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# Friction Sensitivity of the ε-CL-20 Crystals Obtained in Precipitation Process

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**Abstract:** The purpose of this work was to obtain samples of CL-20 by precipitation process in a solvent/nonsolvent system, under variable process parameters such as: antisolvent kind, time of nonsolvent addition, stirrer speed, mass of seeded crystals of ε-CL-20. Received samples were studied in the aspect of their sensitivity to friction. As the results of the crystallization processes were prepared crystals of different sizes and shapes depend on applied parameters. It was affirmed, that applied antisolvent has essential influence on type of received crystals. CL-20 crystals of cuboid shape and sizes of 80-200 μm were obtained by recrystallization from ethyl acetate/chloroform. As the result of the recrystallization from ethyl acetate/xylene crystals with rounded edges were obtained. Crystals, from both samples, were mostly single and showed the lowest sensitivity to friction. Also, the crystals of irregular shape and sharp-edged agglomerates were obtained from systems with n-heptane, isooctane, cyclohexane and toluene, which revealed the highest friction sensitivities.

**Keywords:** CL-20, crystallization, friction sensitivity, shape and size of crystal

## Introduction

The development of high energetic materials of the reduced sensitivity is the main direction of investigations. Crystal morphology of these materials plays a vital role in the sensitivity aspects.

Hexanitrohexaazaisowurtzitane (CL-20) is a novel high energy density material (HEDM) [1]. The theoretical maximum density for CL-20 is 2.044 g $cm^{-3}$ and detonation velocity, extrapolated to this density, is 9800 m $s^{-1}$ [2]. These superior properties are due to its unique caged structure with characteristic high density, strained ring, and high branching. These advantages have made CL-20 a possible alternative for the currently used polynitroamines RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Five different polymorphs *α, β, ε, γ, ζ* of CL-20 have been identified [3, 4]. Due to the high energetic performance, high density, and low friction sensitivity compared to the other polymorphs, epsilon form is more desirable for use in propellant and weapons systems [5-7].

A problem of the sensitivity of CL-20 was investigated on a number of studies [8-11]. The aim of this work is to decrease the sensitivity of CL-20 relative to HMX and to identify parameters that control the CL-20 sensitivity. It is commonly known that the quality of the crystal directly affects the CL-20 sensitivity [12]. The physical characteristics of high energetic materials such as crystal size, shape, morphology, purity, internal and external defects and the microstructure of inter crystalline voids play vital role in the sensitivity of HEDMs [10]. One of the ways to lower the sensitivity towards mechanical stimuli is to control the crystal size and morphology to cubic or spherical shape. Another factor that may affect CL-20 sensitivity is the presence of impurities.

The theory of “hot spots” [13-15] attempts to explain the phenomenon of initiating of explosive material by external mechanical stimulus, e.g. friction or shock. Under influence of stimulus in some areas of explosive material develop the quick chemical reactions. These areas are the places where mechanical tensions caused by an initiating stimulus accumulate, referred as “hot spots”. The chemical reaction, initiated at hot spots, extends on next layers of explosive material, which leads in consequence to detonation. The “hot spots” are for instance, air bubbles, inclusions, empty spaces, crystal lattice defects, sharp edges of a crystal, etc.

The research show that crystallization process is suitable technique to improve the quality of CL-20, particularly to decrease the sensitivity [11]. Precipitation by an antisolvent is the suitable method of obtaining the crystallites of the CL-20 [8, 9]. When the antisolvent is added to the solution, solubility of the solute decreases and the solution becomes supersaturated. Upon reducing the solubility a supersaturation is created which induces the nucleation of crystals in solution. The various crystallization parameters such as temperature, antisolvent addition rate and agitation are adjusted to get the required final crystal size and morphology. The solvent-antisolvent ratio, time of crystallization and yield of the product are the key factors for controlling antisolvent based precipitation process.

The purpose of these investigations was to identify the parameters that control CL-20 friction sensitivity. The method applied to obtain ε-CL-20 was precipitation carried out with change of parameters such as: the kind of the antisolvent, speed of stirring and mass of nuclei. Further, the study brings out the advantages of use the precipitation process as well as the friction sensitivity of CL-20 obtained using this process.

