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Recrystallization of CL-20 and HNFX from Solution for Rigorous Control of the Polymorph Type: Part II, Experimental Studies

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The recrystallization of CL-20 and HNFX to form different polymorphs was investigated by employing various experimental analyses, including micro-crystallization under myriad conditions, novel means of crystallization, analysis of polymorphs using powder diffraction, and Rietveld analysis. In the investigation all three groups of solvents: polar protic, non-polar aprotic, and dipolar aprotic solvents were employed. These results are reported in two parts with the experimental results reported here and the mathematical modeling results reported in Part I of this paper. The conventional crystallization techniques included combinations of solvent and anti-solvent system (including high molecular weight polymer melts), combination of solvents, the use of habit modifiers, and seeding. Other recrystallization techniques, which were also investigated included recrystallization under UV, under microwaves, upon freeze drying, upon annealing, in the presence of high molecular

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weight polymers, and under different hydrodynamic and hence different micro-mixing conditions.

As will be seen in Part I of this paper (this issue) our computations suggest (in agreement with earlier studies) that multiple polymorphs with various densities for both CL-20 and HNFX are possible. However, the recrystallization studies reported here revealed only one type of polymorph for HNFX, i.e., the Ci R-3 polymorph. On the other hand, CL-20 gave rise to indeed multiple polymorphs which changed with the crystallization conditions, especially with the solvent/anti-solvent systems utilized. An X-ray based method was used to determine the types of polymorphs and also the percentages of the polymorphs generated upon crystallization. The presence of multiple polymorphs or polymorph impurities in CL-20 may have significant ramifications in the sensitivity and other ultimate properties of energetic grains containing CL-20. On the other hand the existence of only one low-density polymorph for HNFX significantly limits the application areas for HNFX.

Keywords: CL-20, conventional crystallization, HNFX, micro-crystallization, polymorph analysis, powder diffraction, Rietveld analysis

Introduction

The performance characteristics of energetic formulations, including the detonation velocity and pressure during combustion are directly linked to the density of the energetic crystals [1]. The stumbling block to the development of various nitramines as suitable materials for use in energetic formulations is the difficulty of generating specific gravity values that approach or surpass a specific gravity of 2.0.

One of the most interesting energetic materials containing the difluoramine group synthesized recently is 3,3,7,7-tetrakis (difluoramino) octahydro-1, 5-dinitro1, 5-diazocine (HNFX) [2] HNFX was synthesized by the nitrolysis of 3,3,7,7-tetrakis (difluoramino) octahydro-1,5-bis(4-nitrobenzenesulfonyl)-1,5-diazocine with HNO_3/CF_3SO_3H at 55°C for 40 h [3]. However, the only known polymorph of HNFX is of specific gravity,

i.e., around 1.8 and thus is not suitable without the ability to generate polymorphs with higher density. The second material of our study, CL-20 was developed as a crystalline explosive at Naval Weapons Center at China Lake in 1989 [4]. Several polymorphs of CL-20 crystal exist due to the presence of different molecular conformations and arrangements in the lattice. ε, α, β, and γ forms of CL-20 can be prepared by recrystallization techniques and generally the mixture of polymorphs are present in the product. Currently the epsilon phase is the most desirable and under extensive investigation. It provides high density and high-energy output upon detonation. In general, the epsilon CL-20 is highly soluble in the solvents with carbonyl groups, and is relatively insoluble in hydrocarbons and materials containing ether linkages [4].

The objective of the overall investigation was to mathematically model the crystallization process to predict the polymorph/s to be generated and develop methods to detect the polymorph type using X-ray diffraction, XRD, in conjunction with Rietveld analysis. In Part I of this publication (this issue) various methods for the mathematical modeling of the crystallization from solution of CL-20 and HNFX were outlined and typical results for CL-20 and HNFX were provided. Here experimental results are provided aiming to investigate the efficacy of myriad methods of crystallization to influence the type of polymorph to emerge from the recrystallization process.

Experimental Methods

Our experimental methods included the following:

- Solubility tests for CL-20 and HNFX
- Microcrystallization of CL-20 and HNFX
- Material characterization by DSC, TGA, SEM and XRD.
- Polymorph analysis and validation using powder diffraction and Rietveld.

Several factors are involved in selecting a solvent for the recrystallization process. Besides health, safety and environmental concerns, other issues need to be considered such as

chemical reactivity, molecular bonding interactions, product yield, and the degree of solubility of the solute in the solvent, etc. A poor choice of solvent may limit the yield of crystals obtained during processing and also may limit the effectiveness of the separation. Hence, special attention is required in solvent selection. In this study we wished to obtain relevant data for all types of solvents; accordingly, a group of twenty one solvents, from three main categories were selected, to be investigated in the simulations and in the parallel experimental studies. The list of solvents with their chemical formulae and respective densities is presented in Tables 1 and 2. A brief description for each category is presented below.

Based on the nature of their molecular bonding interactions, solvents may be divided into three main classes [5].

- polar protic, e.g., water, methanol, acetic acid.
- dipolar aprotic, e.g., nitrobenzene, acetonitrile, furfural
- non-polar aprotic, e.g., hexane, benzene, ethyl ether

In polar solvents, the solvents molecules interact by forming strong hydrogen bonds. To have a reasonable solubility, the solute must be capable of forming hydrogen bonds, either because the solute itself is hydrogen bonded or because it is sufficiently basic to accept a donated hydrogen atom to form a hydrogen bond. If the solute is aprotic and not basic, it cannot form strong bonds with the solvent molecules and therefore will have a very low solubility.

In dipolar aprotic solvents, the solvent molecules interact by dipole-dipole interactions. If the solute is also dipolar and aprotic, it can interact readily with the solvent molecules forming similar dipole-dipole interactions. If the solute is non-polar it cannot interact with the dipoles of the solvent molecules and cannot dissolve. Protic solutes are soluble in basic dipolar aprotic solvents because strong hydrogen bonds are formed, replacing the hydrogen bonds between the solute molecules in the solid state. If a dipolar aprotic solvent is not basic, a protic solute will have a low solubility, because the strong hydrogen bonds in the solid state can only be replaced by weaker dipole-dipole interactions.

Table 1
Solvents used in this study

Solvents	Chemical formula	MW (g/mol)	Boiling temp (°C)	Density (g/ml)	δ (calculated)	δ^* (literature)
Acetic acid	CH_3COOH	60.05	117.9	1.049	–	12.4
Acetone	CH_3COCH_3	58.08	56.2	0.780	9.454	9.6
Acetonitrile	CH_3CN	41.05	81.6	1.340	–	11.7
Acetophenone	$C_6H_5COCH_3$	120.15	202.1	1.030	–	11.9
Chloroform	$CHCl_3$	119.38	61.2	1.492	–	9.2
Cyclohexane	C_6H_{12}	84.16	80.7	0.774	7.358	8.2
Cyclohexanone	$C_6H_{10}O$	98.15	155.0	0.947	–	–
Dichloromethane	CH_2Cl_2	84.93	39.8	1.325	–	9.6
Dimethyl sulfoxide	CH_3SOCH_3	78.13	189.0	1.101	12.93	12.8
DMF	$HCON(CH_3)_2$	73.10	153.0	0.944	12.14	11.5
Ethanol	C_2H_5OH	46.07	78.3	0.794	12.92	12.0

**Journal of Paint Technology*, Vol. 39, No. 505, Feb 1967.
**Handbook of Solubility Parameters*, CRC Press, 1983.
δ = Calculated solubility parameter from the Group molar attraction constants at 25°C.

Table 2
Solvents used in this study

Solvents	Chemical formula	MW (g/mol)	Boiling temp (°C)	Density (g/ml)	δ (calculated)	δ^* (literature)
Ethyl acetate	$CH_3COOC_2H_5$	88.10	77.1	0.902	8.918	9.1
Formamide	NH_2COH	45.04	210.0	1.134	–	–
Formic acid	HCOOH	46.03	100.8	1.220	–	–
Heptane	C_7H_{16}	100.21	98.4	0.684	7.460	7.4
Hexane	C_6H_{14}	86.18	68.7	0.659	7.341	7.3
Lactic acid	$CH_3CHOHCOOH$	90.08	122	1.219	–	–
Benzene	C_6H_6	78.11	80.1	0.874	–	9.2
Benzyl alcohol	$C_6H_5CH_2OH$	108.14	205.5	1.045	–	–
1,4-dioxane	$C_4H_8O_2$	88.11	101.2	1.034	–	10.0
THF	C_4H_8O	72.11	66.0	0.889	–	9.1
Toluene	$C_6H_5CH_3$	92.14	110.6	0.865	–	8.9
Water	H_2O	18.02	100.0	1.000	–	21.0

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**Handbook of Solubility Parameters*, CRC Press, 1983.
δ = Calculated solubility parameter from the Group molar attraction constants at 25°C.

