperatures are 227°C and ~286°C respectively. The results of the DSC analyses at heating rates of 2 and 5°C min^{-1} follow the same pattern as for 10°C min^{-1} although the peaks show less intensity.

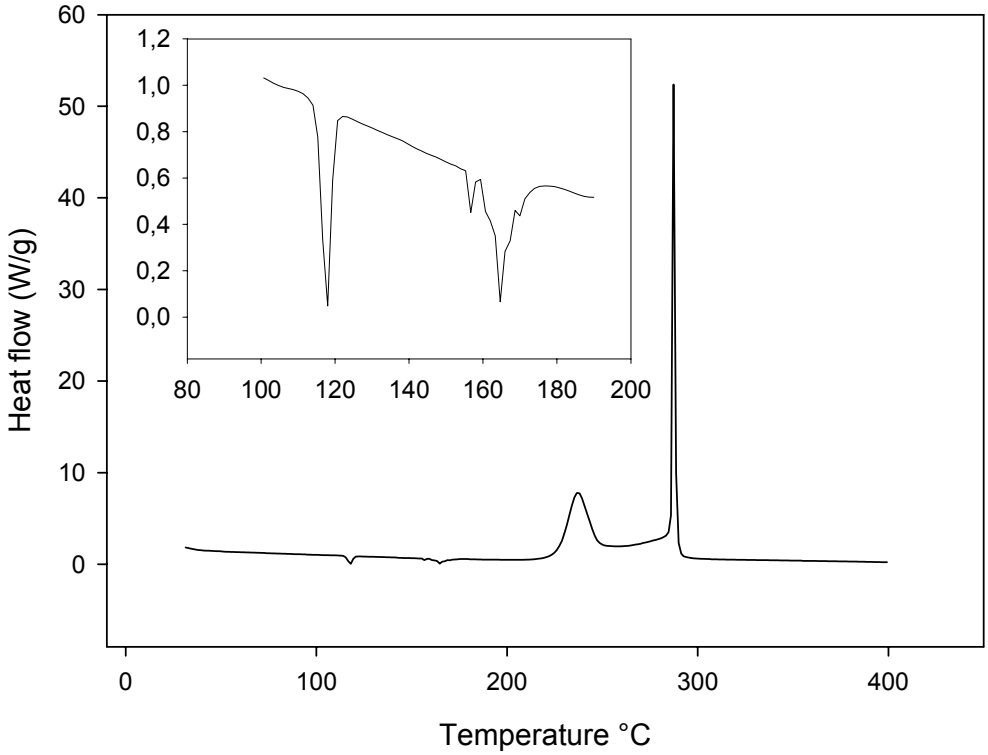

Figure 9 FOX-7 crystallised in NMP/water (2002-7033). DSC analysis between 30°C and 400°C at a heating rate of 10°C /min.

Thermogravimetric analysis of FOX-7 crystallised in NMP/water (Eurenco Bofors 2002-7033) reveals a three stage weight loss process, Figure 10. The weight loss occurs in a three stage process. The first stage starts from ~155°C to ~165°C with a ~3 to 5 % weight loss. The second and third stage begins at ~220°C and ends at ~290°C with a total weight loss of approximately 88%. A shoulder is observed at ~240°C after a weight loss of ~30%, forming the beginning of the third stage. Thus, the calculated weight loss due to the overall reaction is 94%. Thermogravimetric analysis obtained at heating rates of 2 and 5°C/min follow the same pattern. The SDTA curve calculated from thermogravimetric data reveals small endothermal peaks at ~115°C and ~155°C and exothermal peaks at ~235°C and ~290°C, see Figure 11. The calculated SDTA curve is in correspondence with the obtained DSC thermogram. The SDTA data shows two exothermal peaks that are in good agreement with the second and third stage shoulder observed within the thermogravimetric analysis.

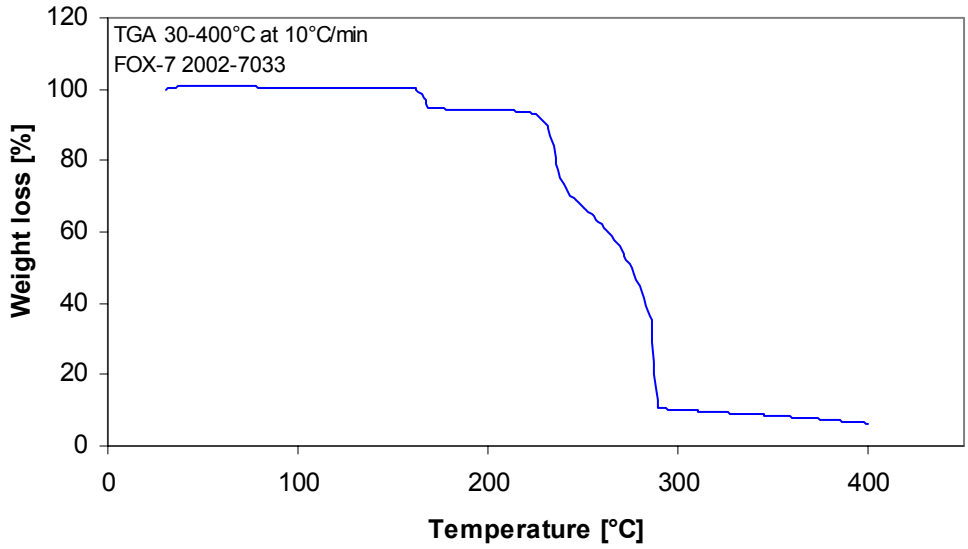

Figure 10 FOX-7 crystallised in NMP/water (2002-7033). Thermogravimetric analysis between 30°C and 400°C at a heating rate of 10°C/min.

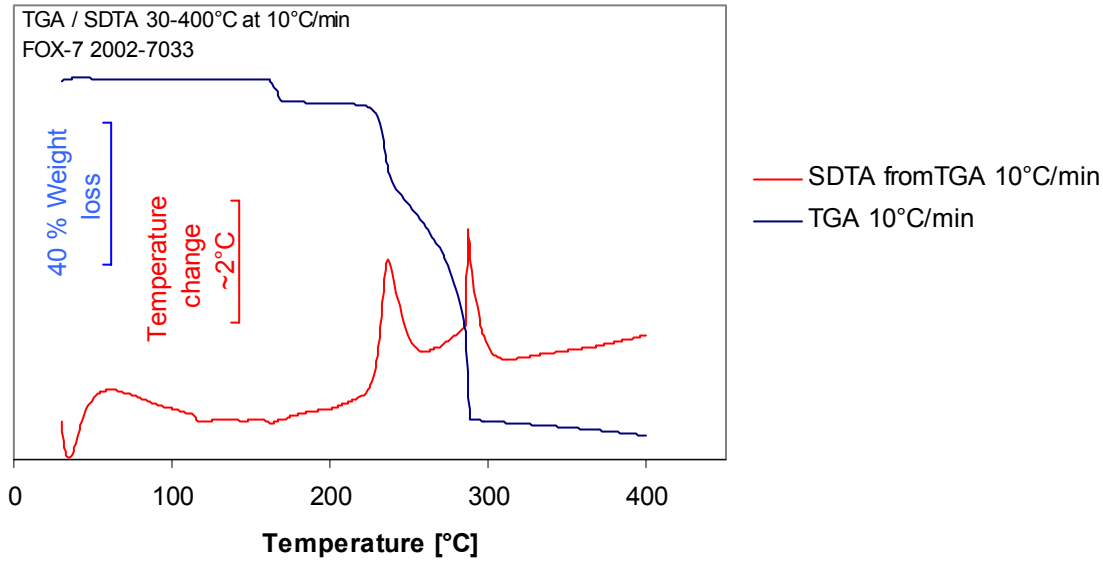

Figure 11 SDTA curve calculated from TG data of FOX-7 (2002-7033) with the heating rate of 10°C /min.

The DSC analysis between 30°C and 400°C of FOX-7 crystallised in GBL is shown in Figure 12. The first endothermal peak at ~114°C and the two exothermal peaks at ~224°C and ~278°C respectively is detected at lower peak temperatures than the corresponding peaks (at

~117°C, ~230°C and ~280°C) detected in DCS analysis of the larger GBL crystals. The second endothermal peak appears as a broad peak at ~172°C during analysis of the small GBL crystals. The corresponding second endothermal peak at ~159°C in the larger crystals grown in the GBL filtrate is a split. The TG analysis of the large GBL crystals shows a weight loss at the same temperature as the second endothermal peak during DSC analysis whereas the small GBL crystals do not (Figure 13). The major weight loss of the small GBL crystals is seen as two steps. The first starts at ~220°C and approximately 40 wt-% is instantaneously lost. A slower weight loss is then detected up to approximately 285°C.A total weight loss of the overall reaction for the small GBL crystals is ~90 wt-%.The major weight loss of the large crystals from GBL starts at ~240°C and ~80 wt-% is lost during one instantaneous step. The large crystals then continue to slowly loose weight and the total weight loss of the overall reaction is ~90wt-%.

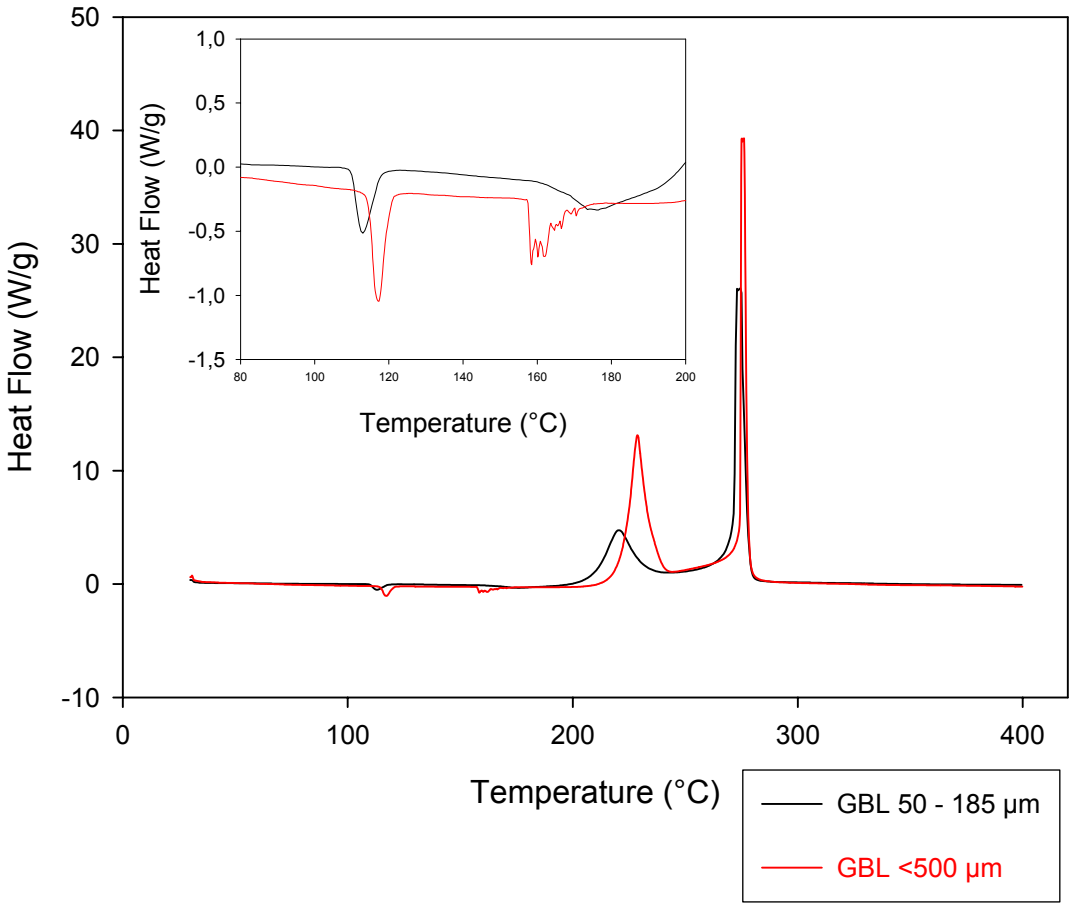

Figure 12 FOX-7 crystallised in GBL (black) and grown in the GBL filtrate (red). DSC analysis between 30°C and 400°C at a heating rate of 10°C /min.

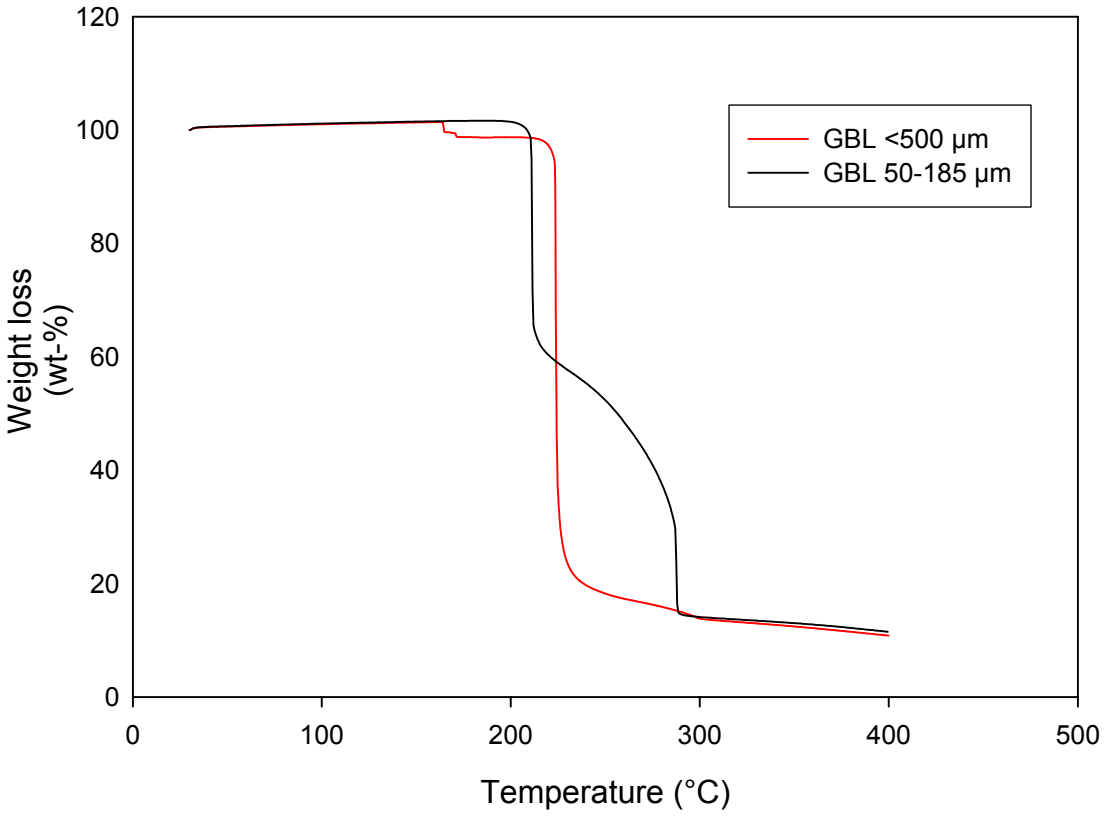

Figure 13 FOX-7 crystallised in GBL (black) and grown in the GBL filtrate (red). Thermogravimetric analysis between 30°C and 400°C at a heating rate of 10°C /min.