## Materials and Methods

### Materials

All the reagents and chemicals used in present work are listed below:

- CL-20, obtained in the High Energy Materials Laboratory, Warsaw University of Technology, Department of Chemistry. The purity of the crystalline powder of HNIW was examined with HPLC and was 95.1%;
- ethyl acetate, POCH Gliwice, analytical purity grade;
- xylene, pure, Aldrich;
- chloroform, pure, POCH Gliwice;
- cyclohexane, for HPLC, POCH Gliwice;
- toluene, pure, POCH Gliwice;
- n-heptane, p. a. PsPark;
- n-hexane, p. a. Aldrich, cz.d.a. Chempur;
- isooctane, p. a. Fuka, cz.d.a. POCH;
- methanol, pure, POCH Gliwice;
- tetrahydrofuran, CHROMASOLV® Plus, for HPLC, ≥99.9%, Sigma-Aldrich;
- water, HPLC Grade, Rathburn.

### Recrystallization Technique

In this study CL-20 has been recrystallized using a nonsolvent to precipitate the CL-20 from solvent. The solution (solute + solvent) was taken in a three-necked flask fitted with an incorporated mechanical stirrer and equipped with a dropping funnel. 10 g of CL-20 was dissolved in 30 ml of ethyl acetate and then CL-20 was precipitated by adding 120 ml of antisolvent gradually. To obtain epsilon form CL-20, the solution was seeded with several crystals of **ε**-hexanitrohexaazaisowurtzitane during the recrystallization process. The recrystallizations were carried out with change of parameters such as: the kind of the antisolvent, time of antisolvent addition, stirrer speeds. The precipitated CL-20 was filtered, washed with methanol, air-dried and characterized.

**Qualitative analysis of presence of polymorphic form ε**

The samples were measured by analysis FT-IR spectra in the "fingerprint" region 800-900 $cm^{-1}$. The IR spectra were recorded on Nicolet FT-IR 6700 spectrophotometer in KBr matrix [5].

**HPLC analysis of hexanitrohexaazaisowurtzitane**

The CL-20 purity was measured by HPLC using a chromatographic system Shimadzu (Japan), binary gradient system (LC-10AD pumps, SPD-10A UV detector, CTO-10A oven) using detection at 254 nm. The separation was carried out on analytical LiChroCART Purspher RP-18 5 µm 125x4 mm column (Merck, Germany) and 5x4 mm precolumn packed with the same material.

**Optical Observations**

The samples were analyzed for morphology with the Eduko model SK 392 optical microscope combined with the Olympus model C560 photographic camera. Photographs of the obtained crystals were taken, and a visual assessment of their quality was performed.

**Analysis of Particle Size Distribution**

The size distribution of the obtained crystals has been measured with the IPS-U infrared particle sizer mark 8.12. The device provides an automatic measurement of the size of particles of solids or liquids irrespectively of their physical and chemical properties. The principle of operation consists of measuring variations in the infrared radiation beam, which is dispersed by the particles that are moving about in the measurement zone. Variations in the IR radiation beam, following an electronic processing, are recorded with a computer. On completion of the measurement of a given sample, results are presented in terms of statistical parameters of the set, as well as in the form of distribution of various properties of particles.

**Friction Sensitivity**

Friction sensitivity of the samples CL-20 was determined on a BAM friction apparatus. The test was performed by a series of trials until there was no explosion/ignition in six consecutive test samples at that weight. The lower limit of sensitivity is defined as the lowest load at which the result "explosion" is obtained from at least one out of six trials [16].

## Results and Discussion

Samples of ε-CL-20 of different shapes and sizes, were received by recrystallization of CL-20 under variable conditions. All samples were obtained applying as a solvent ethyl acetate. The number of organic compounds, listed in Table 1, was applied as an antisolvent. The speeds of stirrer applied, to individual recrystallizations, were in the 300-500 RPM range. In the process of the recrystallization the solvent was added in by 3-5 hours. Chemical purity of the samples after recrystallization were determined by HPLC and it was between 95-97% (Tables 1 and 2). Figure 1 shows the chromatograms of crude and recrystallized CL-20. In both chromatograms the peaks from 4,6,8,10,12-pentanitro-2-acetyl-2,4,6,8,10,12-hexaazaisowurtzitane (PNAIW) and 2,8-diacetyl-4,6,10,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (DATNIW) and other impurities are present. In the process of recrystallization the contamination of the CL-20 were only partially removed. Figure 2 shows the FTIR spectra of the polymorphs after synthesis and recrystallized sample 7 of the CL-20, measured in the "fingerprint" region of 900-800 $cm^{-1}$. FTIR measurement confirmed that $\alpha$-polymorph was present after the synthesis. The presence of peak ε at 820 $cm^{-1}$ in the spectra of the samples after recrystallization shows that as a result of all the tests epsilon form was received. The influence of variable factors on recrystallization process was described in next subsections.