In non-polar aprotic solvents, molecules interact by weak van der Waals forces. Dipolar and polar protic solutes are generally found to have very low solubilities in these solvents, except in cases where non-polar complexes are formed. We selected seven of each group for a total of twenty-one for both the simulations and the experimental studies. Simulations and experiments were carried-out in parallel. The selected solvents, and the solubility parameter of each solvent (for which data were available for the calculation or in the literature) are shown in Tables 1 and 2.

Solubility Experiments of CL-20 and HNFX

Solubility is a measure of the quantity of solute that will dissolve in a given quantity of solvent at a given temperature. Several factors can influence the solubility of a compound, among them: the nature of the solute and the solvent, it includes the molecular size and polarity. The polarity dictates the type of interactions in the solution. Other very important factors are the molecular weight, temperature and pressure. A description of the procedure used for the determination of the solubility of CL-20 and HNFX is given below.

a. Solubility at Room Temperature
Samples of HNFX and CL-20 were tested for solubility at room temperature. Small quantities of HNFX and CL-20 were weighed in transparent glass vials. Solvent at room temperature was added to each sample slowly in a drop wise fashion followed by a continuous swirling until step changes in refractive index associated with solubility limits could be observed.

b. Solubility at High Temperature
HNFX and CL-20 were also tested for solubility at temperatures greater than room temperature. The procedure followed was similar to the procedure specified above, except that in this case the solvent was initially at a greater temperature. Small quantities of HNFX were weighed in transparent glass vials. Solvent at the targeted temperature was added to each sample

slowly in a drop wise fashion followed by a continuous swirling till solubility changes were observed.

Micro-crystallization Experiments

Crystallization from homogeneous and supersaturated solutions is widely employed in the chemical and pharmaceutical industries as a solid liquid separation technique. While the process in the industry is typically applied in large volumes, understanding of the molecular level process plays a key role in the optimization and quality of the crystalline product. In our study micro-crystallization experiments were performed in parallel to the simulations for solvent screening and the validation of the numerical simulations. The experiments aimed at identifying the best solvent system for crystallization and to achieve higher density polymorphs.

Several conventional methods exist for crystallization. We have primarily used the methods of cooling, solvent evaporation, vapor-diffusion, and liquid-liquid diffusion methods. The sublimation method was not attempted here because of the energetic nature of the materials. Since we had limited quantities of HNFX (we worked with total sample sizes of 2 g in each shipment from China Lake) and CL-20 the experiments were carried out using sample sizes which were as small as possible. The typical weight of the HNFX used in each crystallization run was thus limited to be less than 50 mg. Some of the runs used only 10 mg of HNFX. Based on the computations and the solubility tests, solvents and antisolvents systems were selected, and the various crystallization methods were applied. The conventional procedure used for crystallization was as follows:

1. HNFX and CL-20 samples were dissolved in different solvents and solvent combinations at a given temperature. (To prevent any reaction to happen, the solvent was heated separated and added to the solute, HNFX and CL-20, slowly).
2. The solution was kept under continuous stirring under isothermal conditions, until supersaturation was

obtained (If antisolvent was included it was also added and the solution was allowed to cool).
3. The sample was placed either at room temperature (for solvent evaporation slowly) or in the freezer (for cooling to decrease the solubility of the HNFX and CL-20) to generate HNFX and CL-20 crystals.
4. The HNFX and CL-20 crystals obtained were kept under vacuum at least overnight.
5. After drying the crystals were observed under polarized microscopy and SEM first and then analyzed using powder diffraction, XRD. (Some of the samples were also crystallized over longer time periods in attempts to obtain single crystals, which were adequate for single crystal X-ray analysis).
6. Recrystallization in presence of additives or habit modifiers and with micromixing as a parameter were also attempted.

In our efforts to identify a new polymorph of HNFX, recrystalization in conjunction with other novel techniques were also investigated. These additional recrystallization experiments included the following.

- Recrystallization upon freeze drying
- Recrystallization under UV exposure
- Recrystallization after annealing
- Recrystallization after microwave exposure
- Recrystallization in a viscous gel

The method of choice for the recrystallizations was a slow evaporation method except in the case of freeze drying and microwave. A description of each technique follows.

Recrystallization by Lyophilization (Freeze Drying)

Lyophilization, commonly referred to as freeze drying, is the process of removing water or solvent from a product by sublimation and desorption. This technique is occasionally used for drying of high-quality products in the pharmaceutical and food industries. In the field of material science, only few cases

have been reported regarding the use of this method (for example in the synthesis of $PbTiO_3$, $Ba_2Ti_9O_{20}$ powder and lead magnesium pyrochlore phase) [6]. The freeze-drying process is known to ensure high quality grains with a homogeneous distribution of particles. For pharmaceutical compounds that undergo degradation, lyophilization offers a means of improving their stability and shelf life.

From a general point of view, the freeze drying method involves the dehydration of a frozen product (which is a solution in the case of crystallization) based on solvent sublimation. The conditions in the process are varied (according to the material being treated) to ensure that the resulting product has the desired physical and chemical properties and that the required stability is achieved. The fundamental process steps are [7]:

1) Freezing: The product is frozen. This provides a necessary condition for low temperature drying. The freezing is usually performed by vaporization of the solution under liquid nitrogen or carbon dioxide. The goal is to freeze the mobile water or solvent in the product. A fast freezing is important for the homogeneity of the product.
2) Vacuum: After freezing, the product is placed under vacuum. This enables the frozen solvent in the product to undergo sublimation.
3) Heat: Heat is applied to the frozen product to accelerate sublimation.
4) Condensation: Low temperature condenser plates remove the vaporized solvent from the vacuum chamber. This completes the process.

The lyophillization equipment used consisted of a drying chamber with temperature controlled shelves, a condenser to trap water or solvent removed from the product, a cooling system to supply refrigerant to the shelves and condenser, a vacuum system to reduce the pressure in the chamber, and another condenser to facilitate the drying process. Based on the understanding of the differences in the molecular configuration and thermal vibration of molecules at low temperatures

and in different solvents, we investigated the possibility of growing HNFX by the freeze drying process.

Recrystallization solutions of 10 mg of HNFX were prepared in acetic acid, formic acid, and water. These solvents were selected because of their low freezing points, and their ability to crystallize HNFX, especially in the case of acetic acid and formic acid. Water was used as a standard for verification. The recrystallization solutions were initially frozen by using carbon dioxide. The recrystallized HNFX samples were then analyzed by XRD. Each experiment was reproduced a number of times.

Recrystallization in the Presence of Habit Modifiers

The presence of impurities or additives in a crystallizing system can have a drastic effect on the nucleation and growth of crystals. Various impurities can suppress growth entirely. On the other hand some impurities can enhance growth, while others may exert a highly selective effect, acting only on certain crystallographic faces and thus modifying the crystal habit. Some impurities can exert an influence at very low concentrations, less than one part per million, while others need to be present in fairly large amounts before having any effect [5].

Myerson [8] has listed common additives affecting the growth of crystals and their possible morphology changes. These additives are mostly metal ions, which can be purposely added but are more often unavoidably present in the crystallization solution. The relationship between the chemical structure of the ionic additive and the structural characteristics at the crystal-liquid interface is known to be of importance in determining the relative efficacy of many of these additives [9].

An important class of additives are the so-called ''tailor-made'' additives, which are designed to interact in very specific ways with selected faces of crystalline materials. These additives are designed to contain some chemical groups or moieties that mimic the solute molecules and are thus readily adsorbed at the growth side on the crystal surface. The effect of these additives on crystallization is significant growth reduction

and enlargement of the affected faces. Based on this approach, it is potentially feasible to systematically modify the morphology of the crystals by tailoring additives to bind at pre-selected faces, thus changing growth rate in a predictable manner [10].

The effects of additives in the growth of HNFX were investigated by using hydrated sodium borate, (Borax), ethylenediaminetetra acetic acid, (EDTA), sodium citrate, and malic acid. Recrystallization solutions of 10 mg of HNFX were prepared in ethanol and ethylacetate and small quantities (< 1 mg) of the additives Borax, EDTA, sodium citrate and malic acid were added (independently) to the recrystallization solutions.

