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Thermal Properties and Decomposition Mechanism of Propyl-Nitroguanidine(PrNQ)

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Abstract: Both thermal decomposition behaviors and non-isothermal decomposition reaction kinetics of propyl-nitroguanidine (PrNQ) were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) method. Its decomposition mechanism was studied through *in-situ* FTIR spectroscopy technology and the compatibilities of PrNQ with 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX), hexanitrohexaazaisowurtzitane (CL-20) and 5,5'-bistetrazole-1,1'-diolate (TKX-50) were also achieved by DSC experiment. The results show that the melting point of PrNQ is around 99 °C, which is very suitable for the application of melt-cast technology. The thermal stability of PrNQ is good and the difference between the melting point and decomposition temperature of PrNQ is about 137 °C, which is large enough to guarantee the safety of the melt-cast process. The compatibilities between PrNQ and HMX or TKX-50 are also excellent, with ΔT_p of -0.3 K and 1.36 K, respectively.

Key words: energetic material; thermal decomposition; compatibility; melt-cast; propyl-nitroguanidine(PrNQ)

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1 Introduction

The development of energetic materials contributed enormously to the progress and prosperity of mankind^[1-3]. Meanwhile, heavy casualties caused by their accidental explosion and serious environmental pollution always plague the researchers, thus, the application of greener and more insensitive explosives is required^[4-6]. Generally, insensitive explosives are divided into two categories based on their preparation processes. One is “cast-cured explosives”, since the preparation is achieved through cast cured process^[7]. The other is “melt-cast explo-

sives”, which is melted and cast into shells during their preparations^[8]. Compared with melt-cast explosives, cast-cured ones are more difficult to process and recycle, and more expensive^[9], therefore, there are increasing interests for insensitive melt-cast explosives in the past decades^[10-11].

2,4,6-Trinitrotoluene (TNT) acts as an ideal organic solvent in melt-cast process due to its capability in the dissolution of numerous energetic materials, which results in an acceptable processing viscosity^[12]. Currently, TNT based melt-cast explosives are no doubt the most important “melt-cast explosives” with intensive studies^[13], however, strong toxicity and high vapor-pressure of TNT often lead to fatal harmful effect and the relatively high sensitivities cause significant risks during the production and application processes of TNT^[14]. In recent years, developing new insensitive explosive to replace TNT has become a key research direction in the field of melt-cast explosives^[15-16].

Nitroguanidine (NQ) is widely applied and known for its inherent insensitivity. Propyl-nitrogua-

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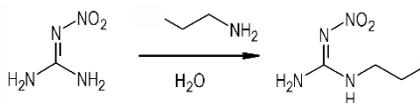
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midine (PrNQ) is an alkylated analog of NQ, with a propyl moiety effectively reduces the melting point while nitroguanidine portion of the molecule provides the explosive power. PrNQ has a detonation velocity of $7.76 \text{ km}\cdot\text{s}^{-1}$ with a density of $1.64 \text{ g}\cdot\text{cm}^{-3}$, which is higher than TNT^[17]. In contrast, the ERL impact and BAM friction sensitivity data are higher than 100 J and 360 N, which are lower than those of TNT (88 J and 220 N)^[18]. The good detonation and insensitivity performances make PrNQ an important potential candidate to replace TNT. However, studies on its thermal behaviors and compatibilities with other high explosives, which are crucial for its further applications, are still limited. Herein, in this work, we reported the thermal behaviors, non-isothermal kinetics of thermal decomposition, and decomposition mechanism of PrNQ as well as its compatibility with some important high explosives. The thermal decomposition process of PrNQ was studied by DSC-TG method while the compatibilities of PrNQ with 1, 3, 5-trinitroperhydro-1, 3, 5-triazine (RDX), 1, 3, 5, 7-Tetranitro-1, 3, 5, 7-tetrazoctane (HMX), hexanitrohexaazaisowurtzitane (CL-20), 5, 5'-bistetrazole-1, 1'-diolate (TKX-50) were investigated by DSC experiments. The intermediates formed during the pyrolysis process were also characterized through *in-situ* FTIR spectroscopy technologies to reveal the intrinsic decomposition mechanism of this novel nitroguanidine derivative.