DSC analysis of crystals from the DMF/water mix (Figure 14) show endothermal peak temperatures of ~116°C and ~162°C , and the exothermal peak temperatures are ~234°C and ~281°C respectively. The DMF/water crystals also show a split second endothermal peak. The major weight loss of the DMF/water crystals is seen in one step (Figure 15). Approximately 80 wt-% is instantaneously lost at ~230°C. A total weight loss of the overall reaction for the DMF/water crystals is ~85 wt-%. The DSC analysis of crystals from acetonitrile show a first endothermal peak at ~119°C and two exothermal peaks at ~229°C and ~278°C (Figure 16). A small heat flow decrease is detected before the onset of the first exothermal peak. The major weight loss in the TG analysis is seen as two steps (Figure 17). Approximately 70 wt-% is instantaneously lost at ~220°C. A slower weight loss is then detected up to approximately 295°C.A total weight loss of the overall reaction for the acetonitrile crystals is ~90 wt-%.

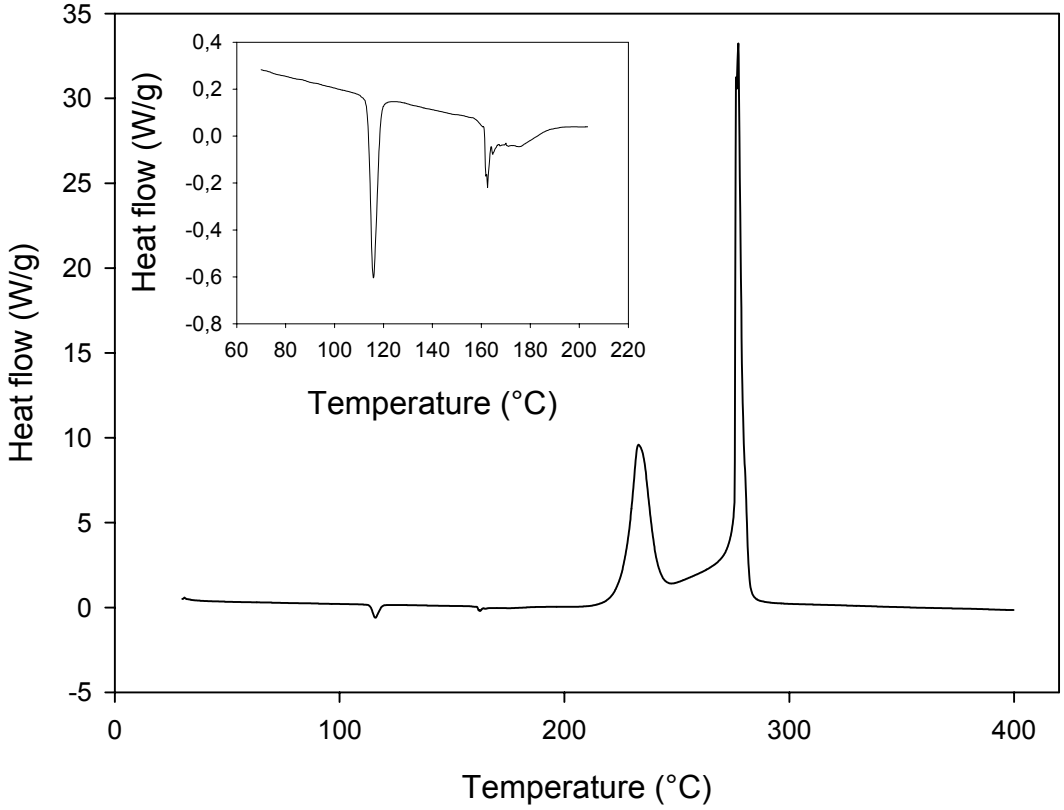

Figure 14 FOX-7 crystallised in DMF/water. DSC analysis between 30°C and 400°C at a heating rate of 10°C /min.

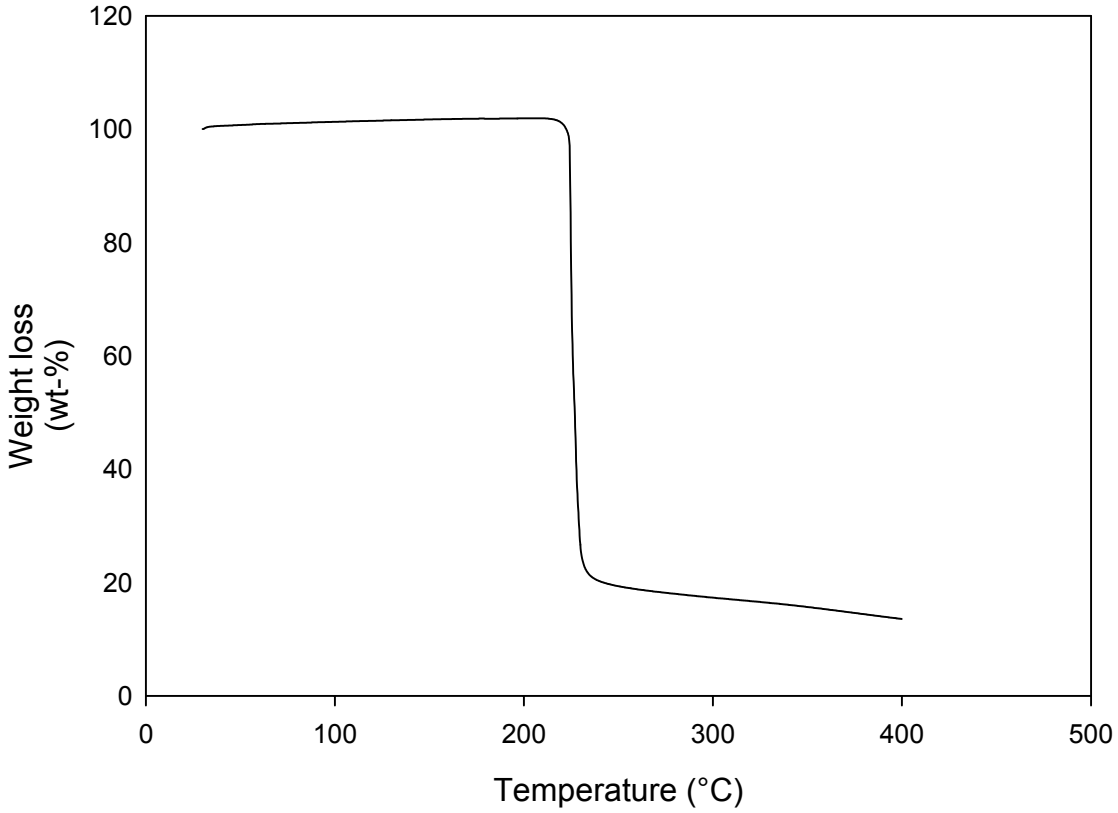

Figure 15 FOX-7 crystallised in DMF/water. Thermogravimetric analysis between 30°C and 400°C at a heating rate of 10°C /min.

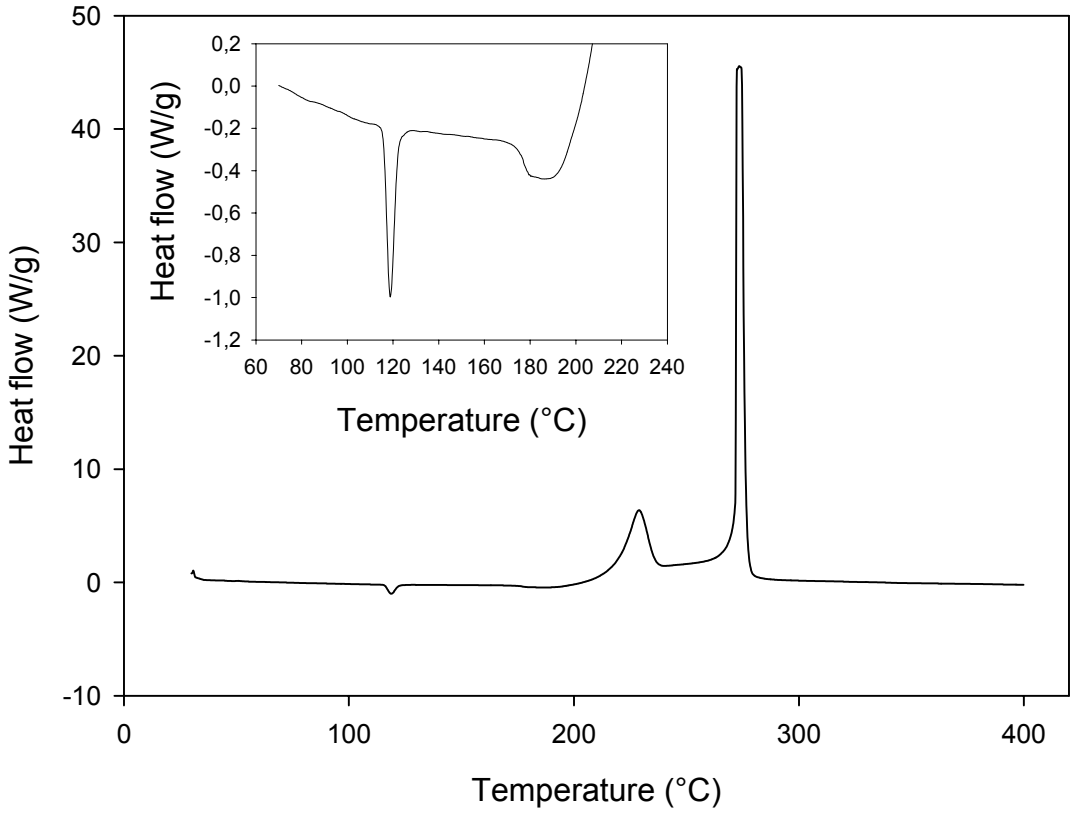

Figure 16 FOX-7 crystallised in acetonitrile. DSC analysis between 30°C and 400°C at a heating rate of 10°C /min.

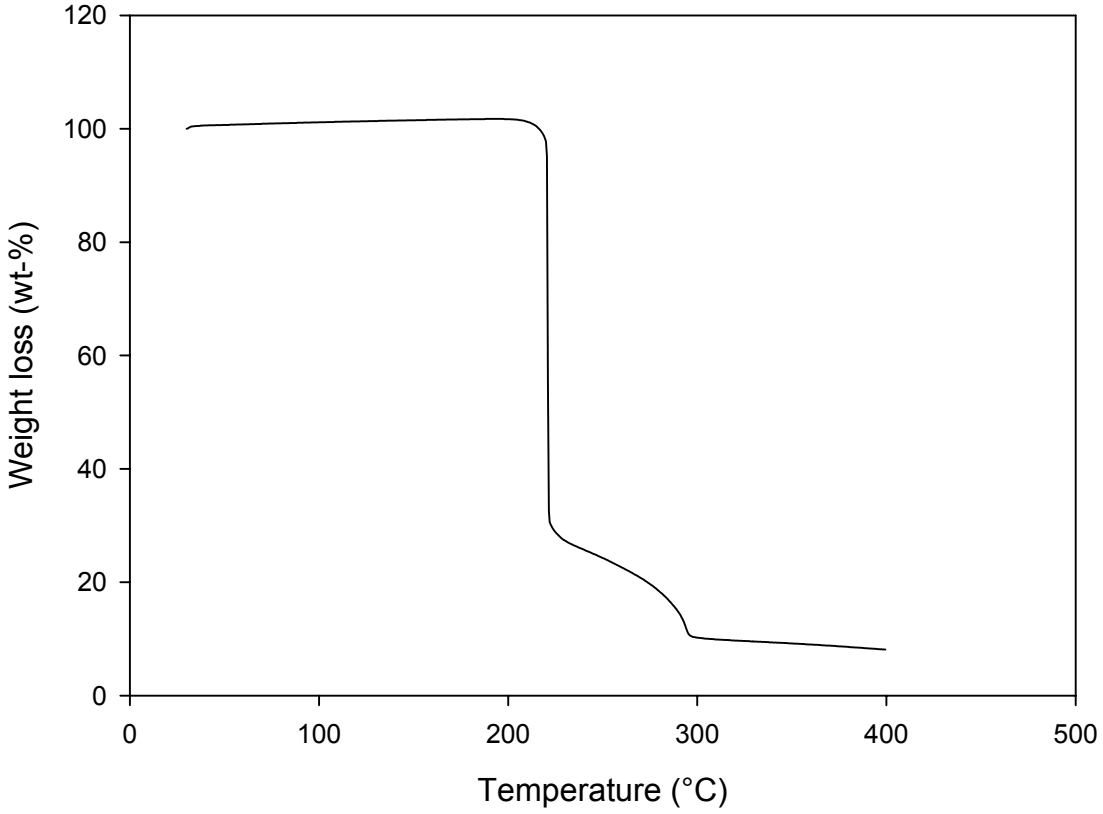

Figure 17 FOX-7 crystallised in acetonitrile. Thermogravimetric analysis between 30°C and 400°C at a heating rate of 10°C /min.

5.2.1 Cyclic repeated DSC and TG analysis

Cyclic repeated DSC analysis between 30°C and 135°C show one endothermal peak during heating and one exothermal peak during cooling (Figure 18). The peaks appear repeatedly in each heating and cooling cycle with unchanged peak areas. The endothermal peak in the first heating cycle appears at a higher temperature than in the following cycles. The exothermal peak in the first cooling cycle is registered at a lower temperature compared to the following cycles.