Recrystallization by Using Seeding

Recrystallization by seeding with other energetic materials which exhibit relatively high densities including HMX and RDX was also performed. In this case acetic acid was used as the solvent. A small amount (< 1 mg) of the seed HMX or RDX, was added to the recrystallization solutions. In all cases the slow evaporation method was used. The recrystallized samples were then examined by XRD analysis.

Recrystallization under UV Exposure

Ultraviolet (UV) light with wavelengths between 100 and 400 nm is divided into four sub-bands with the division in sub-bands connected to the human skin sensitivity. UV light is capable of disinfecting water, and/or air purification in order to render any pathogens inactive or initiate photochemistry that can remove (i.e., oxidize) chemical contaminants or cause chemical transformations on a surface. The effect of UV light in HNFX crystallization was investigated. Recrystallization solutions of HNFX in acetic acid and DMSO were prepared and set under UV light overnight. We have used both short and long waves.

- Short Wave Length, or UVC ranging from 200–280 nm, the UVC has general germicidal power. These wavelengths are absorbed by proteins, DNA and RNA and

it can lead to cell mutation. In microorganisms it can lead to their "inactivation." Eye and skin protection is required.

- Long Wave Length or UVA ranging from 320–380 nm.

Crystals were grown over 24 hours period. The samples obtained were analyzed by XRD.

Recrystallization upon Exposure to Microwaves

The microwaves can be used to drive chemical reactions. This in situ mode of energy conversion has many attractions to chemists [11,12] on the basis of reaction selectivity. Some of the advantages of this method are given in [13]. Recrystallization of HNFX was also carried out upon microwave exposure. The crystals grown by this method were then subjected to microscopy and analyzed by XRD. The typical procedure was as follows.

1. 30 mg of HNFX was placed in a 25 ml Erlenmeyer flask
2. 5 ml of acetonitrile solvent was added to this sample
3. The sample was placed in a microwave oven and irradiated for 20 seconds at 100 Watts
4. It was taken out from the microwave when all the solid was dissolved
5. 10 ml of hexane solvent was added
6. The entire mixture was placed again in a microwave oven and irradiated for 30 seconds at 100 Watts.
7. The sample was taken out when the volume of the residual liquid was about 6 ml.
8. It was allowed to cool in a hot water bath to room temperature when white crystals appeared.
9. The sample was set apart and allowed to complete the crystallization
10. After complete crystallization, the solution was filtered and crystals were collected
11. The crystals were dried in an oven at 30°C
12. The sample was analyzed by XRD

Recrystallization under Different Micro-Mixing Regimes

Mixing is critical to attain product quality and uniformity and is an important parameter in the crystallization process. We have investigated the effect of micro-mixing on the crystallization of HNFX. The effect was investigated by using three common micro-mixing techniques: sonication, vessel rotation at 600 rpm, and magnetic stirring while the crystallization took place. The procedure followed is the same as described for a general micro-crystallization experiment, except that a given type of micro mixing technique was used during the crystallization process. The crystals obtained in each case were examined in the same fashion as the other samples and the effect of micro-mixing was evaluated as a function of particle size. In these experiments the solvent used was benzene. This solvent was selected because its unusual ability at growing HNFX in very large crystals shapes (mostly hexagonal, cubic or square) thus offering an interesting packing feature for HNFX.

Recrystallization after Annealing

Annealing process is generally used to relax residual stresses, to induce softness, to modify ductility, and to alter electrical, magnetic, or other physical and mechanical properties, to change the crystalline structure, to remove gases, and to produce a definite microstructure. We have carried out our recrystallization experiments of HNFX after annealing HNFX at various temperatures for different lengths of time. The size of the sample, the temperature, and the annealing times were selected upon consideration of the inherent limitations of the material (such as the energetic nature of the material, the decomposition temperature of the material) and the appropriate safety practices of the experiment.

Temperatures of 50, 100, and 150°C were used for annealing of the HNFX powder, prior to dissolution, using durations of thirty minutes, one, two, four, and six hours. The size of the sample was 15 mg and the solvent used was ethanol. The

Table 3
Crystallization after annealing at different temperatures and different length of times

HNFX (mg)	Annealing temperature (°C)	Annealing time (h)	Solvent (ml)
15	50	30 minutes	Ethanol
15	100	30 minutes	Ethanol
15	150	1 hour	Ethanol
15	150	2 hrs	Ethanol
15	150	4 hrs	Ethanol
15	150	6 hrs	Ethanol

temperature and respective annealing time used in each experiment are shown in Table 3.

Recrystallization in the Presence of High Molecular Weight Polymers

In addition to all the recrystalization experiments described above, recrystallization in the presence of high molecular weight polymers used as antisolvents was also carried out. The use of the polymer increases the viscosity of the medium and can alter the dynamics of the crystallization by especially altering diffusion rates during crystallization. In these experiments the slow evaporation method was used in conjunction with polyethylene glycol and poly(dimethyl siloxane).

Material Characterization and Polymorph Analysis

In our study we have used thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray- powder diffraction (XRD), scanning electro microscopy, and polarized microscopy for the characterization of the morphology and polymorph type of HNFX crystals along with their decomposition characteristics. TA Instruments DSC Q1000 and a TGA

Q500 were used. We have used a Miniflex Rigaku X-ray diffractometer in conjunction with Jade 3.1 for the powder diffraction analysis of the crystals and the characterization of their polymorph types. The recrystallized HNFX was always ground prior to XRD to eliminate texturing and orientation effects.

Rietveld analysis was carried out for the validation of the conclusions of the powder diffraction experiments. In the Rietveld method the least-squares refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models of the crystal structure. Rietveld analysis represents a solid link between theoretical and experimental studies by providing insight into structure-property relationships, and allowing the further refinement of the structural model using the experimental data and the accurate determination of structural parameters and relative phase proportions on samples with multiple polymorphs or containing polymorph impurities.

For Rietveld analysis we have used the Rietveld module of Cerius^2. The Rietveld module functions in Cerius^2 are performed via an interface to the DBWS-9006 program of Sakthivel and Young for Rietveld refinement of crystalline structures and via an interface to the Structural Analysis System (GSAS) program of Larson and Von Dreele. Both the Rietveld (DBWS) and the Rietveld (GSAS) use the least square refinement techniques [Cerius^2].

Rietveld refinement iteratively improves the parameters of an approximate (trial) structure to maximize the agreement between simulated and experimental X-ray diffraction patterns. The process usually requires many successive stages. A periodic crystal model is used. Once the trial structure has been built or read and an experimental powder diffraction pattern has been loaded, the refinable parameters are chosen, and the Rietveld refinement is run. When a refinement run is completed, the model and the parameter values are automatically updated with all the calculated changes. Differences of the experimental and simulated diffraction patterns are displayed. A summary of the procedure is the following.

1. Load the trial structure
2. Load the experimental powder pattern
3. Calculate a diffraction pattern
4. Calculate the Rietveld R-factor
5. Perform the Rietveld refinement
6. First refinement stage: Background, intensity factor, and cell dimensions
7. Second refinement stage: peak profile refinement
8. The experimental and simulated patterns differences are displayed
9. Examine the result

Results and Discussion

Solubility tests for HNFX in twenty one solvents that included three classes of solvents (polar, dipolar aprotic, and non-polar aprotic solvents) were performed at two temperatures. In general, polar protic solvents such as acetic acid, ethanol, and methanol dissolve HNFX very well. The same is true for dipolar aprotic solvents such as acetonitrile, DMSO, and dimethyl formamide. Non-polar aprotic solvents such as chloroform, dichloromethane, hexane and heptane give rise to relatively low solubility of HNFX. Water, which is a polar protic solvent also exhibits low solubility. The solubility results for all the solvents at ambient temperature are shown in Tables 4 and 5. Acetone, acetophenone, acetonitrile, benzyl alcohol, cyclohexanone, 1-4-dioxane, ethyl acetate, and DMSO exhibited high solubility for HNFX at room temperature. Ethanol, acetic acid, and formamide exhibited moderate solubility at ambient temperature. Benzene, chloroform, dichloromethane, hexane, heptane, lactic acid, toluene, and water exhibited low solubility at ambient temperature.