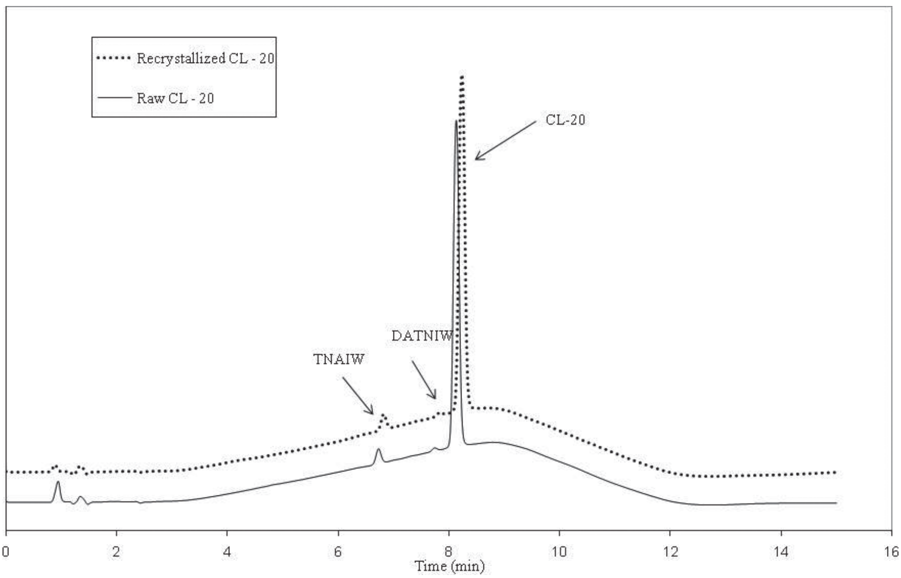



**Figure 1.** HPLC chromatograms of the raw and recrystallized CL-20 samples.

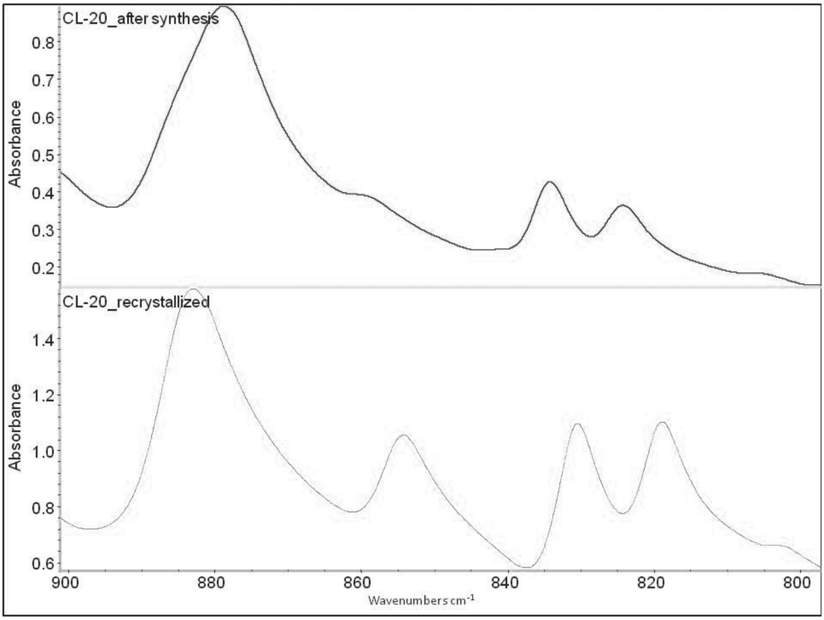



**Figure 2.** The FTIR spectra of the polymorphs after synthesis and recrystallized CL-20.

**The influence of antisolvent on morphology of the CL -20 crystals**

Seven different antisolvents were applied to the crystallization of the CL-20. The antisolvent was dropped for 4 hours. Samples: 1, 2, 3 were received at a stirrer speed of 400 RPM, next four samples at 300 RPM. As a result of all the tests was epsilon form received. The highest efficiency was obtained for the recrystallization from ethyl acetate/n-heptane system. Not satisfactory efficiencies were received for toluene and xylene.