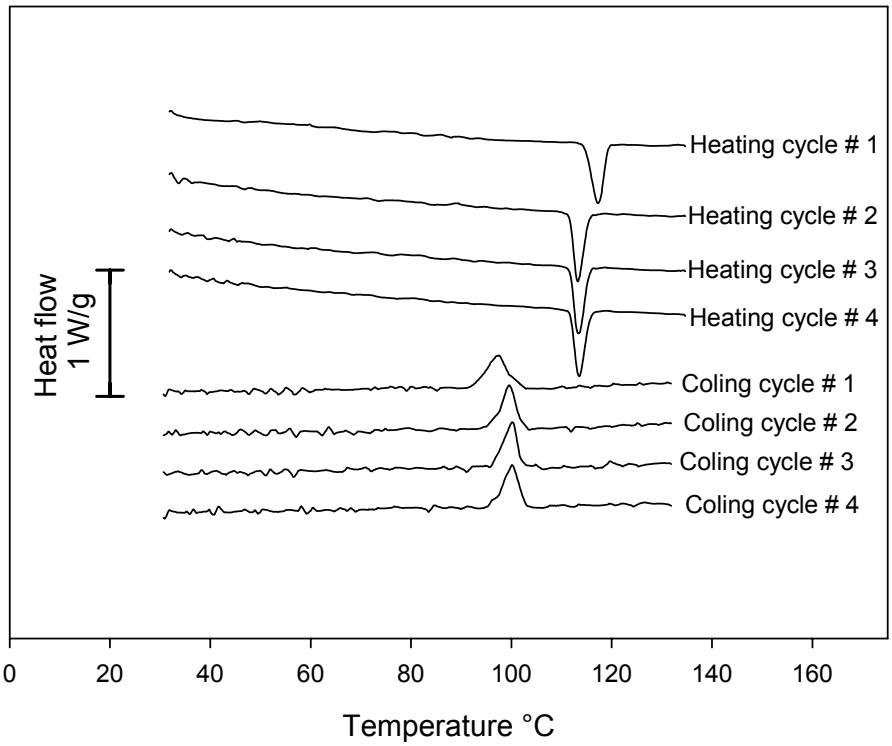

Figure 18 DSC thermogram of cyclic repeated analysis of FOX-7 crystallised in NMP/water. The analysis was performed between 30°C and 135°C and back to 30°C at a rate of 5°C/min.

Cyclic repeated DSC analysis between 30°C and above the second endothermal peak of crystals from NMP/water (Figure 19), the larger fraction from GBL (crystals grown in the GBL filtrate)(Figure 20) and DMF/water (Figure 21) show two endothermal peaks during heating. The endothermal peaks appear repeatedly in each cycle at approximately the same temperature. However, there are decreased peak areas for each cycle. The shape of the second endothermal peak shifts from a divided peak in the first cycle to a single peak in the following cycles. During temperature decrease one exothermal peak is detected in NMP/water and in the larger fraction from GBL (crystals grown in the GBL filtrate).

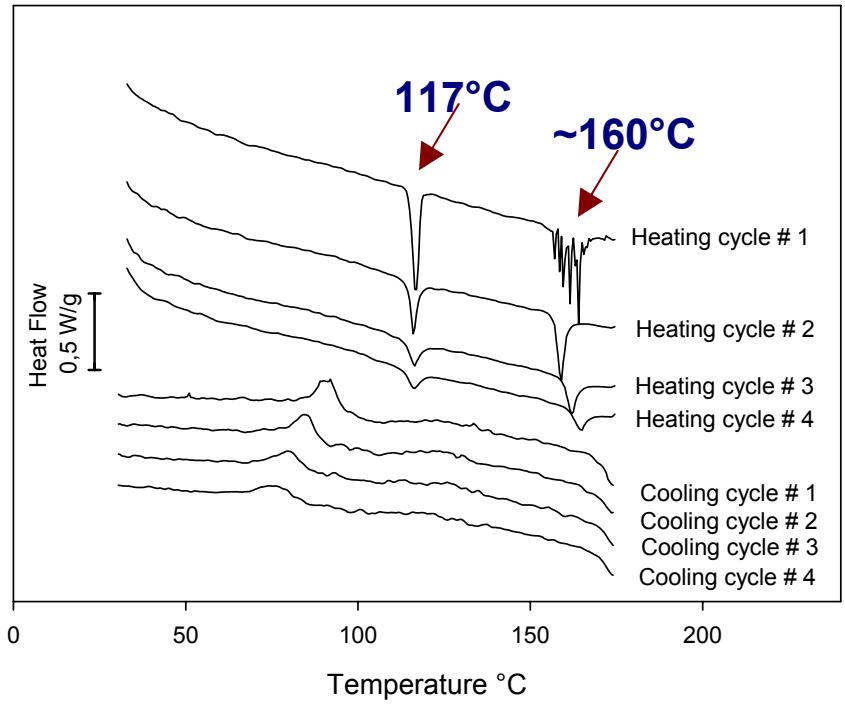

Figure 19 DSC thermogram of cyclic repeated analysis of FOX-7 crystallised in NMP/water. The analysis was performed between 30°C and 175°C and back to 30°C at a rate of 5°C/min.

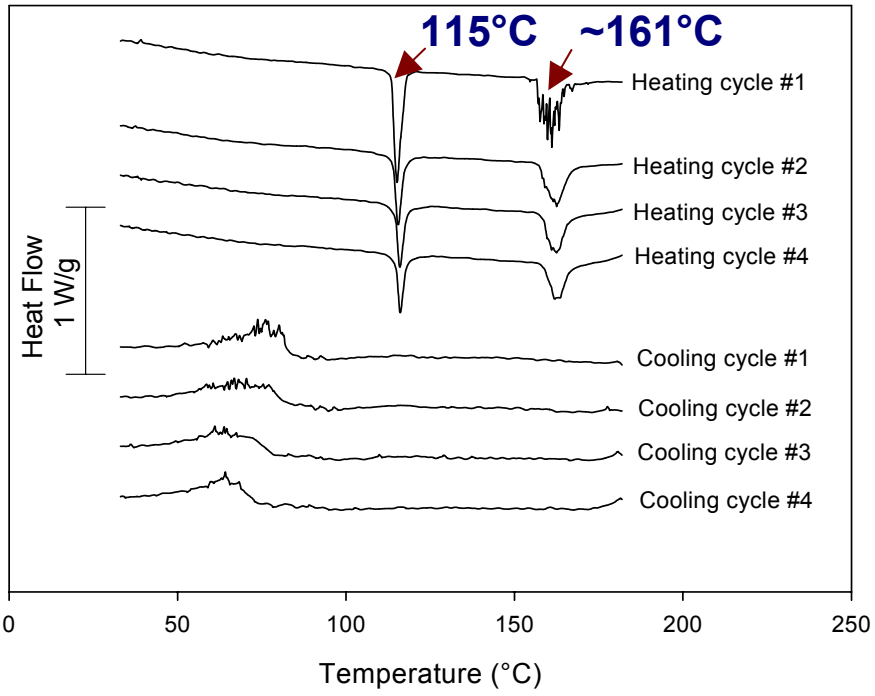

Figure 20 DSC thermogram of cyclic repeated analysis of the larger FOX-7 fraction from crystallisation in GBL (crystals grown in the GBL filtrate). The analysis was performed between 30°C and 185°C and back to 30°C at a rate of 5°C/min.

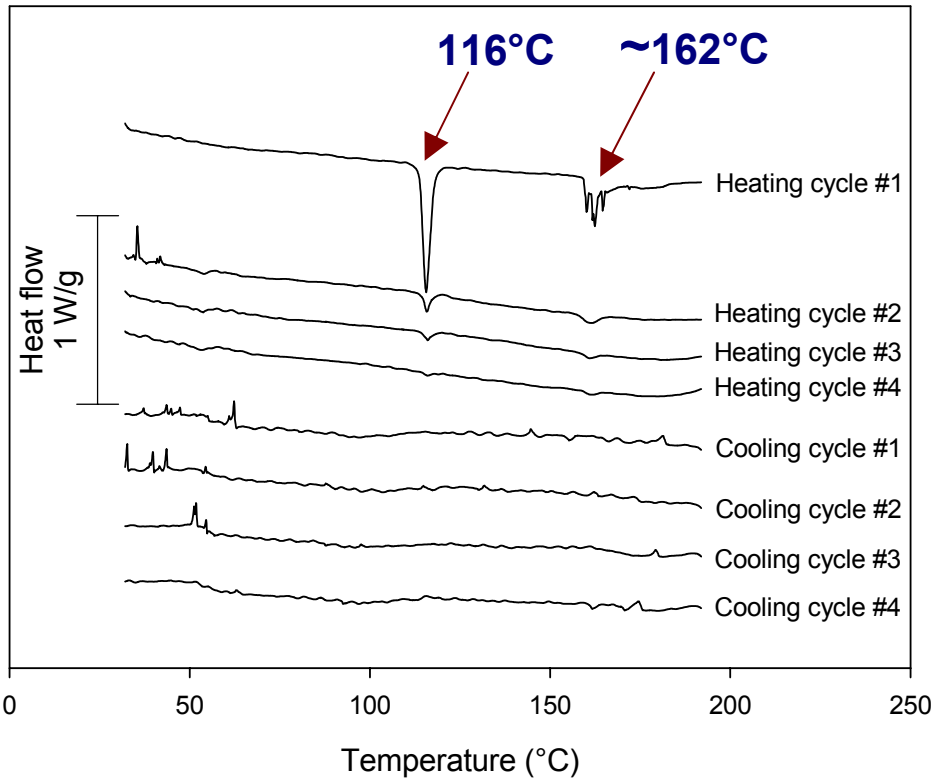

Figure 21 DSC thermogram of cyclic repeated analysis of FOX-7 crystallised in DMF/water. The analysis was performed between 30°C and 195°C and back to 30°C at a rate of 5°C/min.

Compared to NMP/water and the larger GBL fraction the crystals from DMF/water show smaller peak areas and the last heating cycle does not show any peaks at all. The cyclic repeated DSC analysis of the smaller crystals recrystallised from GBL also show endothermal peaks at ~111°C and ~175°C (Figure 22). However, the second endothermal peak at ~175°C is not divided but has a broad shape. Both peaks are repeatedly obtained with a decreased area in each new heating cycle. The repeated analysis of the crystals obtained from acetonitrile produces one endothermal peak in each heating cycle at ~118°C (Figure 23). A hint of an endothermal peak at ~170°C is also obtained during the first heating cycle but not in the following.

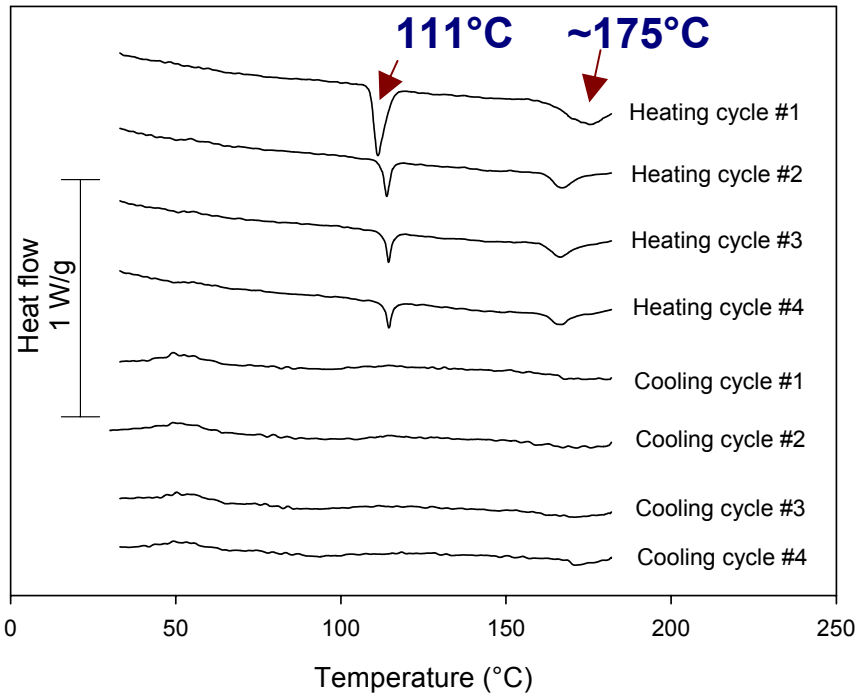

Figure 22 DSC thermogram of cyclic repeated analysis of the smaller FOX-7 fraction from crystallisation in GBL. The analysis was performed between 30°C and 185°C and back to 30°C at a rate of 5°C/min.

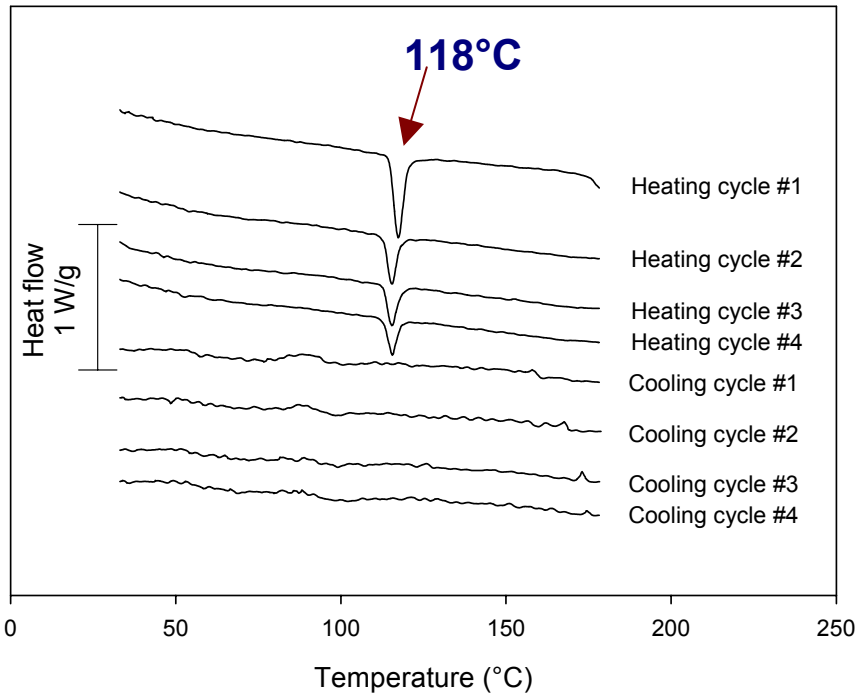

Figure 23 DSC thermogram of cyclic repeated analysis of FOX-7 crystallised in acetonitrile. The analysis was performed between 30°C and 185°C and back to 30°C at a rate of 5°C/min.