2 Experimental

2.1 Sample

The sample of PrNQ used in this work was prepared through one step synthesis from nitroguanidine (NQ) and propylamine (Scheme 1).



Scheme 1 Preparation of PrNQ from NQ

2.2 Apparatus and Measurements

The thermal analysis experiments of PrNQ were performed on a model TG-DSC STA 449C instru-

ment (NETZSCH, Germany) as well as a DSC Q200 instrument (TA, America). The operation conditions were: sample mass, 0.6 mg; atmosphere, dynamic nitrogen, $50 \text{ mL}\cdot\text{min}^{-1}$; aluminum cell was used.

IR spectra were recorded on a Nicolet 60SX FT-IR spectrometer employing an HgCdTe detector. The *in-situ* FTIR spectroscopy experiment was carried out with a Nicolet 60 SXR FTIR spectrometer. The operation conditions were: sample mass, 0.6 mg; heating rate, $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$; $17.8 \text{ file}\cdot\text{min}^{-1}$ and $16 \text{ scans}\cdot\text{file}^{-1}$ were recorded at a resolution of 4 cm^{-1} ; temperature range, $20\text{--}450 \text{ }^\circ\text{C}$.

3 Results and Discussion

3.1 Thermal Behaviors of PrNQ

Thermal decomposition behavior is regarded as one of the most important indexes on evaluating the quantity of explosives and studies of thermal properties of PrNQ were first carried out through DSC measurements. From the DSC curve in Fig. 1, an endothermic peak with summit peak at $99.39 \text{ }^\circ\text{C}$ could be clearly observed and the highly sharp shape of this peak indicates that it most likely to be a physical change. To clarify this physical process, TG-DTG technology was carried out. It finds that the mass of PrNQ maintains during the process, which demonstrates that PrNQ melted around $99.39 \text{ }^\circ\text{C}$, which is an ideal melting point for the preparation of melt-cast explosives. With the rise of the heating temperature, a major exothermic decomposition peak near $236.10 \text{ }^\circ\text{C}$ appears in DSC curve. It is clear that the mass of PrNQ lost completely around this temperature in the TG-DTG curve (Fig. 2). The discrepancy between melting temperature and decomposition temperature of PrNQ is about $137 \text{ }^\circ\text{C}$, which is large enough to guarantee the safety of the melt-cast process as the heating temperatures are generally under $150 \text{ }^\circ\text{C}$ in the preparation of melt-cast explosives.

For better evaluation of application prospect, DSC experiments of TNT under same conditions

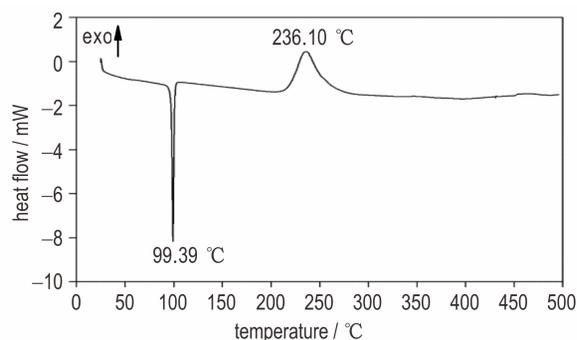


Fig.1 DSC curve of PrNQ at a heating rate of $10\text{ °C}\cdot\text{min}^{-1}$

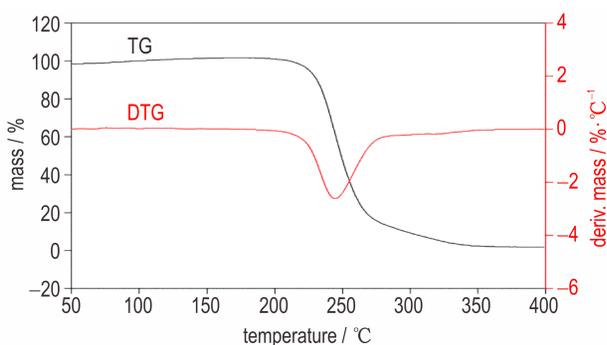


Fig.2 TG-DTG curve of PrNQ at a heating rate of $10\text{ °C}\cdot\text{min}^{-1}$