The solubility results for all solvents at the higher temperature (60 to 100°C, selected on the basis of the boiling point limitations of the solvent) are shown in Tables 6 and 7. Acetone, acetophenone, acetonitrile, acetic acid, benzyl alcohol, cyclohexanone, DMSO, ethyl acetate, ethanol, formic acid, tetrahydrofuran (THF), and lactic acid gave rise to relatively high

Table 4
Solubility of HNFX at room temperature

Solvents	Temp (°C)	Solubility
Acetone	24	√
Acetophenone	24	√
Ethyl acetate	24	√
Heptane	24	Δ
Water	24	Δ
Chloroform	24	Δ
Dichloromethane	24	Δ
Hexane	24	Δ
Ethanol	24	Δ√
Cyclohexanone	24	√
Acetonitrile	24	√

√ = High solubility.
Δ√ = Moderate solubility.
Δ = Low solubility.

Table 5
Solubility of HNFX at room temperature

Solvents	Temp (°C)	Solubility
Acetic acid	24	Δ√
Formic acid	24	Δ√
Formamide	24	Δ√
Dimethyl sulfoxide	24	√
Lactic acid	24	Δ
1-4-dioxane	24	√
Toluene	24	Δ
Benzene	24	Δ
Benzyl alcohol	24	√
Tetrahydrofuran	24	√

√ = High solubility.
Δ√ = Moderate solubility.
Δ = Low solubility.

Table 6
Solubility of HNFX at higher than ambient temperatures

Solvents	Temp (°C)	Solubility
Acetone	68.8	√
Acetophenone	100.0	√
Ethyl acetate	77.0	√
Heptane	98.4	Δ
Water	100.0	Δ
Chloroform	61.0	Δ√
Dichloromethane	40.0	Δ√
Hexane	68.7	Δ
Ethanol	77.0	√
Cyclohexanone	100.0	√
Acetonitrile	81.0	√

√ = High solubility.
Δ√ = Moderate solubility.
Δ = Low solubility.

Table 7
Solubility of HNFX at higher than ambient temperatures

Solvents	Temp (°C)	Solubility
Acetic acid	100.0	√
Formic acid	100.0	√
Formamide	100.0	Δ√
Dimethyl sulfoxide	100.0	√
Lactic acid	100.0	√
1-4-dioxane	100.0	√
Toluene	100.0	Δ√
Benzene	80.0	Δ√
Benzyl alcohol	100.0	√
Tetrahydrofuran	66.0	√

√ = High solubility.
Δ√ = Moderate solubility.
Δ = Low solubility.

solubility of HNFX at the higher temperature. HNFX in benzene, chloroform, dichloromethane formamide, and toluene exhibited moderate solubility. HNFX in heptane, hexane and water exhibited low solubility at the higher temperatures.

Micro-crystallization Experiments and Analysis of HNFX Crystals

Conventional Crystallization Experiments. Micro-crystallization experiments (in a single solvent or in a solvent-antisolvent system) were performed in parallel to the simulations for solvent screening and the validation of the numerical simulations. While all the main methods commonly used for crystallization, such as cooling, evaporation, vapor-diffusion, and liquid-liquid diffusion were used, due to the energetic nature of the material, easiness and safety, the slow cooling and slow evaporation methods were the preferred methods. Since we had access to only limited quantities of HNFX (4 g total for the two shipments received), the sample size in the experiments was limited to 10 mg in most of the cases. The procedure used for the crystallization was described earlier in the method section.

The crystals obtained from the micro-crystallization experiments in each of the solvents tested were characterized by analytical techniques available at HFMI (described in the methodology section). The presence of polymorphs was investigated by microscopic observation and powder diffraction techniques. All the crystallized samples were evaluated. As basic reference scanning electron micrographs and the XRD patterns of the starting material received from China Lake are shown in Fig. 1. The typical morphological features of the crystals upon optical microscopy obtained from our initial experiments are presented in Fig. 2. The corresponding XRD pattern is also presented in Fig. 2. These samples were grown using chloroform. Overall, the morphologies obtained and the powder diffraction pattern results were reproducible. The powder diffraction patterns and the subsequent Rietveld analysis invariably revealed the crystallization of solely the R-3 polymorph, which

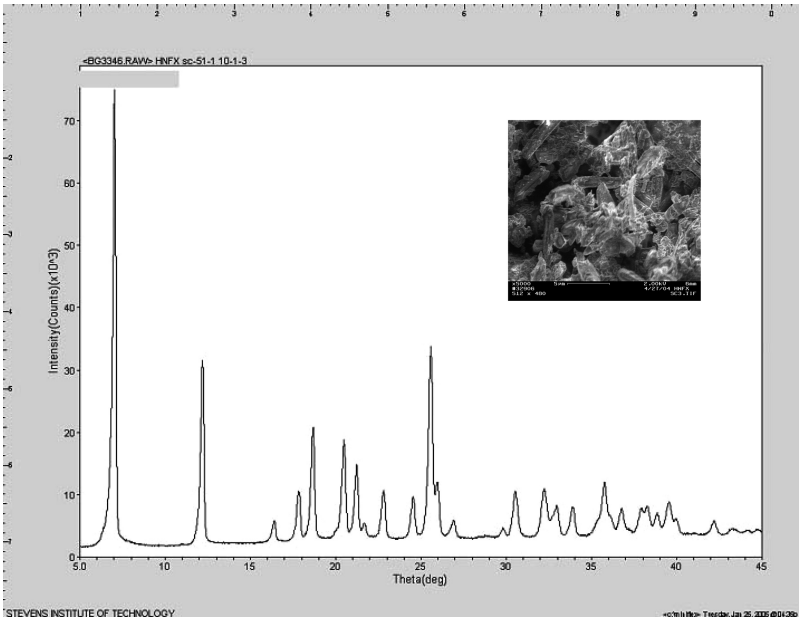

Figure 1. XRD pattern of HNFX original sample.

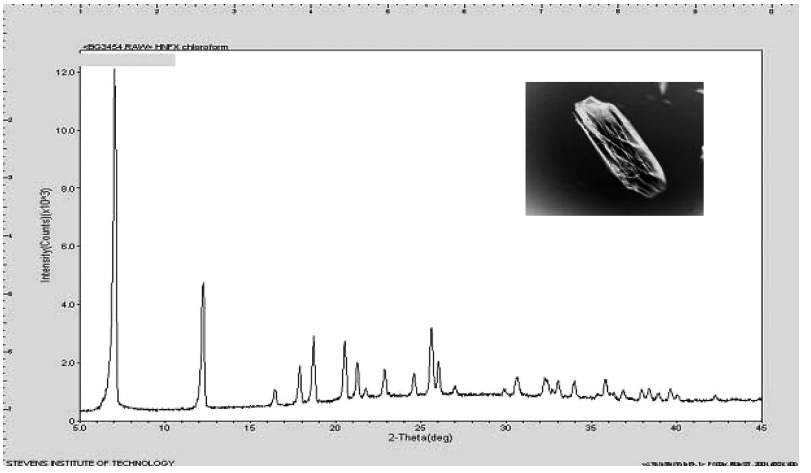

Figure 2. HNFX in chloroform ($CHCl_3$).

is the same low-density polymorph of the original HNFX received from China Lake.

Typical micrographs obtained from the micro-crystallization experiments in a single solvent or in solvent-antisolvent system, as well as their respective XRD patterns are shown in Figs. 3 to 10. The typical crystallization result for a polar protic solvent, i.e., benzyl alcohol, is shown in Fig. 3. Figure 4 exhibits the result for dipolar aprotic solvents, i.e., cyclohexanone. This is one of the cases, which generated a false positive change in the diffraction pattern, which turned out to be related to chemical changes and not a change in the polymorph type (similar effects in Fig. 10). Figure 5 presents the typical recrystallization results for non-polar aprotic solvents, i.e., benzene here. In all of these results, along with

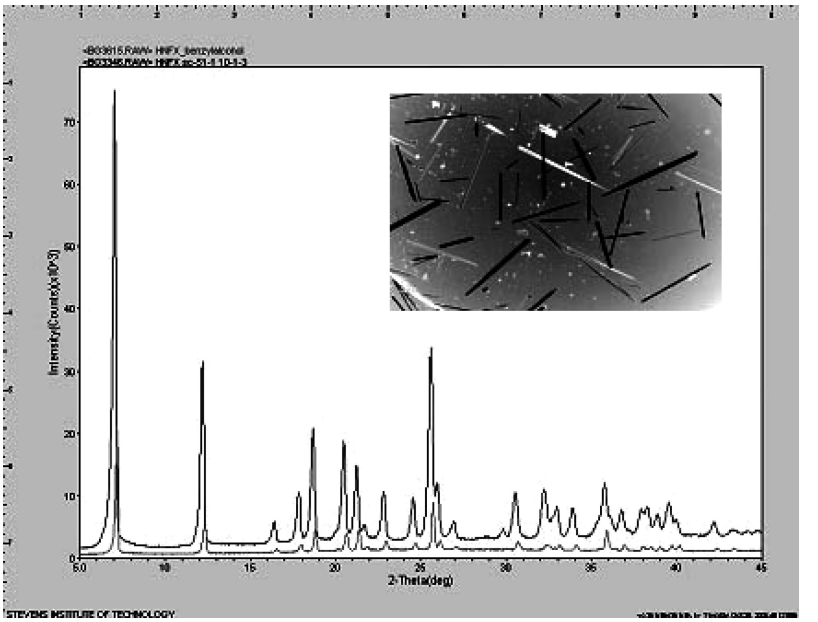

Figure 3. A comparison of the XRD pattern of the sample from benzyl alcohol with the HNFX XRD pattern of HNFX original sample.