The repeated thermogravimetric analyses of crystals from NMP/water (Figure 24) and the larger fraction from GBL(Figure 25) show weight losses in the first heating cycle. The weight loss is registered at the corresponding temperature of the second endothermal peak in the DSC analysis. The NMP/water crystals have a weight loss of approximately 2 weight-% and approximately 1 weight-% is lost from the larger crystals obtained from GBL. A small weight loss of 0.1 weight-% is also obtained with the crystals from DMF/water (Figure 26). The cyclic repeated TG analysis obtained from the small crystals of GBL (Figure 27) and from acetonitrile (Figure 28) does not show any significant weight loss at the corresponding temperature of the second endothermal peak obtained in the DSC analysis. Table 3 shows a summary of DSC and TG data obtained during cyclic repeated analysis between 30°C and above the second endothermal peak detected in DSC analysis.

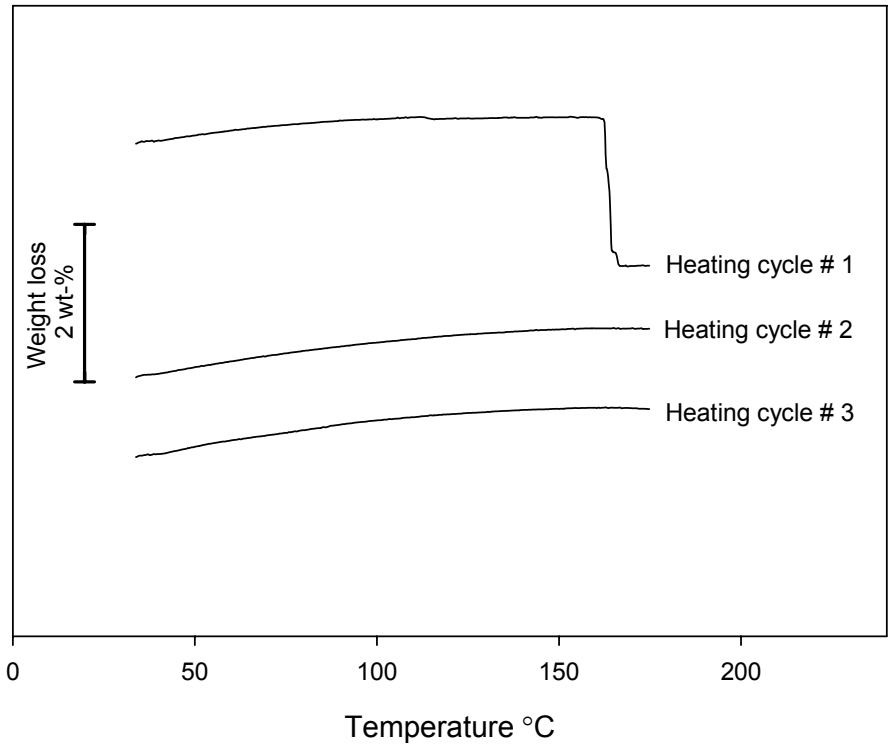

Figure 24 Thermogravimetric cyclic repeated analysis of FOX-7 crystallised in NMP/water. The analysis was performed between 30°C and 175°C at a heating rate of 5°C/min.

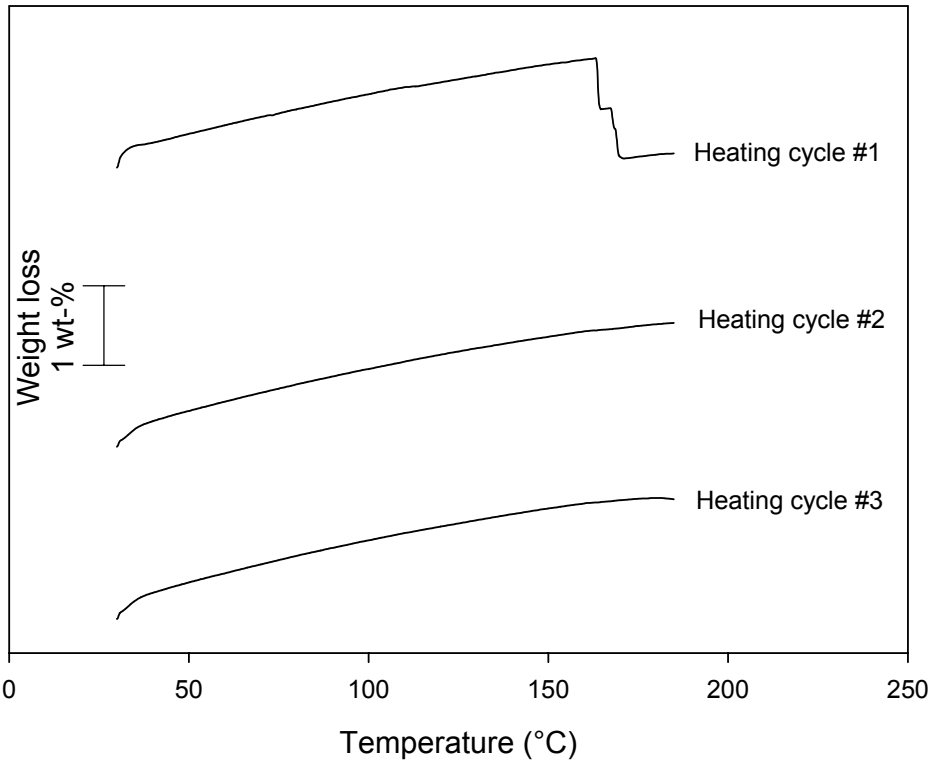

Figure 25 Thermogravimetric cyclic repeated analysis of the larger FOX-7 fraction crystallised in GBL. The analysis was performed between 30°C and 185°C at a heating rate of 5°C/min.

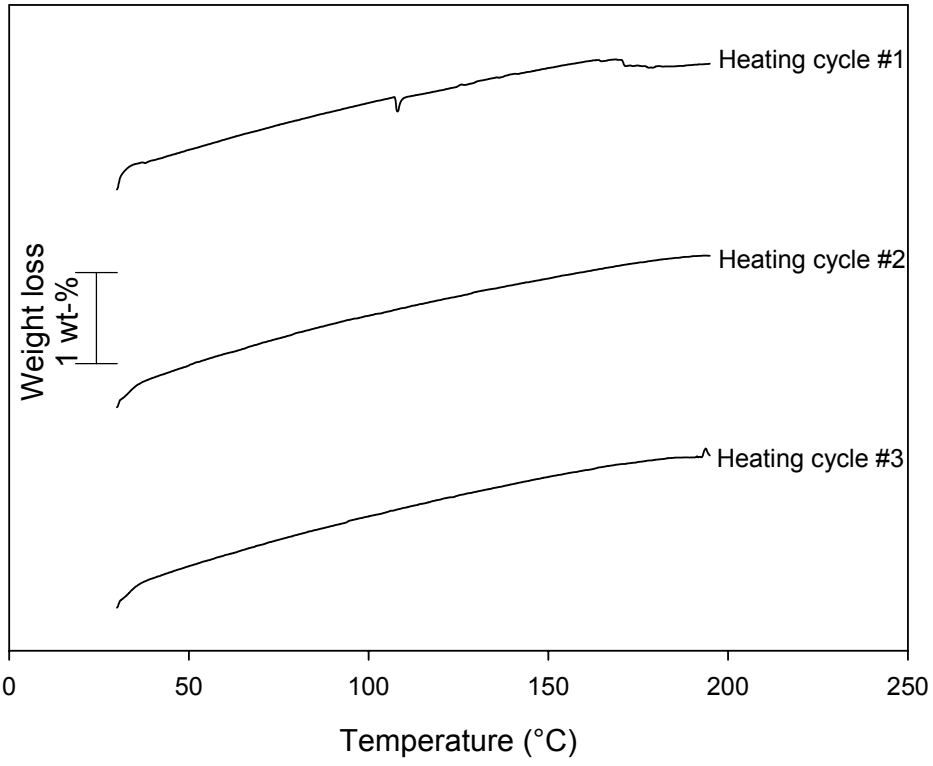

Figure 26 Thermogravimetric cyclic repeated analysis of FOX-7 crystallised in DMF/water. The analysis was performed between 30°C and 195°C at a heating rate of 5°C/min.

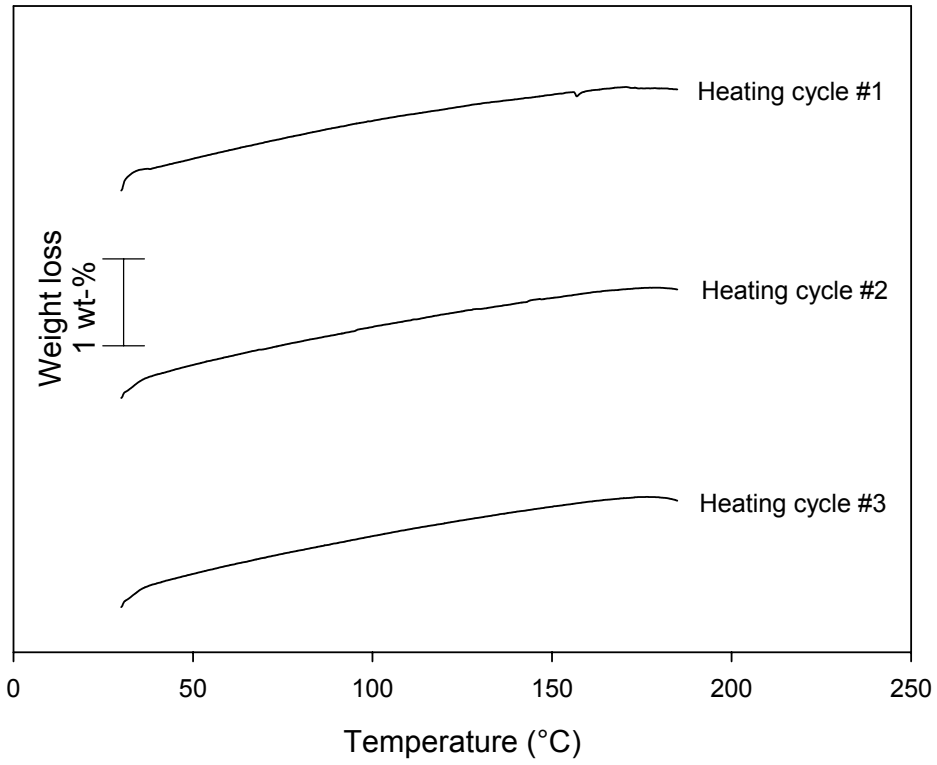

Figure 27 Thermogravimetric cyclic repeated analysis of the smaller FOX-7 fraction crystallised in GBL. The analysis was performed between 30°C and 185°C at a heating rate of 5°C/min.

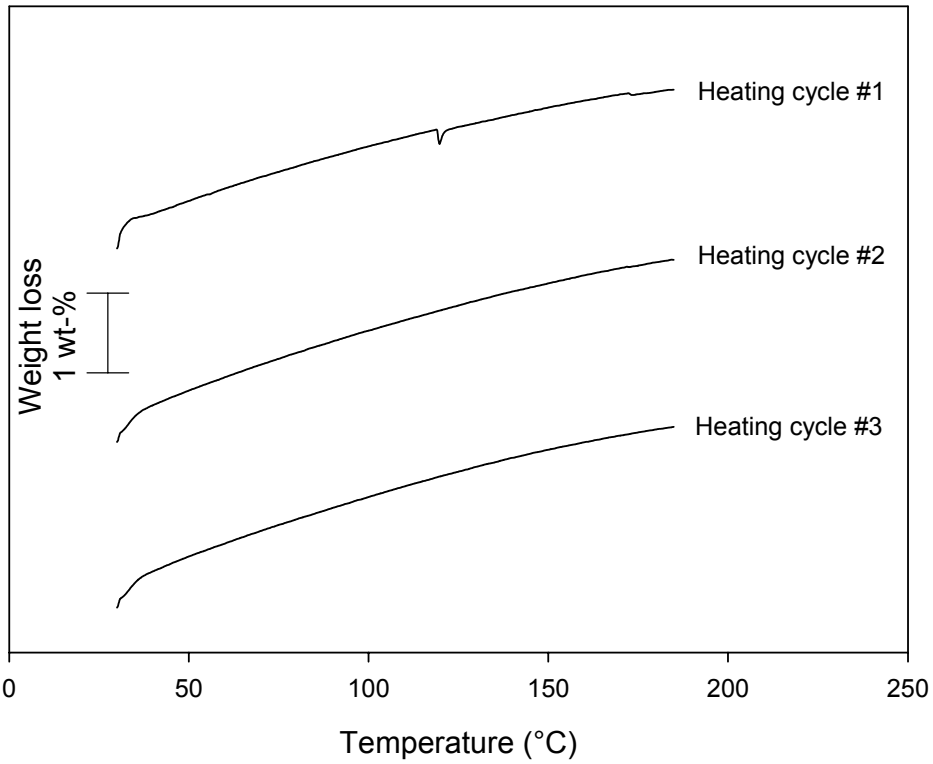

Figure 28 Thermogravimetric cyclic repeated analysis of FOX-7 crystallised in acetonitrile. The analysis was performed between 30°C and 185°C at a heating rate of 5°C/min.

Table 3 Weight loss of crystallised FOX-7 during the first cycle of repeated thermogravimetric analysis and the corresponding second endothermal peak temperature in the DSC analysis.

FOX-7 crystallisation Solvent	TG analysis		Corresponding endothermal peak temperature in DSC analysis (°C)
	Weight loss during 1st heating cycle	Weight loss temperature (°C)	
NMP/water	2 wt-%	~160	~160
GBL (large crystals)	1 wt-%	~162	~161
DMF/water	0,1 wt-%	~167	~162
GBL (small crystals)	-	-	~175
Acetonitrile	-	-	-

5.2.2 Isothermal thermogravimetric analysis

Isothermal thermogravimetric analyses of FOX-7 crystallised in NMP/water (2002-7033) were made during 120 minutes after heating from 30°C at a rate of 5°C/min. The isothermal analyses were made at temperatures between the second endothermal and second exothermal peak detected in DSC analyses. Figure 29 and Figure 30 shows the weight loss detected at the various temperatures.

Initially an increased weight loss rate is observed with increased temperature. The total weight loss obtained after 120 minutes also increases with increased temperature. The analyses at temperatures below 200°C initially adopt to lower weight loss rates and then the rate increases. While the analyses above 200°C starts off with high weight loss rates and then adopt to lower rates. The weight loss at 230°C is almost instantaneously 75 wt-% of the initial weight followed by a very slow decrease.