were also carried out. TNT melted at a relatively lower temperature of 80 °C . However, with the rise of heating temperature, a spontaneous endothermic volatilization process of TNT was observed, which means a large amount of TNT vapor was generated when the molecule was heated, which could also be observed in TG-DTG studies of TNT^[19]. The existence of TNT vapor obviously will lead to high toxicity and serious safety issues during the melt-cast process of explosives. In comparison of the previous research, it can be concluded that PrNQ has a much lower toxicity and vapor pressure than TNT, showing a good application prospect as the new melt-cast explosives carrier for the replacement of TNT.

3.2 Kinetic Study of PrNQ

In order to obtain the kinetic parameters of the thermolysis process, investigations on the non-isothermal kinetics of thermal decomposition of PrNQ were carried out and DSC curves at different heating rates were employed. Seen from Fig.3, the peak temperatures increase when the heating rate increases, and the decomposition peak temperatures are 215 , 227 , 235 °C and 248 °C at the heating rates of 2.5 ,

5 , $10\text{ °C}\cdot\text{min}^{-1}$ and $20\text{ °C}\cdot\text{min}^{-1}$, respectively. On this basis, we choose both Kissinger's model and Ozawa's model^[20-21] to further calculate the apparent activation energy (E_a) of the decomposition reaction of PrNQ. The results show that two methods coincide quite well and the reaction activation energy of PrNQ is approximately $129\text{ kJ}\cdot\text{mol}^{-1}$ ($128.1\text{ kJ}\cdot\text{mol}^{-1}$ from Kissinger's model and $129.8\text{ kJ}\cdot\text{mol}^{-1}$ from Ozawa's model).

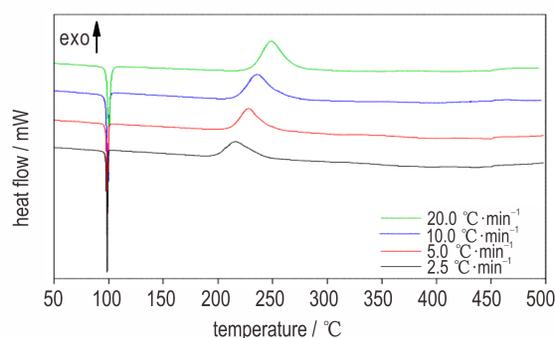


Fig.3 DSC curves of PrNQ at different heating rates

3.3 Structural Transformations During the Decomposition Process of PrNQ

The studies of structural transformations over thermal decomposition process will provide rich information for the decomposition mechanisms of energetic molecules. To better understand the thermal decomposition mechanisms of PrNQ, detailed structural transformations during the pyrolysis process were carefully characterized through *in-suit* FTIR spectroscopy. Fig. 4 demonstrates the *in-suit* FTIR spectroscopy of PrNQ at $20\text{--}450\text{ °C}$. There are no great changes on the peak positions within the first 20 min. With the further rise of heating temperature, the IR peaks are changing rapidly. Seen from Fig.4, the intensity of IR peaks of —NH_2 and —NH— units are first weakened, followed by the intensity of IR peaks of —NO_2 unit and —Pr unit, which indicates that structure unit connected by amine are the most unstable moiety under heating conditions. The new formed IR peak at about $2200\text{--}2600\text{ cm}^{-1}$ is very likely caused by the formation of —CN units during the major exothermic decomposition.