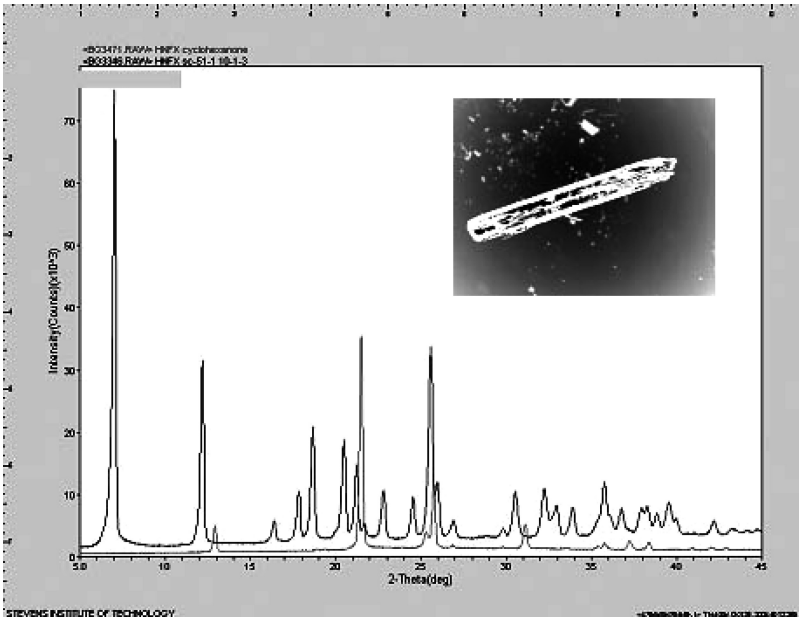

Figure 4. A comparison of the XRD pattern of the sample from cyclohexanone with the HNFX XRD pattern of HNFX original sample.

similar results obtained for the rest of the 21 solvents used in the recrystallization, the powder diffraction pattern and the concomitant Rietveld analysis revealed that only the Ci R3 polymorph of HNFX was obtained. Similar results were obtained upon using mixtures of solvents.

Thus, overall, all of the powder diffraction patterns of the recrystallized HNFX in the various solvents upon conventional recrystallization were the same as the powder diffraction pattern of the starting HNFX sample from China Lake. Thus, none of the conditions tested gave rise to a polymorph, which was different than the starting R-3 polymorph. This was confirmed with the additional precision of the Rietveld analysis, to indicate the dominant formation of the stable R-3 polymorph regardless of which solvent or solvent combination used in the analysis.

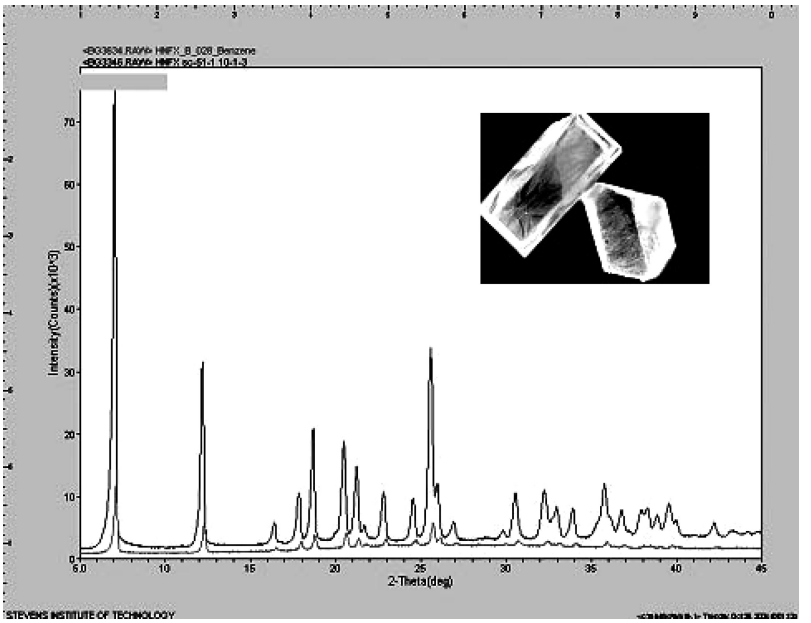

Figure 5. A comparison of the XRD pattern of the sample from benzene with the HNFX XRD pattern of HNFX original sample.

Recrystallization upon Annealing. The samples obtained by re-crystallization of HNFX after annealing at 50, 100 and 150°C for thirty minutes, one, two, four, and six hours, were examined by XRD. The XRD patterns again indicated that there was no change in the polymorph type from the as-received R-3. The resulting crystals exhibited high aspect ratios and were needle like.

Recrystallization by Freeze-Drying. The results for the re-crystallization experiments upon freeze-drying are presented in Fig. 6. Two solvents, acetic acid and formic acid were employed and water was used as the standard for verification. The crystals obtained using acetic acid, formic acid, and water were very small ($<50\,\mu m$), uniform and needle-shaped. However no changes in the polymorph type from the

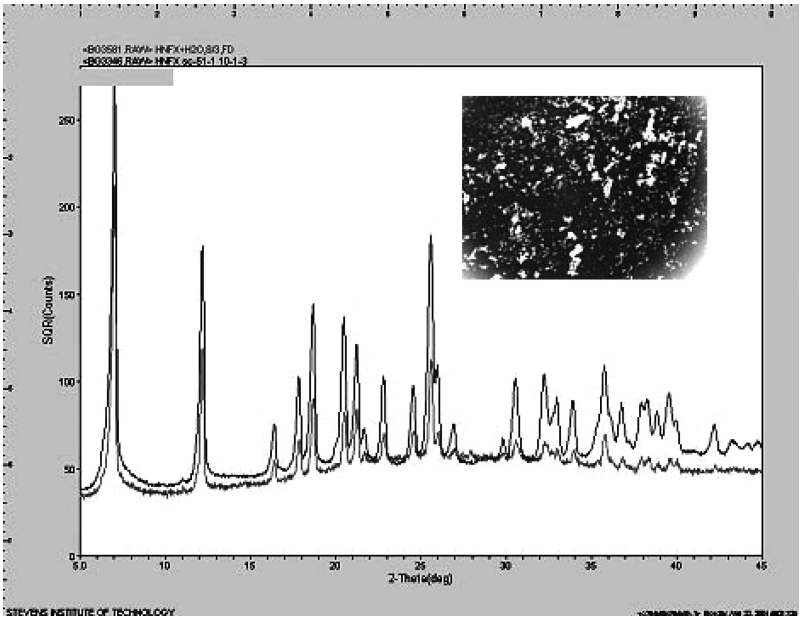

Figure 6. A comparison of the XRD pattern of the sample from water by freeze drying with the HNFX XRD pattern of HNFX original sample.

as-received R-3 upon recrystallization using freeze-drying were detected as shown in the X-ray powder diffraction pattern included in Fig. 6.