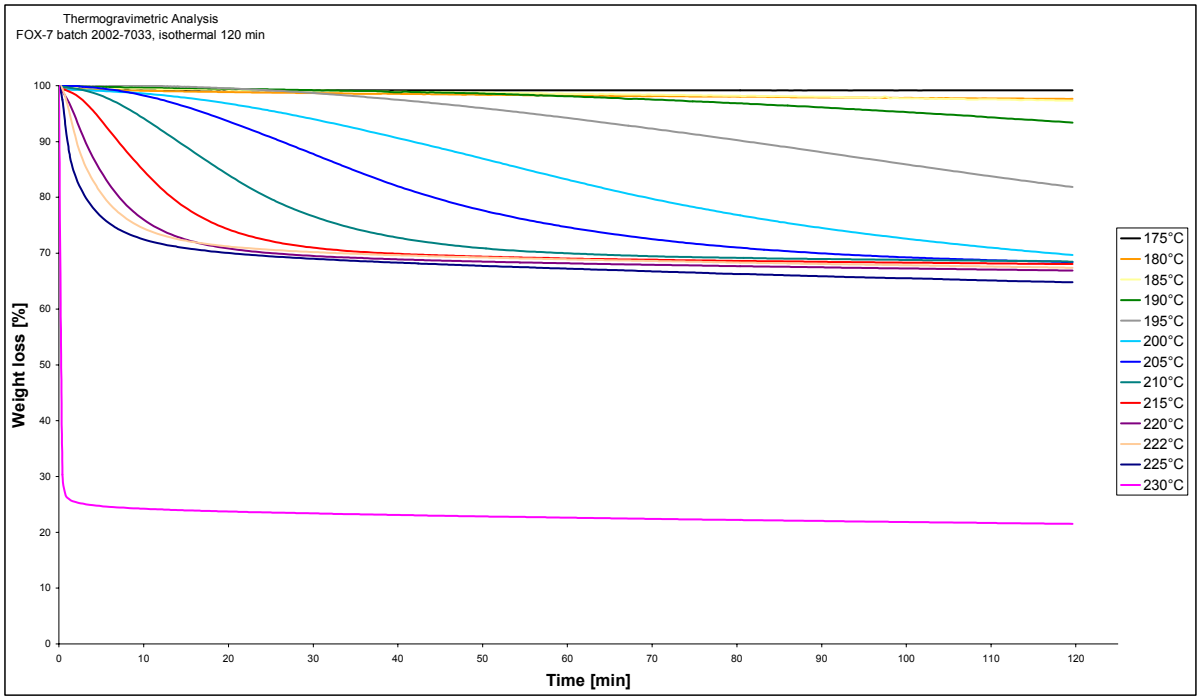

Figure 29 Isothermal TG analyses (after heating from 30°C at a rate of 5°C/min) of FOX-7 (2002-7033) 120 minutes.

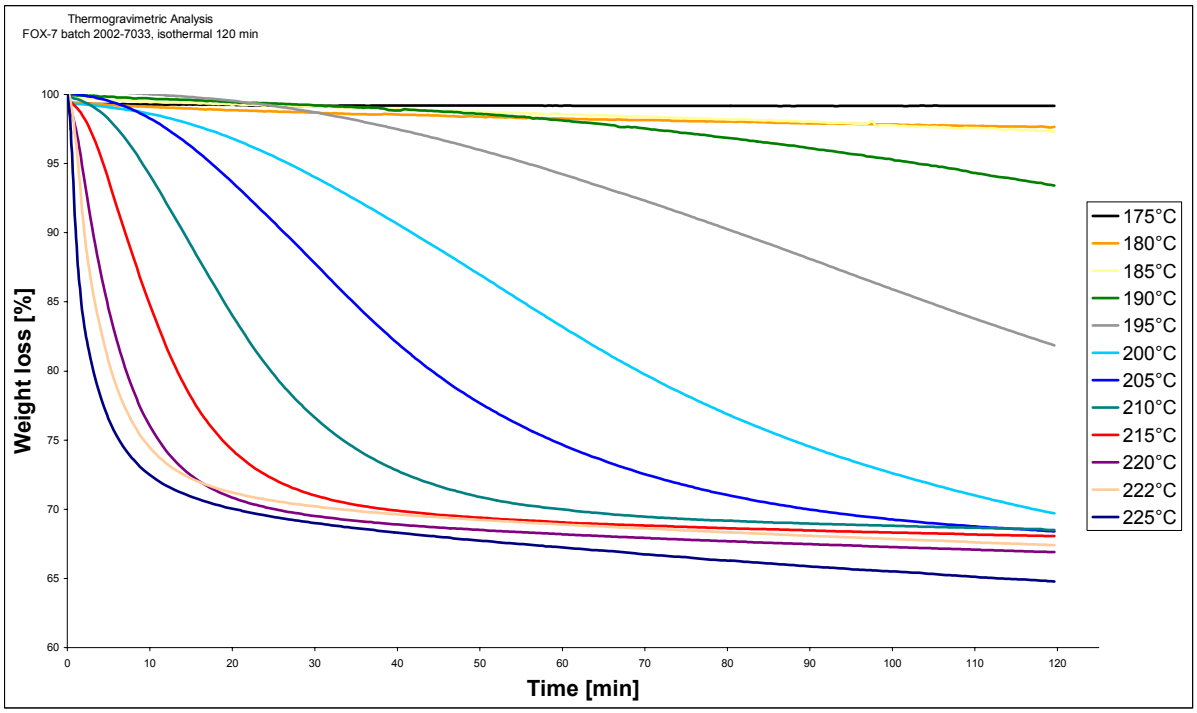

Figure 30 Isothermal TG analyses (after heating from 30°C at a rate of 5°C/min) of FOX-7 (2002-7033) for 120 minutes (data from the analysis above the first exothermal (DSC) peak temperature at 230°C excluded).

Isothermal thermogravimetric analysis of FOX-7 crystallised in NMP/water (2002-7033) at 220°C for 120 minutes were done >20 times. The result of the analyses was very consistent, Figure 31 show the weight loss detected in six analyses. The weight loss of the samples was between 30 and 35% of their initial mass. After the analyses the crystals are gold coloured, non-transparent with some cracks. Figure 32 shows an example of FOX-7 crystals before and after the isothermal TG analysis. The non-transparent material is further on in this report referred to as preheated FOX-7. The material left in the sample pan after analysis at 230°C has a dark brown or black colour.

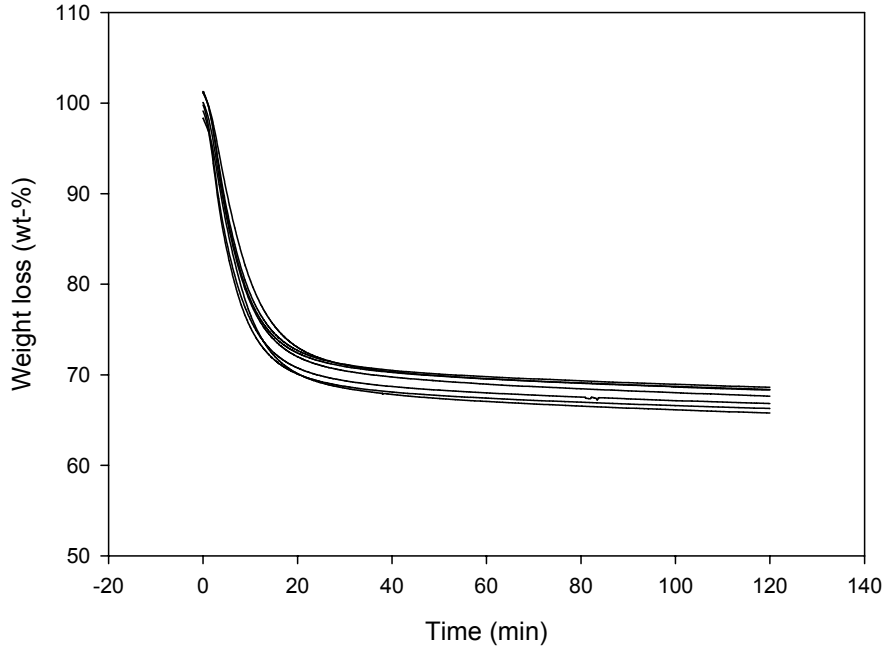

Figure 31 Isothermal TG analyses (after heating from 30°C at a rate of 5°C/min) of six samples of FOX-7 (2002-7033) at 220°C for 120 minutes.

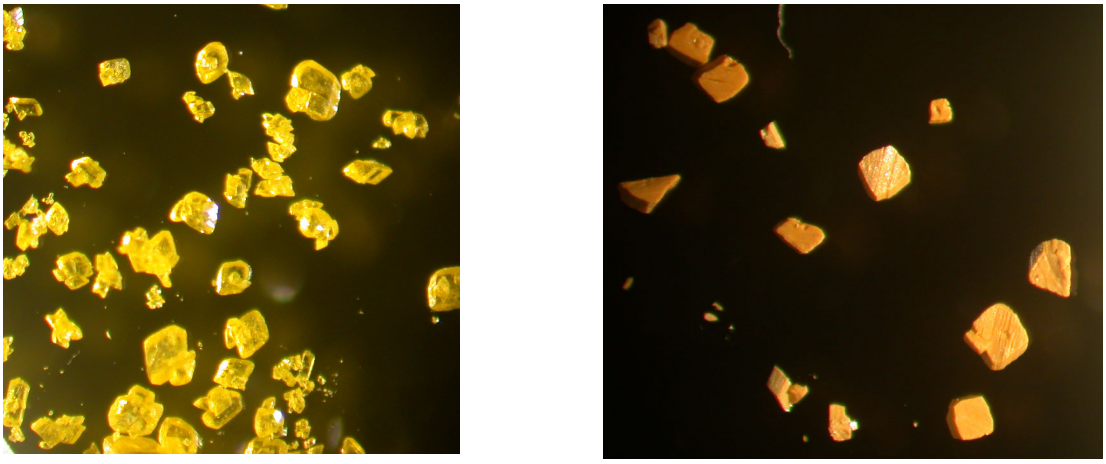

Figure 32 FOX-7 (2002-7033) before and after isothermal TG analysis at 220° for 120 minutes.

The large crystals obtained from crystallisation in GBL were also subjected to isothermal thermogravimetric analysis (Figure 33). This material lost more weight than FOX-7 crystallised in NMP/water at the same isothermal temperatures. During heating of the large crystals from crystallisation in GBL from 30°C to 215°C and 220°C respectively, weight losses were registered. However, isothermal analysis at 210°C formed the gold coloured non-transparent material accompanied with a weight loss of ~25 wt-%.

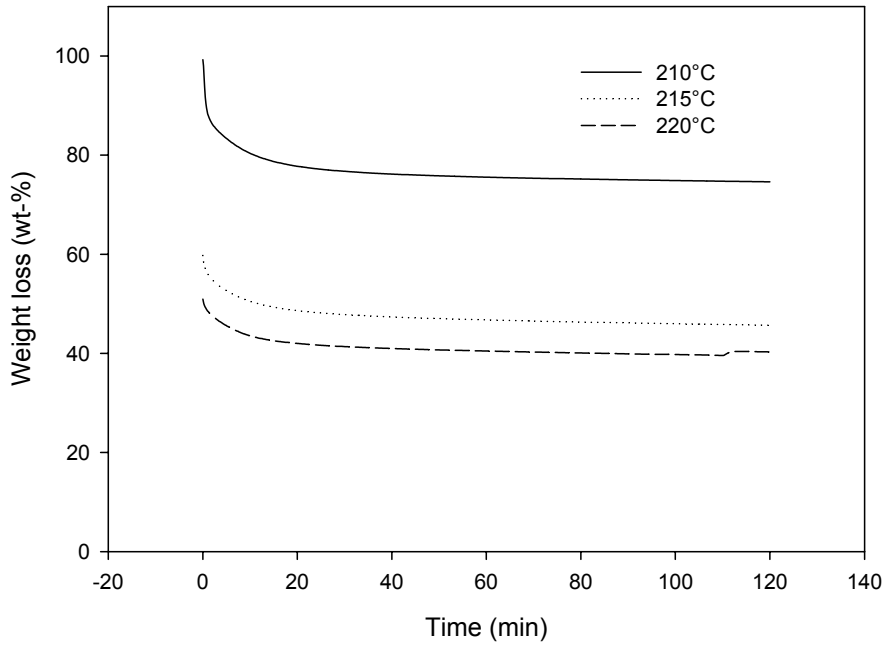

Figure 33 Isothermal TG analyses (after heating from 30°C at a rate of 5°C/min) of the large crystals from crystallisation in GBL.

DSC analysis of preheated FOX-7 (2002-7033) (220°C for 120 min) between 30°C and 400°C at a heating rate of 10°C/min show one exothermal peak (Figure 34). The peak temperature is shifted towards a higher temperature if compared to the second exothermal peak obtained in a corresponding DSC analysis of the FOX-7 (2002-7033) material before preheating.

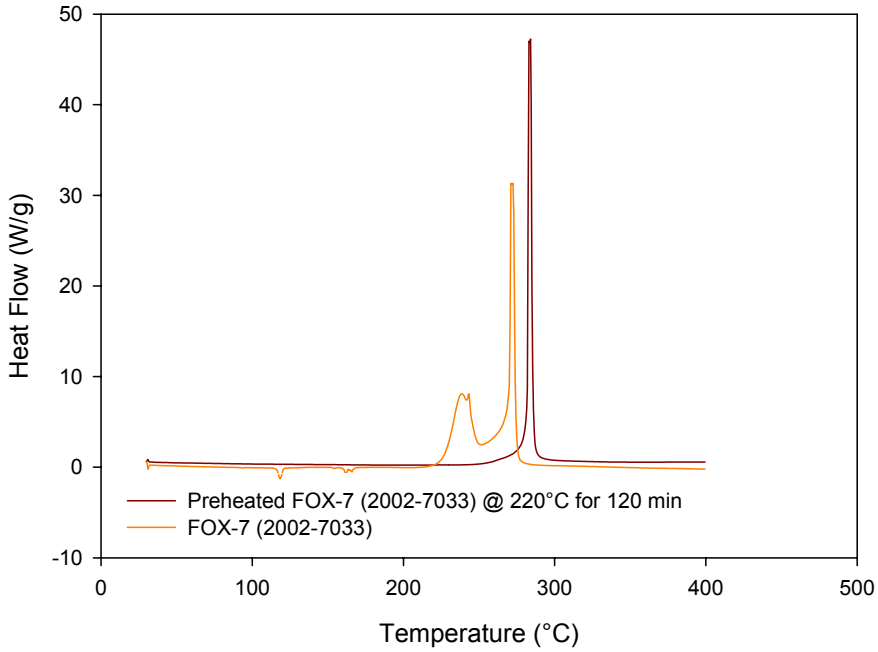

Figure 34 DSC analysis of preheated FOX-7 (2002-7033) and the material before preheating. The analyses were performed between 30°C and 400°C at a heating rate of 10°C/min.