The sample 1 was obtained by recrystallization of CL-20 in an ethyl acetate/n-heptane system with stirrer speed of 400 RPM. The crystals were of irregular shape which for the most part are sharp-edged agglomerates. Figure 3a shows photograph of the obtained crystals.

The sample 2 was obtained by recrystallization of CL-20 in an ethyl acetate/isooctane system with stirrer speed of 400 RPM. They were irregular-shape agglomerates with sharp edges and corners − Figure 3b.

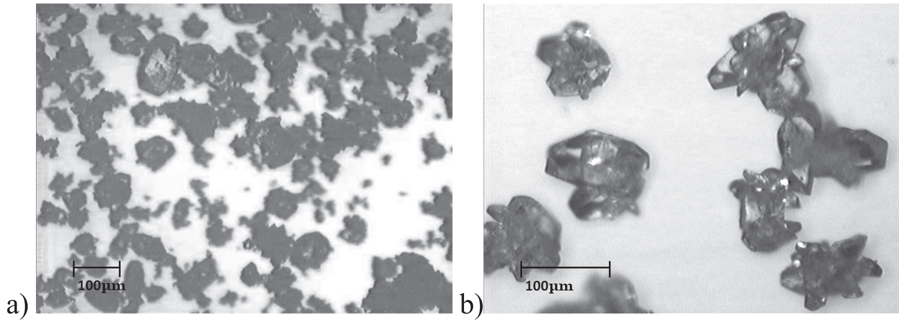



**Figure 3.** Samples number (solvent/nonsolvent, stirrer RPM): a) sample 1, ethyl acetate/heptane, 400 RPM; b) sample 2, ethyl acetate/isooctane, 400 RPM.

Recrystallization 3 resulted in the formation of large regular crystals is shown in Figure 4a. The sample 4 was obtained by recrystallization of CL-20 from an ethyl acetate/chloroform system at a stirrer speed of 300 RPM. The obtained crystals were of regular shapes, and were mostly single crystals. A photograph of the obtained crystals is shown in Figure 4b.

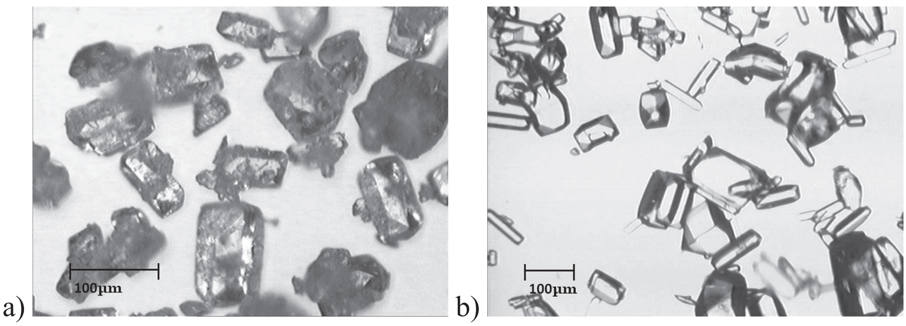
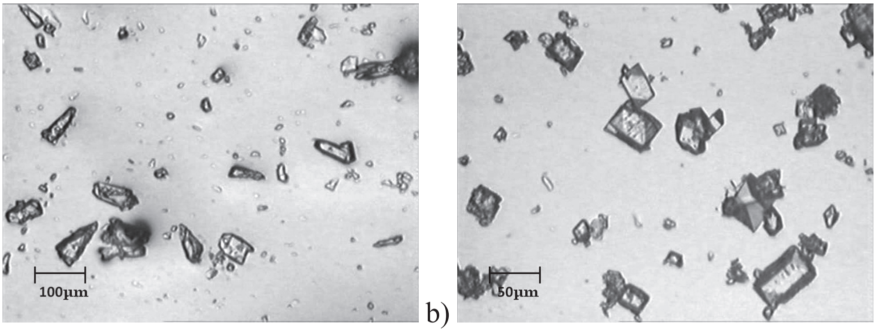



**Figure 4.** Samples number (solvent/nonsolvent, stirrer RPM): a) sample 3, ethyl acetate/n-hexane, 400 RPM; b) sample 4 , ethyl acetate/chloroform, 300 RPM.

The sample 5 was obtained by recrystallization of the CL-20 in an ethyl acetate/cyclohexane system at a stirrer speed of 300 RPM. The crystals of irregular shape are shown in Figure 5a. Owing to their irregular shape the crystals exhibit higher friction sensitivities.