Recrystallization in the Presence of Additives or Habit Modifiers. As indicated earlier, HNFX was also recrystallized in the presence of small quantities ($\sim$1 mg) of various habit modifiers, including, Borax, EDTA, sodium citrate, and malic acid in conjunction with ethanol and ethyl acetate. These additives to crystallization had no influence and the resulting crystals were the same in terms of the polymorph type (R-3) and crystal morphology (high aspect ratio, needle-like crystals) with the HNFX grown in the same solvents and using the same procedures but without the presence of these modifiers. No systematic study of the effect of the concentrations of

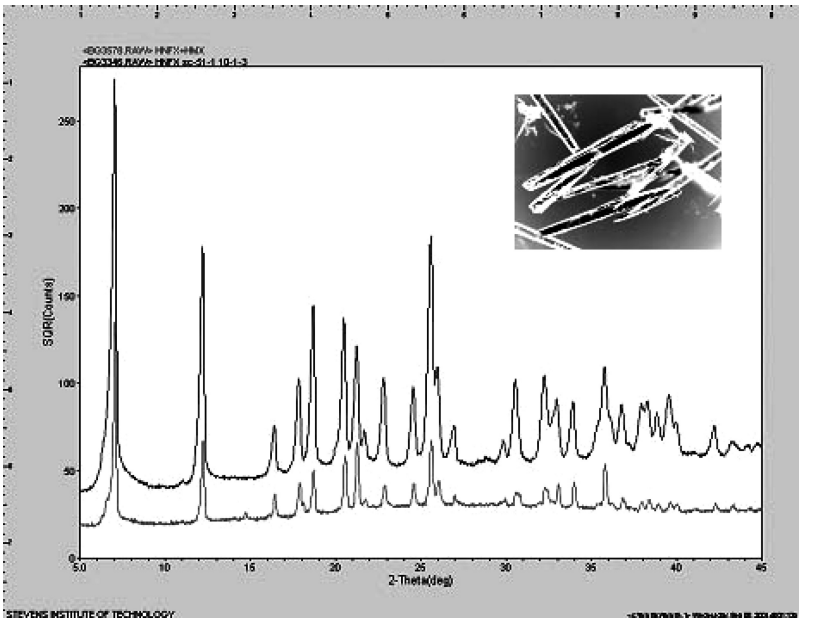

Figure 7. A comparison of the XRD pattern of the sample from acetic acid-HMX by seeding with the HNFX XRD pattern of HNFX original sample.

the potential habit modifiers could be made. The theoretical tools for this task are not very well developed and current efforts without breakthroughs in our detailed understanding as to how the habit modifiers need to be tailored to give rise to a targeted polymorph would be only labor intensive and empirical in nature.

Seeding with Higher-Density Energetic Crystals. Crystals may be crystallized by using seeds of another crystal to act as substrates on which the desired crystal would grow. For example, currently RDX is crystallized industrially by using ground seeds of HMX (typically few pounds of HMX to generate thousands of pounds of RDX). The idea of generating higher density polymorphs by starting with some of the only few available nitramines with the requisite high densities was

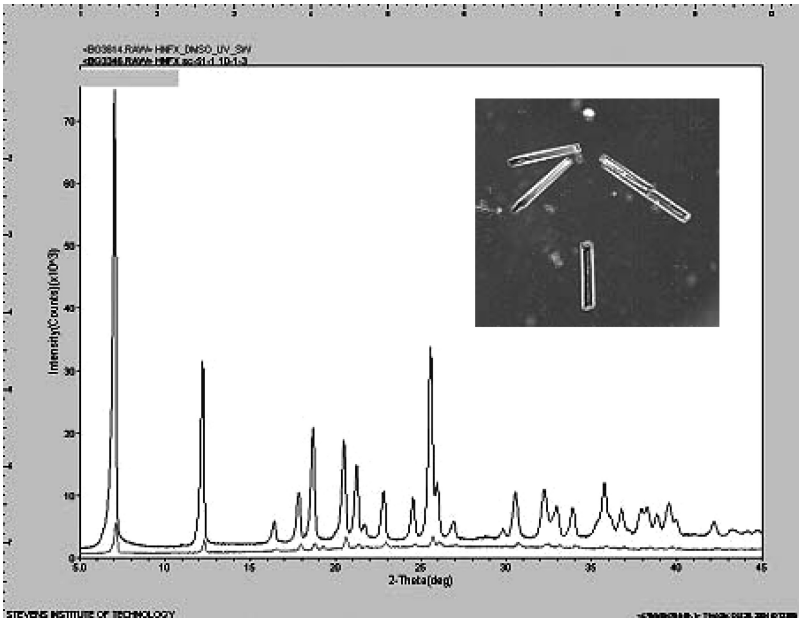

Figure 8. A comparison of the XRD pattern of the sample from DMSO under short wave UV with the HNFX XRD pattern of HNFX original sample.

tested by seeding with HMX and RDX. The typical XRD pattern presented in Fig. 7, i.e., for HMX seed crystals here, suggests that there were no detectable changes in the polymorph from the as-received R-3.

Recrystallization under UV Exposure. The effects of exposing the HNFX during crystallization to UV light were also tested. Solutions of HNFX in acetic acid, and DMSO were set under UV light overnight at short wavelengths (200–280 nm), and long wavelengths (320–380 nm). The typical micrograph and the XRD pattern of the resulting HNFX, i.e., for short-wave UV here, are shown in Fig. 8. For both wavelength ranges, the needle shape was dominant. Recrystallization under short-wave UV produced fast growing needle-shaped crystals. On the other hand, long-wave UV induced defects in the

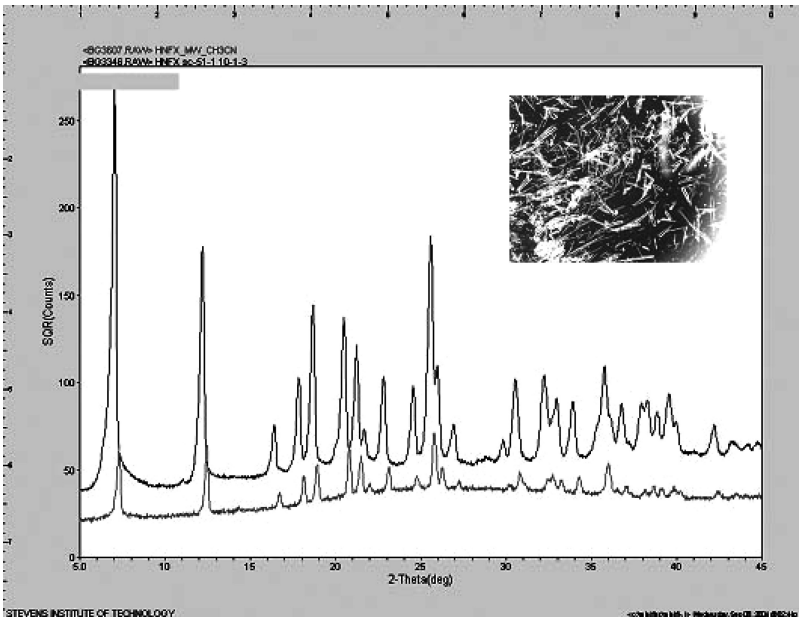

Figure 9. A comparison of the XRD pattern of the sample from acetonitrile after microwave exposure with the HNFX XRD pattern of HNFX original sample.

crystal faces and limited the crystal growth in some cases. Distorted and collapsed crystal shapes were observed in these samples. In contrast to the original needle-shaped crystals of HNFX, bifurcated or split crystal shapes emerged. However, the changes in morphology had no influence on the polymorph type as indicated by the XRD spectra of the samples, which remained similar to the as-received R-3 and no other polymorph impurities were detected.