5.2.3 Karl Fischer analysis of crystallised FOX-7

The water content of crystallised FOX-7 was determined at Analyscentrum AB (Nacka, Sweden) using Karl Fisher titration. Due to difficulties in dissolving FOX-7, the sample amounts were limited to 40 mg. The detection limit was 0.10 %. All samples were analysed in duplicate. The water content was determined to less than 0.10% in all samples. Table 4 shows the results of the Karl Fisher titration of crystallised FOX-7.

Table 4 Results of Karl Fisher titration of crystallised FOX-7

FOX-7 crystallised in (solvent)	Water content (%) (all sample analysed in duplicate)
NMP/water	< 0,10
GBL (large crystals)	< 0,10
DMF/water	< 0,10
GBL (small crystals)	< 0,10
Acetonitrile	< 0,10

5.2.4 Elemental and trace analysis of FOX-7 crystallised in NMP/water

Elemental analyses of both FOX-7 (2002-7033) and preheated FOX-7 (2002-7033) show results that point towards the same elemental composition. Table 5 show both the calculated and analysed elemental composition of FOX-7.

Table 5 Calculated and analysed elemental composition of FOX-7.

Sample	C (wt-%)	H (wt-%)	N (wt-%)	O (wt-%)
FOX-7 (2002-7033)	16,3	2,6	36,3	44,5
Preheated FOX-7 (2002-7033)	17,3	2,6	37,2	42,6
Calculated	16,2	2,7	37,8	43,2

A screening of trace elements in FOX-7 crystallised in NMP/water (2002-7033) was done. Before analysis FOX-7 was dissolved in HCl. The result is shown in Table 6. It should, however, be noted that the corresponding values of the HCl used as solvent are not subtracted from the values below.

Table 6 Trace analysis of crystallized FOX-7 (2002-7033) dissolved in HCl.

Element	Concentration (µg/l)	Element	Concentration (µg/l)	Element	Concentration (µg/l)
Ag	1.7	Hg	0.8	Ru	n.d.
Al	310	Ho	n.d.	S	780
As	n.d.	I	360	Sb	1.7
Au	0.17	Ir	n.d.	Sc	0.05
B	420	K	4800	Se	n.d.
Ba	110	La	0.06	Si	470
Be	n.d.	Li	6	Sm	n.d.
Bi	0.1	Lu	n.d.	Sn	10
Br	10000	Mg	110	Sr	120
Ca	2200	Mn	13	Ta	n.d.
Cd	0.21	Mo	15	Tb	n.d.
Ce	3.2	Na	7000	Te	n.d.
Co	1.4	Nb	0.4	Th	0.21
Cr	160	Nd	0.1	Ti	93
Cs	0.14	Ni	93	Tl	0.55
Cu	92	Os	n.d.	Tm	n.d.
Dy	0.01	P	12	U	0.06
Er	0.006	Pb	16	V	5.2
Eu	n.d.	Pb	n.d.	W	0.6
Fe	700	Pr	n.d.	Y	n.d.
Ga	0.07	Pt	n.d.	Yb	n.d.
Gd	0.03	Rb	5	Zr	2.3
Ge	n.d.	Re	n.d.		
Hf	0.12	Rh	n.d.		

Std dev = ±50% from the reported value except for Br and I.

n.d. = not detected.

5.3 X-ray studies

The first structure investigation of FOX-7 was performed by Bemm and Östmark[4]. It was done at -100°C (173K) and the unit cell (Figure 35) of the model was:
monoclinic; a=6.941(1)Å, b=6.569(1),c=11.315(2),β=90.55(2) and V= 515.9(1)

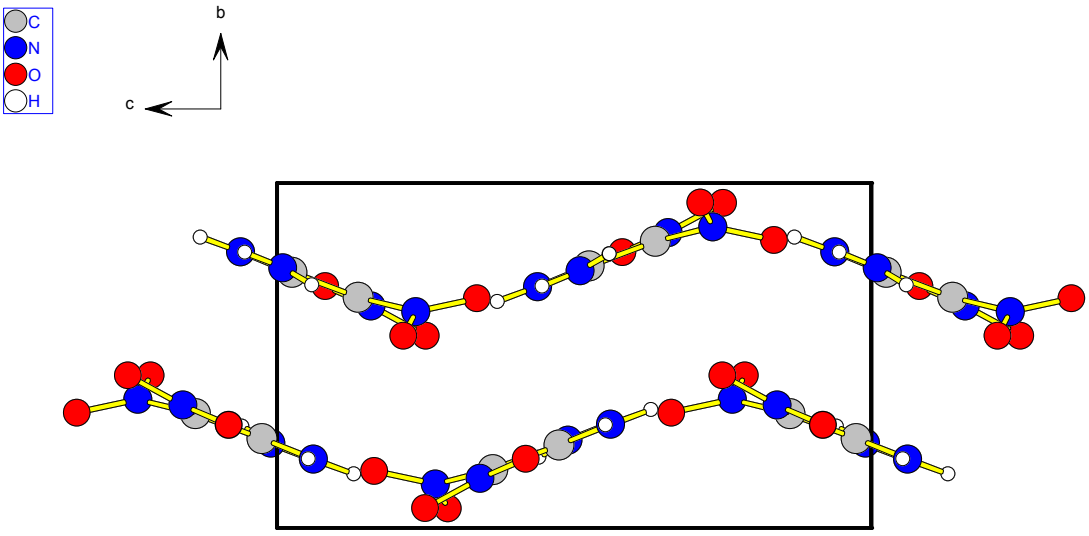

Figure 35 FOX-7 at 173K, view along the b-axis as determined by Bemm and Östmark[4]

The determined structure is further on called the "low temperature phase" in this report. Bemm and Eriksson[3] later suggested that there were an additional phase between 85°C and 125°C. However, there are no signs of this phase from DSC patterns that show the first transition just below 120°C, see Figure 9.

Single crystal investigations on a crystal heated to 130-135°C showed a pseudo orthorhombic unit cell, Figure 36. The solution of the crystal structure was not easy, it was necessary to use space group P1 which only includes translational symmetry in order to solve for all atoms. The cell parameters are similar to what was suggested earlier:
6.951(2), 6.638(2) and 11.336(3) and all angles very close to 90 degrees

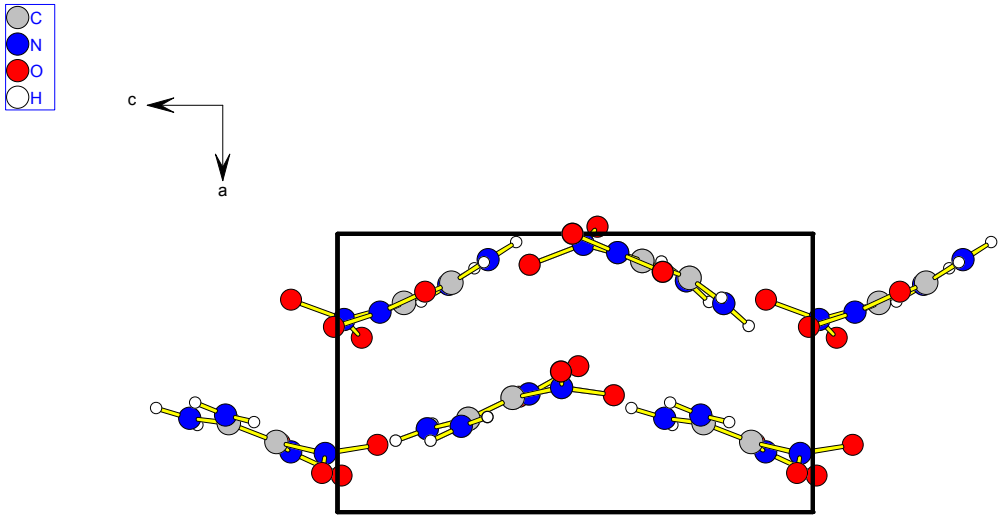

Figure 36 FOX-7 from the sample that was heated to 135°C. Similar view as in Figure 35, only the names of the axes are different. This is not a high quality model but still some indication of dissimilarities with the 173K structure model.

The result file from SHELXL97 is found in Appendix 1. Some problems with the refinements of this ”high temperature” structure model is that there seems to be a lot of twinning present in the crystals. Thus, the model is quite far from publishable quality. However, there seem to be larger deviations of the molecules in the “High temperature phase” than in the “low temperature phase” from Bemm and Östmark[4] , see Figures 37 and 38.

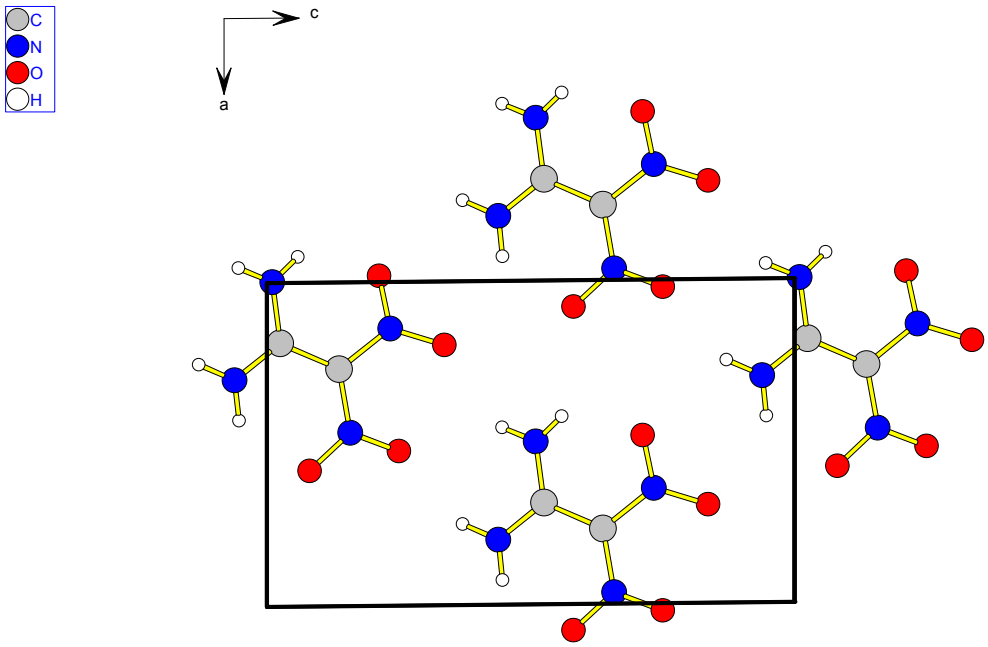

Figure 37 FOX-7, 173K model from Bemm and Östmark[4], 1998, view perpendicular to one layer.

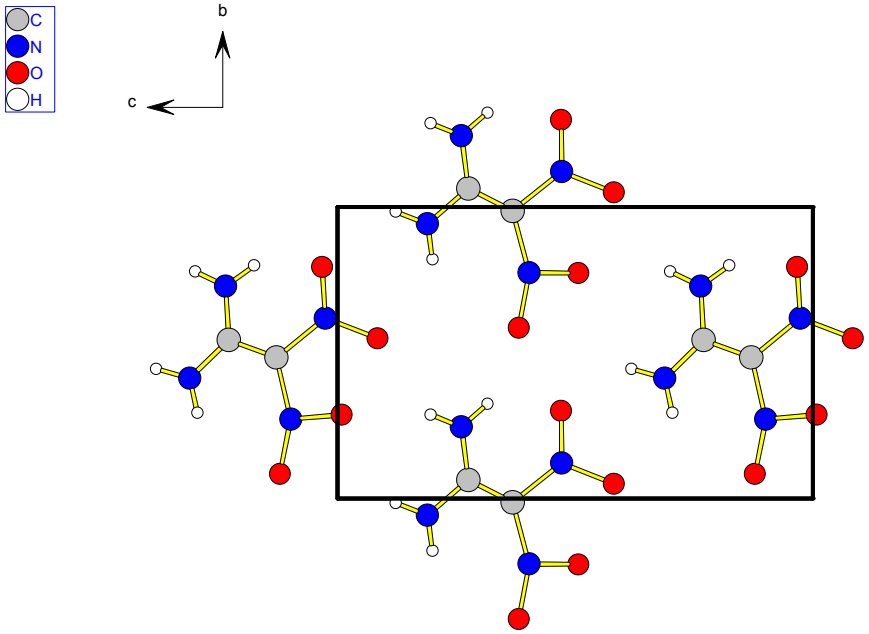

Figure 38 FOX-7 “high temperature”, 135°C, one of the layers. Note that unit cell may not be similar as this high temperature model is done in P1 and no restrictions of the unit cell axes are associated with P1.

FOX-7 (lot no 2002-7033 from Eurenco Bofors) that was heated to 220°C formed a gold coloured non-transparent compound, see chapter 5.2.2 in this report. The material was subjected to X-ray diffraction analysis and preliminary data showed an amorphous structure to X-rays. This result was at least what could be found from a Guinier X-ray diffraction pattern.

5.4 Long term storage stability study of crystallised FOX-7

FOX-7 crystallised in NMP/water (2002-7033) was used for a long term storage stability study. The samples were stored in 2 ml vials at room temperature, 60°C and 80°C. The weight was registered once a month and samples for DSC, TGA and HFC analyses were taken once every second month. The study started in December 2003 and five samples were analysed from each storage temperature during a period of 11 months.