Recrystallization 6 of the CL-20 in an ethyl acetate/toluene system at a stirrer speed of 300 RPM resulted in the formation of irregular crystals is shown in Figure 5b.




a) b)

**Figure 5.** Samples number (solvent/nonsolvent, stirrer RPM) a) sample 5, ethyl acetate/cyclohexane, 300 RPM b) sample 6, ethyl acetate/toluene, 300 RPM.

The sample 7 was obtained by recrystallization of CL-20 from an ethyl acetate/xylene system at a stirrer speed of 300 RPM. The obtained crystals were of round shapes and were mostly single crystals. Crystals of 100-170 µm in size were obtained here, yet crystals of larger size, 180-220 µm, were also present in a quantity of 15%. A photograph of the crystals obtained is in Figure 6.

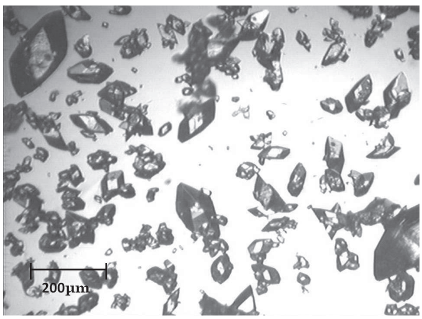



**Figure 6.** Sample 7, ethyl acetate/xylene, 300 RPM.

As seen from Table 1, the less sensitive to friction are samples 4, 6 and 7. These samples were obtained by recrystallization of CL-20 at a stirrer speed of 300 RPM and time antisolvent addition of 4 hours. In samples 4, 7 crystals with rounded edges were obtained, which were in majority single. Owing to their shapes, the crystals reveal lower friction sensitivity. In the sample 7 were obtained crystals of a rectangular shape and sensitivity on the same level. There was not significant relation between the shape of CL-20 crystals and the sensitivity to friction.

**Table 1.** Samples of ε-CL-20 obtained by precipitation with different antisolvent

| Sample | Antisolvent | Stirrer speed [RPM] | Efficiency [%] | Purity [%] | Particle size range [μm] | Friction sensitivity [N] |
|---|---|---|---|---|---|---|
| 1 | n-heptane | 400 | 97 | 96.2 | 50-150 | - |
| 2 | isooctane | 400 | 92 | 95.9 | 50-160 | - |
| 3 | n-hexane | 400 | 83 | 96.4 | 70-160 | - |
| 4 | chloroform | 300 | 74 | 96.5 | 80-200 | 110 |
| 5 | cyclohexane | 300 | 69 | 95.8 | 50-270 | 78 |
| 6 | toluene | 300 | 34 | 96.8 | 70-210<br>280-310 | 110 |
| 7 | xylene | 300 | 52 | 97.1 | 100-170<br>180-220 | 106 |

**The influence of the stirrer speed on friction sensitivity of the CL-20 crystals**

The investigation of influence of the stirrer speed on size distribution of the crystals of CL-20 and their sensitivity to friction was carried out. There were used: ethyl acetate as a solvent and xylene as an antisolvent. The antisolvent was dropped for 4 hours. As a result epsilon form was obtained in all of the tests. The photographs (Figure 7) show crystals received with 170-400 RPM.

In 8 recrystallization process small crystals, 60-80 μm in size, with rounded shapes, were obtained. In this experiment, the seeded ε-CL-20 was not used, which resulted in obtaining crystals of a smaller size. The crystals were single in majority. Their round shape, revealed lower friction sensitivities. A photograph of the obtained crystals is shown in Figure 7a.

The crystals obtained in recrystallization 10 are single crystals in majority, like in the sample 9. Crystals obtained here were of larger size than in the sample 8, 120-180 μm in size, yet crystals of smaller size, 50-90 μm, were also present in a quantity of 10%. A photograph of the obtained crystals is in Figure 7b.