Recrystallization upon Microwave Exposure. Recrystallization of HNFX upon microwave exposure was also examined and the typical micrograph and XRD powder diffraction pattern of the resulting HNFX crystals grown by this method are shown in Fig. 9, i.e., using acetonitrile as the solvent here. The recrystallization upon microwaving also produced needle shape

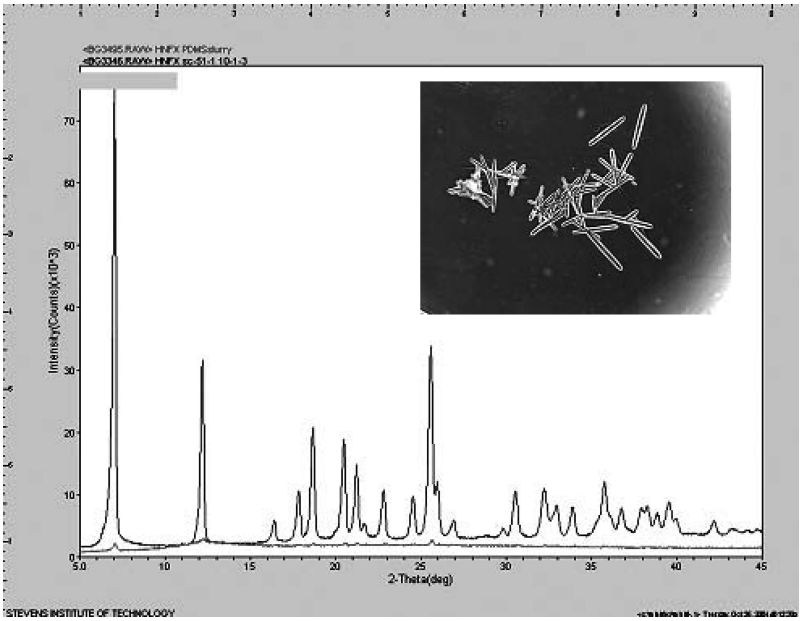

Figure 10. A comparison of the XRD pattern of the sample from PDMS with the HNFX XRD pattern of HNFX original sample.

crystals. The XRD pattern was similar to the R-3 polymorph, as of the as-received HNFX.

Recrystallization with Differing Hydrodynamics and Micro-Mixing Conditions. The effects of three common micro-mixing techniques: sonication, vibration, and magnetic stirring were investigated during the micro-crystallization experiments of HNFX. The crystals obtained in each case were again examined by microscopy and XRD. Different particle sizes could be obtained as a function of the micromixing conditions. However, no changes in the polymorph type were observed.

Recrystallization with High Molecular Weight Polymers. Recrystalization experiments in the presence of polymers including polyethylene glycol, and poly (dimethyl siloxane), PDMS, were

carried out. In some of these experiments the polymer was used as the antisolvent and in some other cases, in spite of the very limited solubility of HNFX in the polymers, the polymer was used as the high molecular weight solvent. The typical results using PDMS and poly(ethylene glycol) are presented in Fig. 10, where very fine uniform crystals are shown to be generated for both polymers. The predominant shape was a needle or rod-like shape. During crystallization the presence of the high molecular weight polymer decreases the rate of diffusion of HNFX and also reduces the rates of convection. However, overall the inclusion of the high molecular weight polymers gave rise to no change in the polymorph type from the as-received R-3.

Other Experimental Techniques for Analysis of Crystallized HNFX. As part of the validation experiments differential scanning calorimetry and thermo gravimetric analyses were performed on the crystallized samples and were compared with the DSC analysis of as-received samples. The TGA experiments were also performed at different temperatures (100, 150, 200, 250°C.) using systematically varied conditions of sample weight and heating rate to determine thermal stability, decomposition temperature, composition, moisture, and volatile contents. The rate of decomposition increased to appreciable values at around 170°C, which stayed consistent from sample to sample, although differences in the rate could be seen.

Overall, the powder diffraction pattern of the as-received HNFX and the HNFX we crystallized under a myriad set of conditions yielded a structure that was consistent with the single crystal data reported in the literature. In our experiments we occasionally ran into significantly different X-ray powder diffraction patterns, which appeared promising initially, but turned out to be related to various types of solvent and chemical reaction effects. We did not make an effort to document these false positives. Thus, all of the experimental conditions using traditional solvents/antisolvents and crystallization methods that we tested resulted in the formation of solely one

polymorph, which pertained to the polymorph type of the as-received HNFX crystals (Ci R-3).

Experimental Results for CL-20

The X-ray diffraction data collected for pure samples of the four different known polymorphs of CL-20 are shown in Figs. 11 to 13 for the ε, α and β polymorphs along with the simulated X-ray powder diffraction patterns for the three polymorphs. The simulated and the experimental powder diffraction patterns agree with each other. These results were used as the basis for the detection and determination of the different types of polymorphs which were predicted to occur with high probability and if possible to select recrystallization conditions which would be more likely to generate the desired pure epsilon polymorph of CL-20.

X-ray diffraction data of the pure polymorphs, as well as the X-ray diffraction patterns predicted for the pure polymorphs

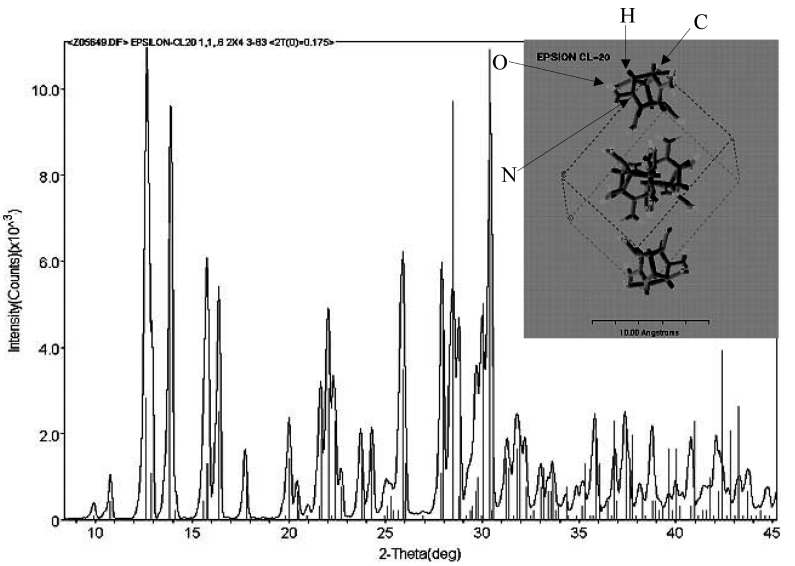

Figure 11. X-ray diffraction pattern for epsilon CL-20.

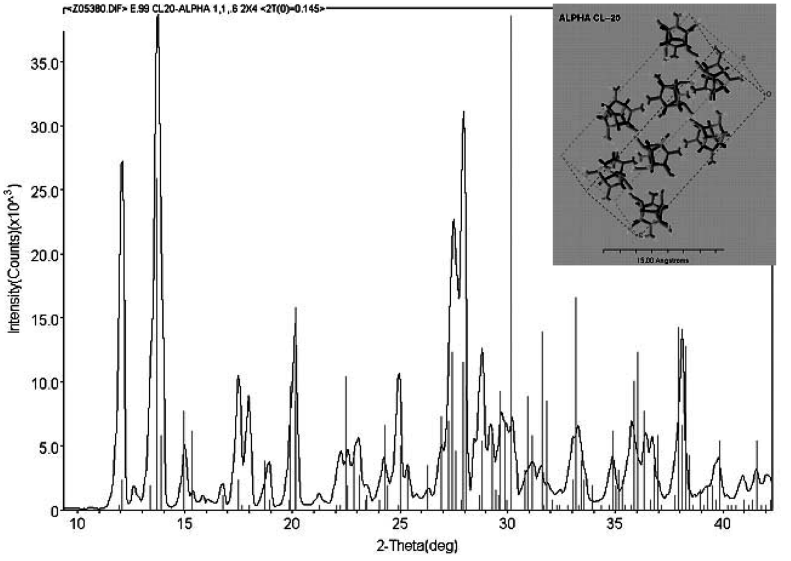

Figure 12. X-ray diffraction pattern for alpha CL-20.

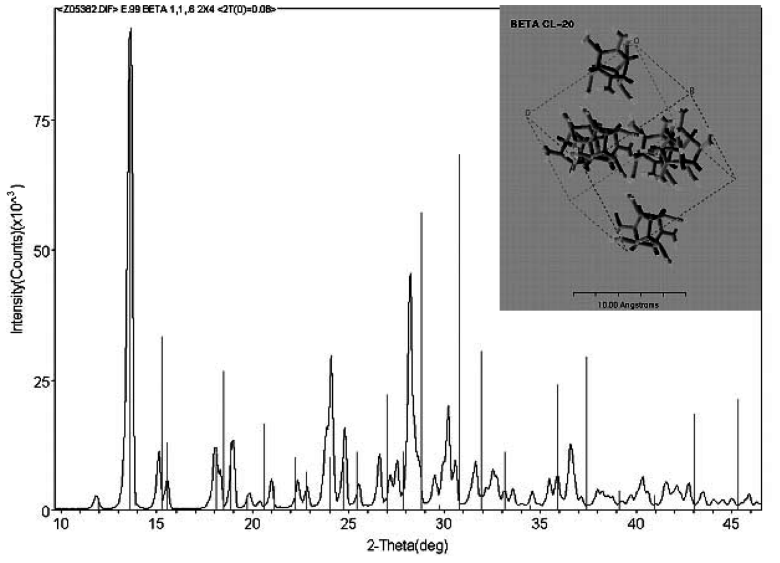

Figure 13. X-ray diffraction pattern for beta CL-20.

reveal the presence of peaks largely associated with various polymorphs. Starting with the available polymorphs samples, their combinations consisting of different percentages of polymorphs were prepared to act as calibration standards for ready determination of the polymorph types in the CL-20 crystallites. For example, Fig. 14 shows the X-ray diffraction data collected with a series of three samples with differing ratios of epsilon to alpha (.2%, 2%, and 5% of alpha in epsilon/alpha mixture). Upon the preparation of easy-to-use calibration curves (Fig. 15), such X-ray diffraction data provided the means to determine the percentages of polymorph impurities generated upon crystallization.