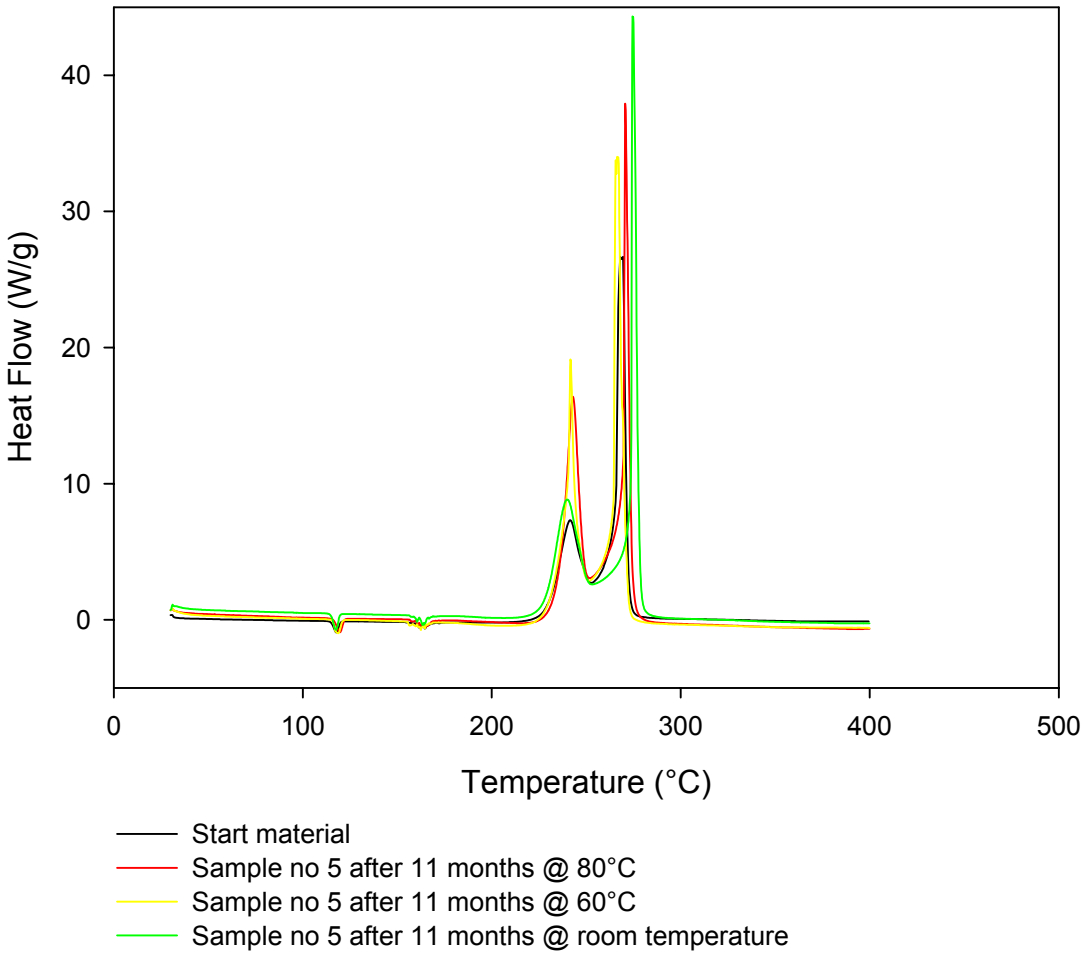

Figure 39 DSC analyses of start material and sample 5 after 11 month storage at room temperature, 60°C and 80°C respectively. The DSC analyses were performed between 30°C and 400°C at a heating rate of 10°C/min.

Figures 39 and 40 show the DSC and TG analyses of start material and sample number 5 from each storage temperature. In all samples two endothermal and two exothermal peaks are detected in the DSC analysis. The peak temperatures are approximately the same for all peaks except for the second exothermal. The second exothermal peak appears within a temperature interval of ~15°C in the DSC thermogram. The proportion between the first and second exothermal peak differs in the samples stored at the elevated temperatures (i.e. 60°C and 80°C) compared to the start material and the sample stored at room temperature. The TG analyses of the start material and the samples stored for 11 months show the same profile. The sample stored at room temperature for 11 months show an increased weight loss during and after the major decomposition step.

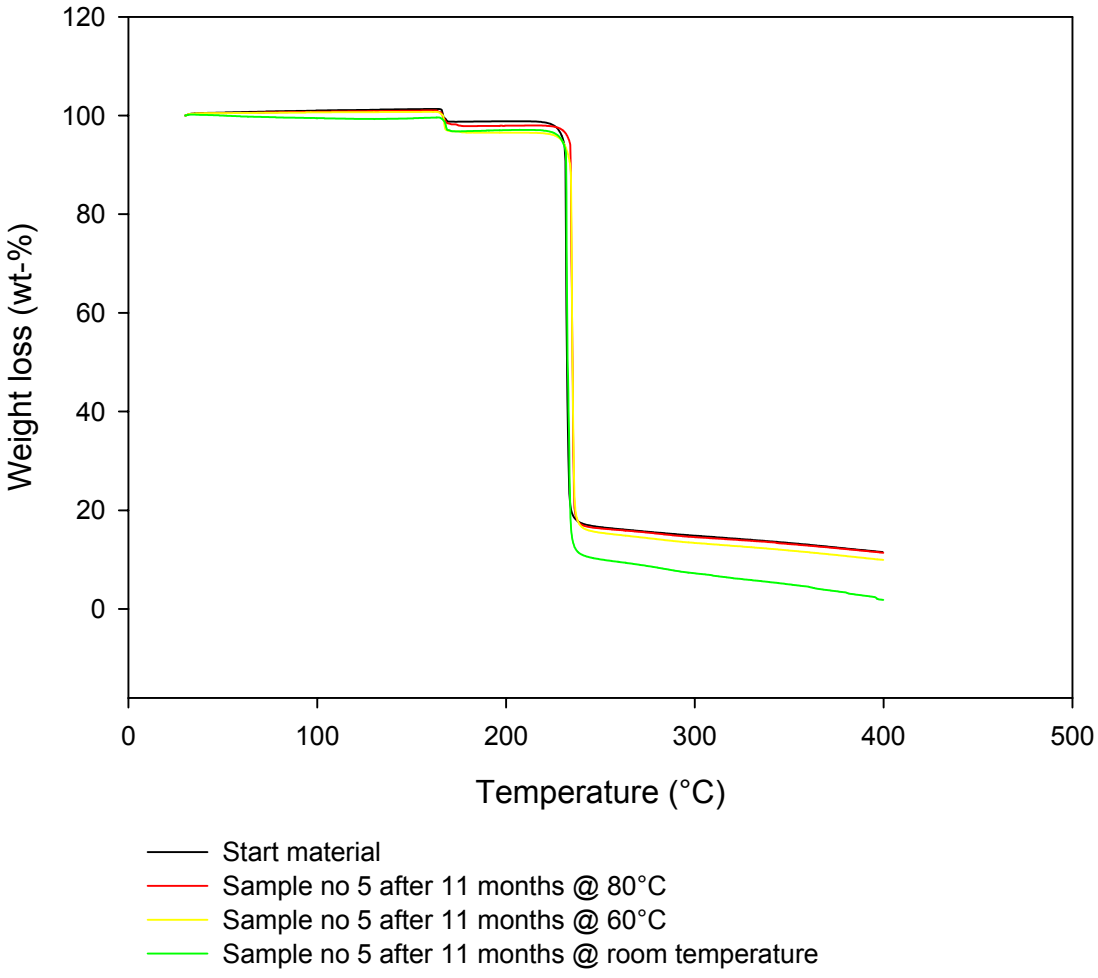

Figure 40 TG analyses of start material and sample 5 after 11 month storage at room temperature, 60°C and 80°C respectively. The TG analyses were performed between 30°C and 400°C at a heating rate of 10°C/min.

In Figure 41 the HFC analysis of the start material is shown. The level of heat flow evolved is stable during the whole analysis. The HFC analyses of samples after 11 months storage are shown in Figure 42. The evolved heat flow of the samples after 11 months of storage show no other profile than the starting material did and there is no evidence of autocatalytic behaviour. The increase detected in the beginning of the analyses is considered to be due to sample adjustment, energy absorption, to the temperature in the measuring cell. The energy evolved during the whole analyses of 19 days per sample is given in Table 7. The heat generation is considered as very low and for all measurements except for the samples analysed after two months storage (sample number 1). However, the samples analysed after two months of storage at room temperature, 60°C and 80°C should be considered as outliers. There were difficulties in calculating the heat generation due to a baseline shift caused by a major power failure during the analysis.

The weight loss of all samples stored during the 11 month period was registered as +/- 0.07 wt-%. This corresponds to a deviation of +/- 0.4 mg in the absolute weight, which can be considered as a normal standard deviation for the procedure.

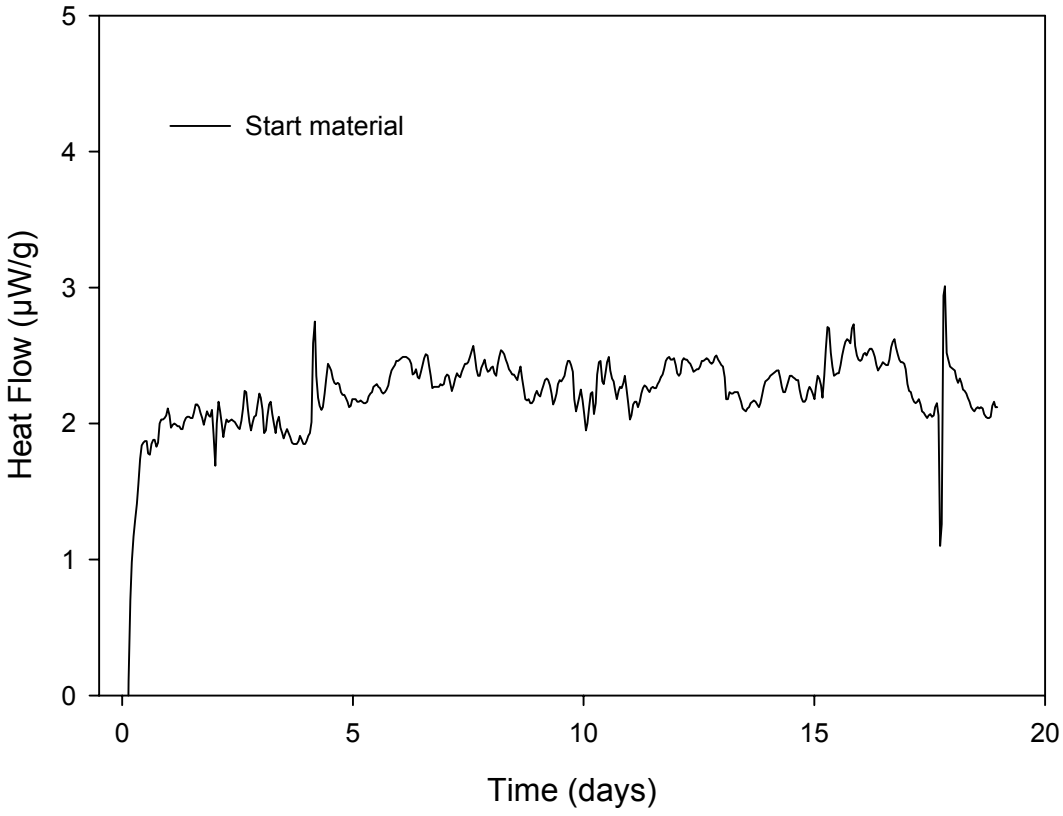

Figure 41 HFC analysis of the start material at 75°C for 19 days.

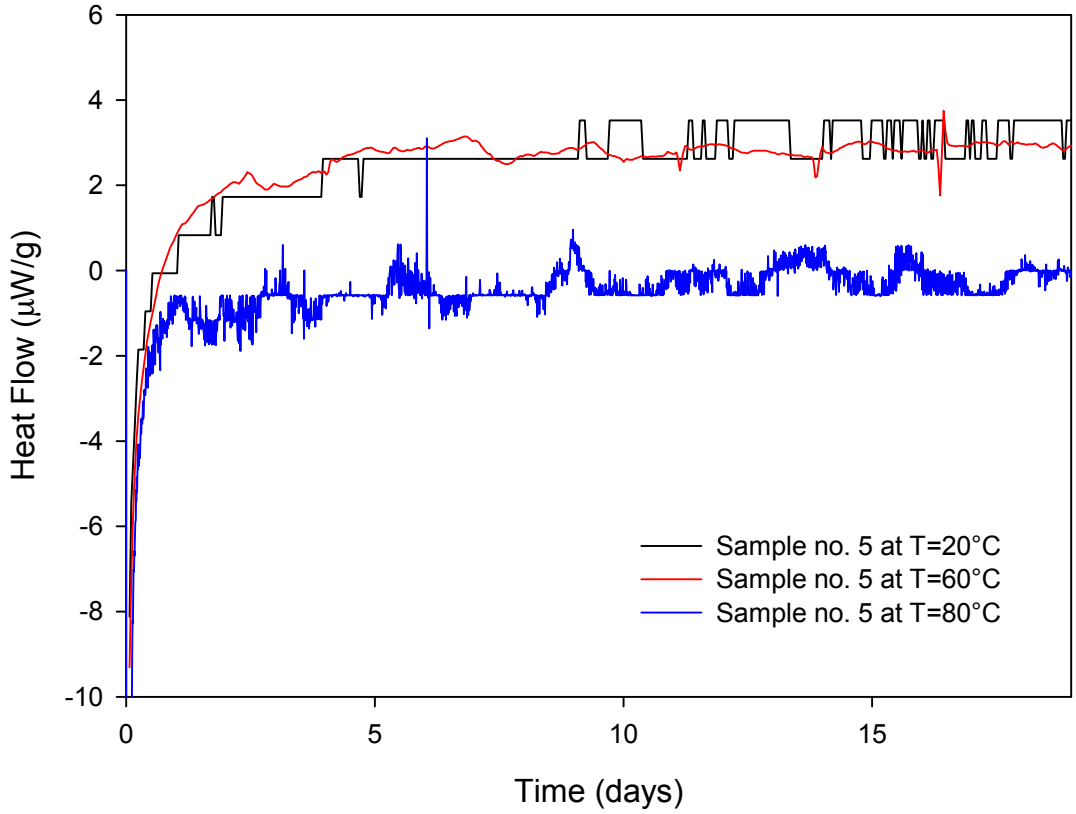

Figure 42 HFC analysis of sample number 5 after 11 month storage at 20, 60 and 80°C. The analysis was done at 75°C for 19 days.

Table 7 Total energy evolved (E_{tot}) during 19 days at 75°C.