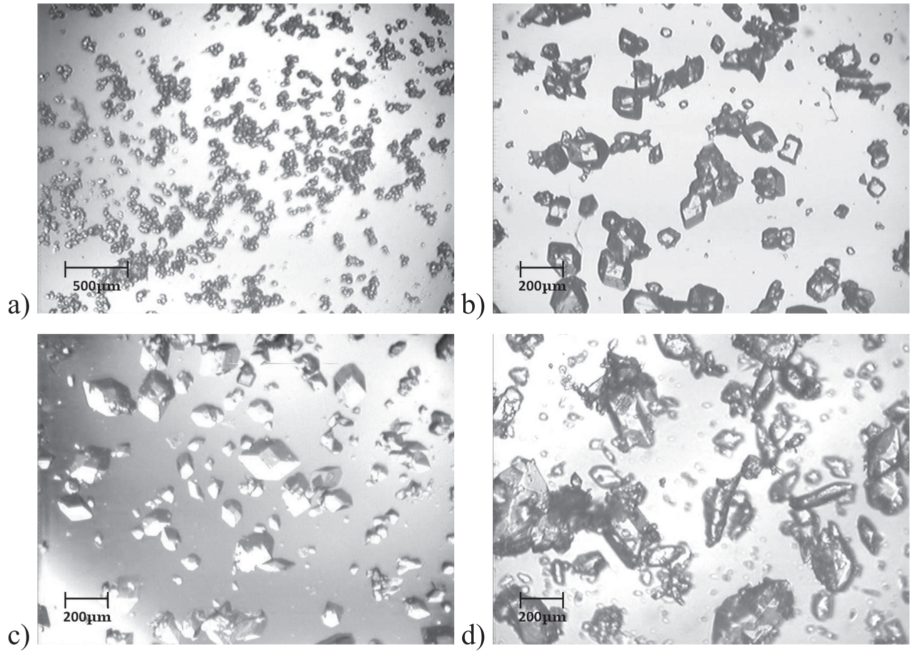



**Figure 7.** Samples number (solvent/nonsolvent, stirrer RPM): a) sample 8, ethyl acetate/xylene, 400 RPM; b) sample 9, ethyl acetate/xylene, 390 RPM; c) sample 10, ethyl acetate/xylene, 200 RPM; d) sample 11, ethyl acetate/xylene, 190 RPM.

**Table 2.** Samples of ε-CL-20 obtained by crystallization with different stirrer speeds

| Sample | Stirrer speed [RPM] | Efficiency [%] | Purity [%] | Particle size range [µm] | Friction sensitivity [N] |
|---|---|---|---|---|---|
| 8 | 400 | 49 | 96.9 | 60-80 | 94 |
| 9 | 390 | 63 | 96.7 | 50-90<br>120-180 | 94 |
| 10 | 200 | 50 | 96.3 | 50-200<br>240-260 | 78 |
| 11 | 170 | 61 | 96.2 | 60-230<br>270-350<br>430-460 | 63 |

As seen from Table 2, less sensitive to friction are the samples 8 and 9. Results show that the smaller grains, received with larger speeds of stirrer, exhibit reduced sensitivity to friction. Moreover, owing to their rounded shapes, the crystals feature lower friction sensitivity.

**The influence of mass of seeded crystals of ε-hexanitrohexaazaisowurtzitane**

Study of the recrystallizations with different mass of the seeded ε-CL-20 was carried out for checking the influence of this parameter on course of precipitation process. 0.3, 1.0, 1.5 g of the seeded ε-CL-20 were applied in the experiments. There were used ethyl acetate as a solvent and xylene as an antisolvent. The antisolvent was dropped for 4 hours.

The photographs (Figure 9) show received crystals. With increasing mass of the seeded ε-CL-20 the shapes of crystals become more spatial and similar to spherical.

The increase of the efficiency together with extension of quantity of the seeded ε-CL-20 were observed. This is relevant that with decrease of the energetic barrier of transition of supersaturated solution in state saturated is disengagement of the solid phase.

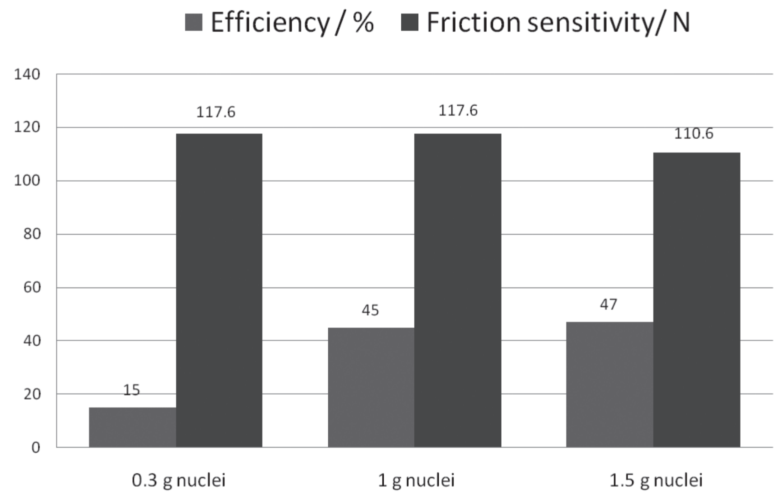



**Figure 8.** The comparison of samples received in recrystallization carried out with different mass of the seeded ε-CL-20.