These methods were then used to determine conditions under which relatively pure polymorphs of CL-20 could be crystallized. As an example, let us consider a set of two crystallization conditions. For both experiments the solvents were acetophenone and xylene. The antisolvent was a high molecular weight polymer, i.e., poly(dimethyl siloxane), PDMS. The crystallization temperature was 10°C. Both batches contained the same amount of epsilon Cl-20 as the seed. However, more

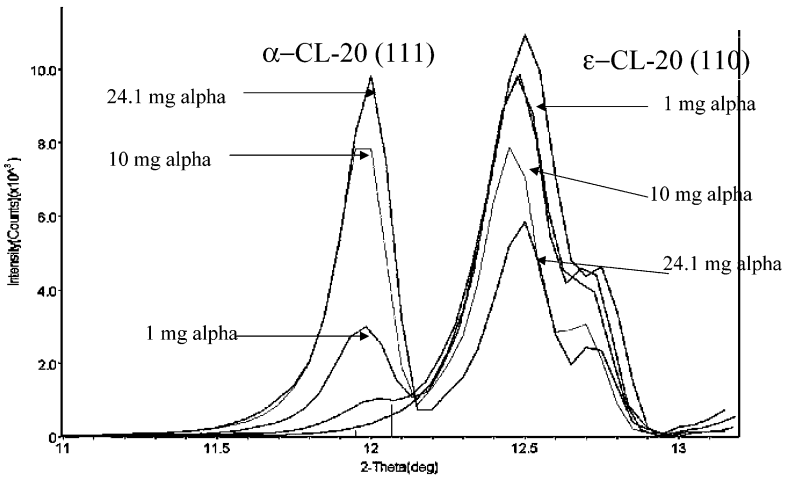

Figure 14. Alpha mixed with 425.7 mg epsilon-CL-20.

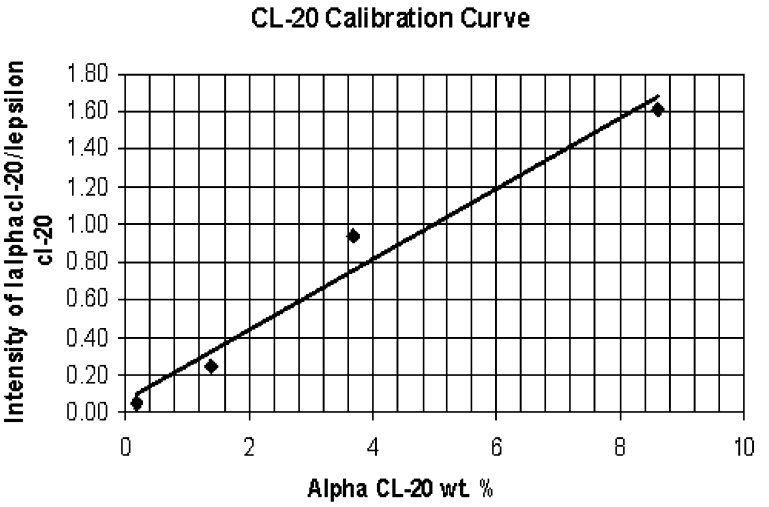

Figure 15.

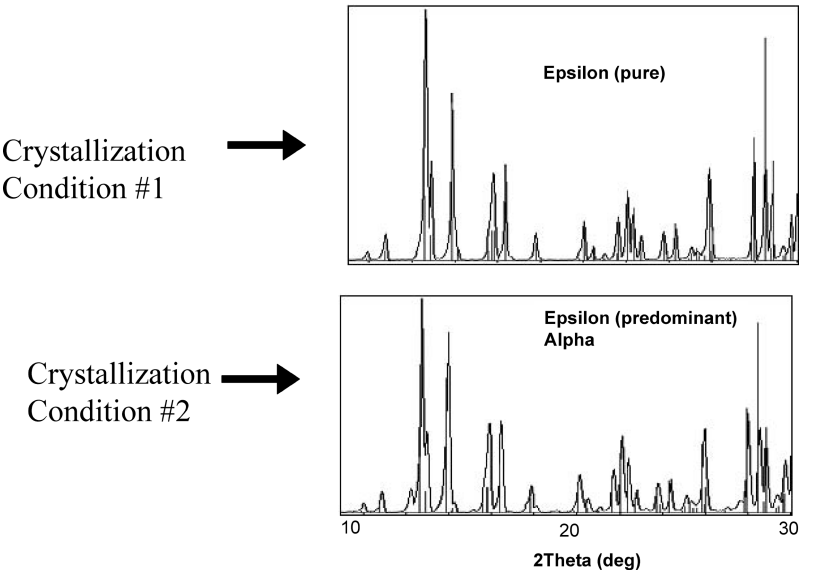

Figure 16. Crystallization conditions and X-ray powder diffraction results.

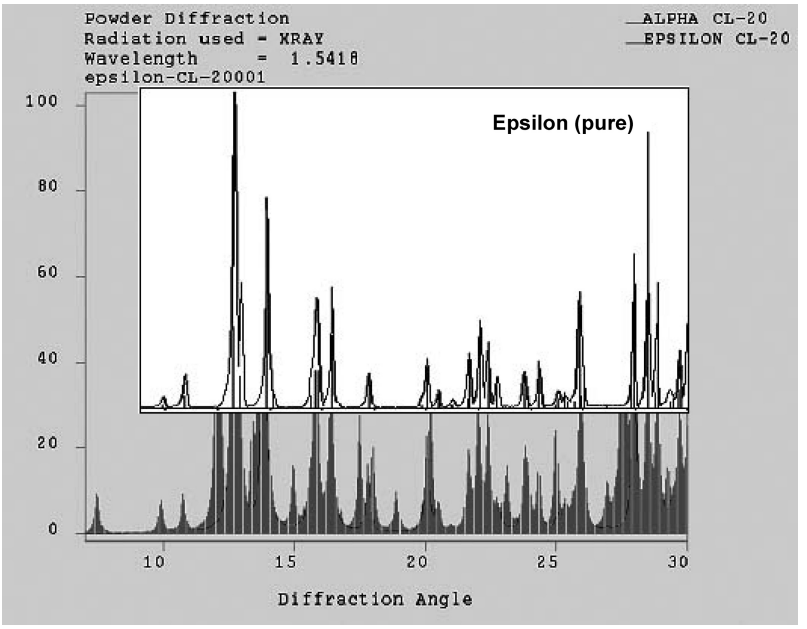

Figure 17. Simulated X-ray powder diffractions of alpha and epsilon CL-20 compare to experimental data.

PDMS was used for the first experiment (about five times more) and more xylene was utilized in the second experiment. The total crystallization times were also different (crystallization duration for Experiment #2 was about 2–3 times longer than that of Experiment #1). The X-ray diffraction results reveal (Figs. 16 and 17) that the second experiment generates an alpha polymorph of CL-20 as an impurity, whereas the first experiment gives rise to relatively pure (alpha not detectable) epsilon.

Conclusions

The recrystallization of two important energetic materials, i.e., CL-20 and HNFX were investigated using multiple experimental means. For HNFX only the Ci R3 polymorph could be obtained regardless of the type of recrystallization method used. On the other hand, consistent with the simulation results

multiple polymorphs could be generated upon recrystallization of CL-20, with mixtures of polymorphs detected under various conditions. X-ray diffraction means were used to identify polymorph impurities and used to identify conditions for the crystallization of CL-20, which would generate CL-20 crystallites which consist of the epsilon polymorph at relatively high purity.

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