Sample	E_{tot} after 19 days (J/g)
Start material	3,597
Sample 1 after 2 months @ room temperature	*(22,999)**
Sample 1 after 2 months @ 60°C	*(18,833)**
Sample 1 after 2 months @ 80°C	*(15,833)**
Sample 2 after 4 months @ room temperature	-0,885
Sample 2 after 4 months @ 60°C	3,349
Sample 2 after 4 months @ 80°C	1,008
Sample 3 after 6 months @ room temperature	2,174
Sample 3 after 6 months @ 60°C	4,039
Sample 3 after 6 months @ 80°C	2,784
Sample 4 after 8 months @ room temperature	-1,210
Sample 4 after 8 months @ 60°C	0,346
Sample 4 after 8 months @ 80°C	-2,990
Sample 5 after 11 months @ room temperature	4,097
Sample 5 after 11 months @ 60°C	4,013
Sample 5 after 11 months @ 80°C	-0,930

* Outliers. Calculated total heat generation is probably not ok. Baseline shift due to major power failure during analysis

6 Discussion

The larger crystals obtained from GBL, NMP/water and DMF/water has the same shape. Surface analysis of the larger crystals indicates a smoother surface of the crystals from GBL and DMF/water than from NMP/water.

Investigations of the phase behavior of crystallized FOX-7 thermal analyses and X-ray diffraction shows that FOX-7 has at least three phases[3,5]. Bemm and Eriksson suggested that there were an additional phase between 85°C and 125°C. However, there are no signs of this phase from DSC patterns that show the first transition just below 120°C. Single crystal investigations on a crystal heated to 130-135°C showed a pseudo orthorhombic unit cell. Some problems with the refinements of this ”high temperature” structure model is that there seems to be a lot of twinning present in the crystals. Thus, the model is quite far from publishable quality. However, there seem to be larger deviations of the molecules in the “High temperature phase” than in the “low temperature phase” from Bemm and Östmark[4]. DSC measurements between 30°C and 400°C of crystallized FOX-7 show two endothermal peaks corresponding to two phase transitions. The endothermal peaks are followed by two exothermal decomposition peaks in connection to a third phase transition.

Cyclic repeated DSC analysis of crystallised FOX-7 between 30°C and 135°C show one endothermal peak during heating[5,6]. A corresponding exothermal peak is also registered during the cooling cycle. The position of the peak shifts after the first cycle and remains unchanged thereafter. This can be explained by storage or thermal memory that causes a different behaviour during the first heating and cooling cycle compared to the following. The peaks appear repeatedly with unchanged peak areas in each heating and cooling cycle. This indicates the fully reversible behaviour of a phase transition, which also is confirmed by X-ray studies[3,5]. However, the peak areas decrease after each new heating and cooling cycle if the heating is extended above the next endothermal peak temperature, i.e. ~160°C.

With the extended heating cycles above the second endothermal peak both endothermal peaks show a decreased peak area for each new heating cycle. The crystals from a mixture of solvent and water and the larger crystals from GBL produce a split second endothermal peak in DSC analysis whereas the smaller crystals from acetonitrile and GBL do not. The shape of

the endothermal peak then shifts to a single peak in the following heating cycles. A possible explanation for this behaviour is evaporation of material from the crystals, such as water, solvent or FOX-7. A fact that supports this is the weight loss registered during the first heating cycle of the repeated TG analyses of these crystals. It appears at the temperature for the appearance of the split peak in the DSC measurements[5,6].

The possibility of evaporation from the crystal structure is produced due to a phase change. The profile of the divided peak reflects the release of material at the same time as the endothermal phase change is registered. The profile of the endothermal peak has then changed to a single peak in the following heating cycles, hence only the phase change is registered in the second, third and fourth heating cycle. The temperature at which solvent or water loss is possible is dependent of the temperature at which the phase change occurs. The theory of water inclusion could be supported by the fact that the water release would be complete during the first heating cycle. The phase change appears at a temperature approximately 60° higher than the boiling point of water which would facilitate a fast evaporation. NMP and GBL have boiling points at 202°C and 205°C respectively. This indicates a slow evaporation at the discussed temperature resulting in possible residue releases in the following heating cycles. Water inclusion is a possibility for all three types of crystals. Even though the GBL crystals were crystallised in dehydrated solvent, the larger GBL crystals may have water inclusions as the growing was made in an open beaker in room temperature for a long period of time. The larger crystals in this study was crystallised in GBL and in a mixture of NMP/water. Also the crystals from DMF/water show the same pattern but produces smaller peak areas than the other two. The weight loss is also smaller for DMF/water crystals than the other.

DSC and TG analyses of the larger crystals show divided endothermal peaks and corresponding weight losses at approximately the same temperature. The smaller crystals does not show any divided endothermal peaks or significant weight losses in the same temperature range. This may indicate a water inclusion during crystal growing that is independent of solvent type. However, Karl Fischer analysis of crystallised FOX-7 indicates that water is not present to such an extent that it would correspond to a 2 % weight loss.

Isothermal analysis of crystallised FOX-7 forms a gold coloured non-transparent product after a 25-35% weight loss. Only one exothermal peak is detected during DSC analysis of the product and this point toward a somewhat different compound than the original FOX-7 sample. This product seems to be more thermally stable, according to the DSC analysis. However, both elemental composition and solid sample mass spectrometry analyses of the product are in agreement and show FOX-7 profiles. The elemental composition of the product is the same as for FOX-7 and the significant FOX-7 decomposition ions are detected during mass spectrometry analysis of the product. Preliminary data from X-ray diffraction analysis of this product showed an amorphous structure to X-rays. This result was at least what could be found from a Guinier X-ray diffraction pattern. Ticmanis et al. explains the mass loss by a presence of an amorphous fraction in the original FOX-7, which decomposes to form the gold coloured non-transparent product[7]. Ticmanis et al also reports the structure of this product to be similar to the structure of the reported FOX-7 phase above ~170°C.

The results from the long term storage stability study show that FOX-7 is thermally very stable. The heat generation is in the same level for all samples and considered as very low. The TG and DSC analyses of both the start material and the samples stored for 11 months show the same profile. This indicates that the samples are thermally very stable. There is however a deviation in the proportion between the first and second endothermal peak. Compared to the start material and the sample stored at room temperature, the proportion between the first and second exothermal peak differs in the samples stored at the elevated temperatures. It may be of interest to investigate this further on.

7 Conclusions

DSC shows two endothermal peaks which are suggested to correspond to phase transitions of the FOX-7 crystal. The first endothermal peak is accompanied by an exothermal peak during cooling indicating a fully reversible instantaneous phase transition. The second endotherm is supposed to reflect a phase transition with an incomplete or slow reversion. The latter phase transition is also suggested to be accompanied with release of FOX-7 in the first transition during heating.

The gold coloured non-transparent product formed when FOX-7 is heated at approximately 220°C for 120 minutes is proposed to be an amorphous structure of FOX-7.

The results from the long term storage stability study show that FOX-7 is thermally very stable. It is however of interest to continue this study and fully investigate and evaluate the results.

8 Future Work

Based on the results of this study a slower cyclic repeated thermal analysis (DSC, TGA) are proposed. In order to understand if the weight loss in connection to the second endothermal peak is depending upon the rate of temperature increase and decrease to trigger the phase transition. Using decreased heating and cooling rate compared to what was used in this study, the phase transition would be done very slowly (for instance 0.5°C or even slower). Will the crystals lose as much weight as was lost during a fast phase transition?

Proposed further X-ray investigations are: Closer spaced and better quality powder diffraction measurements on the different phases of FOX-7 between 50°C and 230°C. Preferably this should be done with synchrotron radiation in order to detect small weak peaks indicating some structural transitions. Possibly the different diffraction patterns from X-ray powder data could be used for solving high temperature structures. Also measurement of one or several high temperature diffraction patterns from a single crystal is proposed, preferably the same crystal, to avoid systematic errors as much as possible. In connection to this correlation between structural changes and observed DSC and TG patterns would be of interest.

A continuation of the long term storage stability study is proposed to fully investigate and evaluate the results. Also to further investigate the difference in proportion between the first end second exothermal peaks after storage at elevated temperatures.

9 Acknowledgement

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Appendix 1.

Result-file from crystallographic calculations with SHELXL97 on ”HT-phase”

```
TITL  FX_RT  STOE IPDS measurement, crystal heated to 135 deg.
CELL  0.71073    6.6382    6.9509   11.3355    90.000    90.000    90.000
ZERR  4          0.0024    0.0016    0.0028     0.000     0.000     0.000
LATT -1
SFAC  C H N O
UNIT  8 16 16 16
merg 0
omit 4
L.S. 10
delu 0.001
dfix  21 0.01 c1a n1a c1a n2a
dfix  31 0.01 n1a o11a n1a o12a n2a o21a n2a o22a
dfix  41 0.01 c1a c2a
dfix  51 0.01 c2a n3a c2a n4a

dfix  21 0.01 c1b n1b c1b n2b
dfix  31 0.01 n1b o11b n1b o12b n2b o21b n2b o22b
dfix  41 0.01 c1b c2b
dfix  51 0.01 c2b n3b c2b n4b

dfix  21 0.01 c1c n1c c1c n2c
dfix  31 0.01 n1c o11c n1c o12c n2c o21c n2c o22c
dfix  41 0.01 c1c c2c
dfix  51 0.01 c2c n3c c2c n4c

dfix  21 0.01 c1d n1d c1d n2d
dfix  31 0.01 n1d o11d n1d o12d n2d o21d n2d o22d
dfix  41 0.01 c1d c2d
dfix  51 0.01 c2d n3d c2d n4d
htab
FMAP 2
PLAN 20
rem ------------------------------------------------------------------------

WGHT    0.010000
BASF   0.96518
FVAR       0.94823   1.52387   1.34254   1.30273   1.29857
C1B   1    0.248082    0.498912    0.860101    11.00000    0.06696
N1B   3    0.308052    0.447471    0.986034    11.00000    0.06632
O11B  4    0.237140    0.448474    1.098058    11.00000    0.12104
O12B  4    0.373669    0.275895    0.949269    11.00000    0.07926
N2B   3    0.281518    0.700189    0.910731    11.00000    0.02193
O21B  4    0.208127    0.796678    0.816082    11.00000    0.00546
O22B  4    0.334474    0.801371    1.007645    11.00000    0.02499
C2B   1    0.175844    0.431686    0.760705    11.00000    0.03919
N3B   3    0.093217    0.545859    0.683378    11.00000    0.28530
AFIX  93
H3B1  2    0.029779    0.498524    0.623936    11.00000   -1.20000
H3B2  2    0.102139    0.668523    0.691800    11.00000   -1.20000
AFIX   0
N4B   3    0.181755    0.245842    0.766143    11.00000    0.05640
AFIX  93
H4B1  2    0.124337    0.178027    0.712328    11.00000   -1.20000
H4B2  2    0.243104    0.190129    0.823572    11.00000   -1.20000

rem ------------------------------------------------------------------------
```

```
C1D   1    0.748177    0.483252    0.128701    11.00000    0.05914
N1D   3    0.789310    0.619289    0.026039    11.00000    0.01584
O11D  4    0.758106    0.549897   -0.084220    11.00000    0.08486
O12D  4    0.859948    0.794419    0.032461    11.00000    0.00001
N2D   3    0.783918    0.271747    0.098586    11.00000    0.05637
O21D  4    0.868507    0.287009   -0.008331    11.00000    0.11137
O22D  4    0.752912    0.084104    0.121465    11.00000    0.15774
C2D   1    0.680719    0.544250    0.229374    11.00000    0.04983
N3D   3    0.662655    0.412450    0.311628    11.00000    0.07786
AFIX  93
H3D1  2    0.626557    0.444716    0.381754    11.00000   -1.20000
H3D2  2    0.686916    0.293833    0.295392    11.00000   -1.20000
AFIX   0
N4D   3    0.651582    0.728170    0.235655    11.00000    0.08629
AFIX  93
H4D1  2    0.676828    0.799930    0.175646    11.00000   -1.20000
H4D2  2    0.606984    0.778558    0.299836    11.00000   -1.20000

rem ---------------------------------------------------------------------

C1C   1    0.589065   -0.013488    0.631281    11.00000    0.04547
N1C   3    0.575965   -0.224971    0.596914    11.00000    0.03516
O11C  4    0.476274   -0.226141    0.493512    11.00000    0.10181
O12C  4    0.586007   -0.414166    0.618313    11.00000    0.13431
N2C   3    0.552508    0.121274    0.528226    11.00000    0.01504
O21C  4    0.494795    0.299835    0.529400    11.00000    0.00142
O22C  4    0.580213    0.049918    0.418758    11.00000    0.06783
C2C   1    0.665274    0.063035    0.725116    11.00000    0.04092
N3C   3    0.692235    0.244947    0.739576    11.00000    0.03121
AFIX  93
H3C1  2    0.658716    0.324079    0.684657    11.00000   -1.20000
H3C2  2    0.743762    0.287322    0.804154    11.00000   -1.20000
AFIX   0
N4C   3    0.701571   -0.057637    0.810990    11.00000    0.05894
AFIX  93
H4C1  2    0.743886   -0.015746    0.877938    11.00000   -1.20000
H4C2  2    0.683133   -0.178909    0.800532    11.00000   -1.20000

rem ---------------------------------------------------------------------
C1A   1    0.097477    1.001737    0.358360    11.00000    0.08088
N1A   3    0.037331    0.942224    0.482667    11.00000    0.05574
O11A  4   -0.025606    0.768195    0.452622    11.00000    0.11514
O12A  4    0.111441    0.946847    0.595394    11.00000    0.09566
N2A   3    0.068001    1.201712    0.410760    11.00000    0.01234
O21A  4    0.136469    1.300070    0.315296    11.00000    0.00026
O22A  4   -0.000489    1.300577    0.505135    11.00000    0.00688
C2A   1    0.158507    0.924855    0.259007    11.00000    0.03627
N3A   3    0.168419    0.740411    0.265910    11.00000    0.03534
AFIX  93
H3A1  2    0.244114    0.677295    0.218024    11.00000   -1.20000
H3A2  2    0.099352    0.680192    0.318412    11.00000   -1.20000
AFIX   0
N4A   3    0.249804    1.041738    0.186819    11.00000    0.08472
AFIX  93
H4A1  2    0.330412    0.996985    0.134145    11.00000   -1.20000
H4A2  2    0.229468    1.163655    0.191835    11.00000   -1.20000
HKLF 4
REM   FX_RT  STOE IPDS measurement
REM R1 =  0.2780 for   3947 Fo > 4sig(Fo)  and  0.4179 for all   8122 data
REM     85 parameters refined using     39 restraints
END
```