a) b) c)

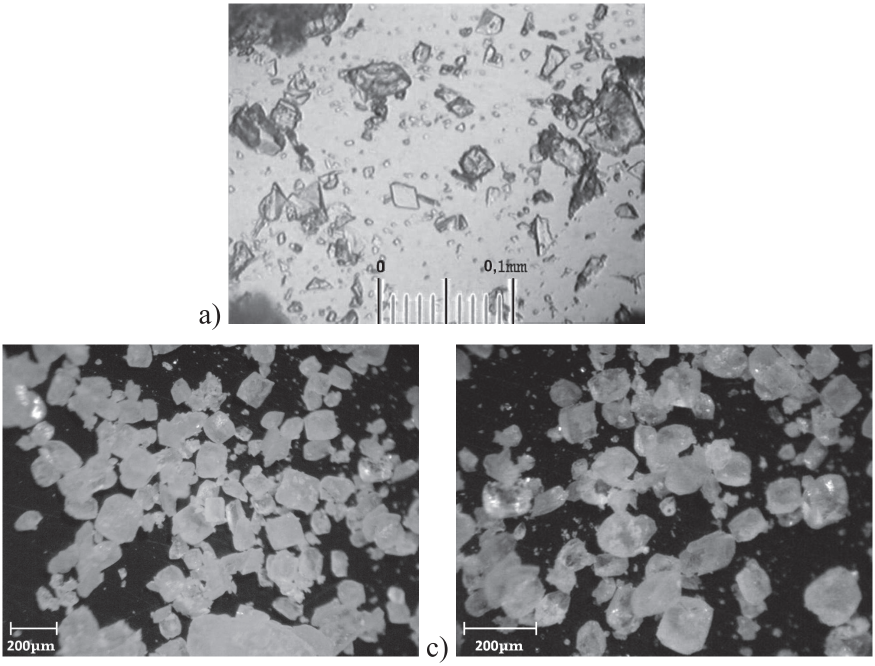



**Figure 9.** Samples obtained with: a) 0.3 g of the seeded ε-CL-20; b) 1.0 g of the seeded ε-CL-20; c) 1.5 g of the seeded ε-CL-20.

# Conclusions

In the present study several antisolvents were examined. The highest efficiency was obtained for the recrystallization from ethyl acetate/n-heptane system. This recrystallization gives crystals of irregular shape. The crystals similar to round were obtained in recrystallizations from ethyl acetate/chloroform system and ethyl acetate/xylene system but the efficiencies were not satisfactory. There was no effect of crystals shape on the sensitivity to friction.

The research on influence of the stirrer speed on friction sensitivity showed that the crystals obtained at 400RPM reveal reduced sensitivity to friction. Moreover, the crystals obtained at lower stirring speeds are more sensitive to friction. It was also found that absence of the seeded ε-CL-20 results in a significant reduction in the size range of crystals. This may be due to the fact that in the process without seeded ε-CL-20 crystals, nucleation occurred later and in shorter time more small crystals was formed.

In studies on the mass of seeded crystals of ε-hexanitrohexaazaisowurtzitane were observed the increase of the efficiency together with increase of quantity of the seeded ε-CL-20. This is relevant that with decrease of the energetic barrier of transition of supersaturated solution in state saturated is disengagement of the solid phase.

The HPLC study showed that impurities intermediates of synthesis of CL-20 were not removed completely in precipitation. Accordingly to the received results it was concluded that it is necessary to use an additional method of purification of crude CL-20 before the process of recrystallization. Research on purification the CL-20 is carried out.

In general, precipitation is useful to produce desired crystals with acceptable shape, and narrow size distribution. However, in the process of precipitation chemical purity of the CL-20 has not been increased to the expected level.

Summarizing these studies showed that recrystallization processes described in this paper are suitable technique to obtain crystals of epsilon polymorph of the CL-20 of reduced sensitivity to friction.

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