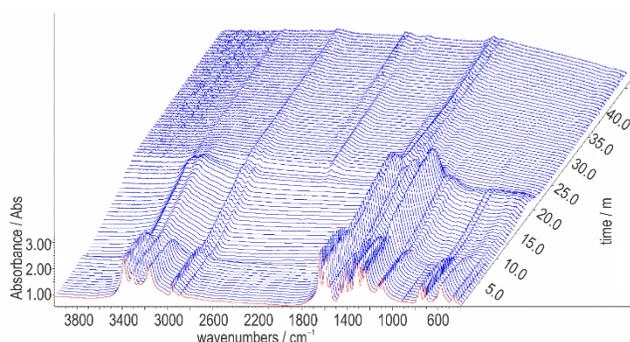
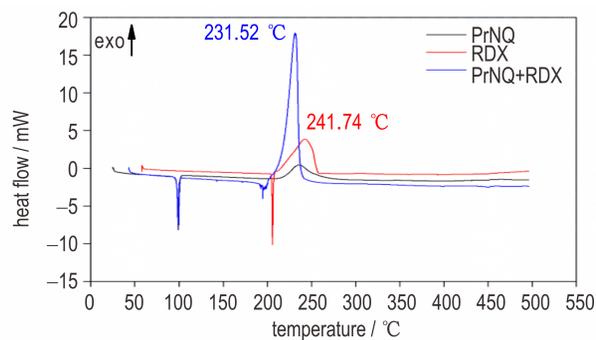


Fig.4 In-suit FTIR spectroscopy of PrNQ at heating temperatures

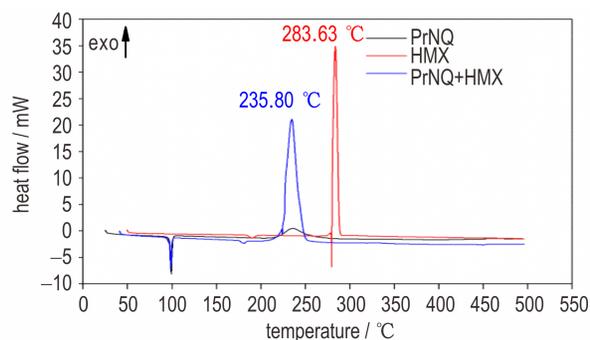
3.4 Compatibility of PrNQ with Some High Explosives

As a potential formula carrier for melt-cast explosives, it requires not only excellent thermostability but also good compatibility with existing high explosives. From application perspectives, compatibility of PrNQ with other energetic materials is one of the most important characters. RDX, HMX, CL-20 and TKX-50 are among the most potent chemical explosives manufactured and the compatibilities of PrNQ with RDX, HMX, CL-20, TKX-50 were investigated by means of DSC technique. The experiments were carried out according to method 602.1 in GJB 772A-1997, and the results are shown in Fig.5 and Table 1.

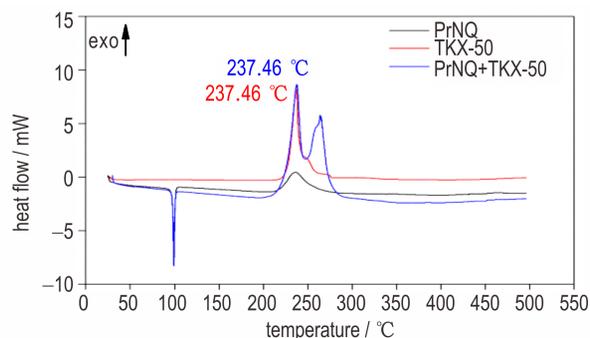
The major exothermic peaks of RDX at 241 °C and PrNQ at 236 °C are caused by the rapid decomposition reactions. Affected by the decomposition process of each other, the major exothermic peak of the mixture moves forward to 231 °C. The decrease of exothermic peak value of the mixture demonstrates the incompatibilities of PrNQ with RDX. Similarly, when PrNQ mixes with CL-20, the major exothermic peak of the mixture at 192 °C is much lower than the exothermic peak of PrNQ and CL-20, indicating a poor compatibility between them. In contrast, the major exothermic peak of PrNQ-HMX mixture is almost the same with the major exothermic peak of PrNQ, showing a good compatibility of PrNQ with HMX. When PrNQ is mixed with TKX-50, there are two major exothermic peaks of the mixture. One major exothermic peak of the mixture



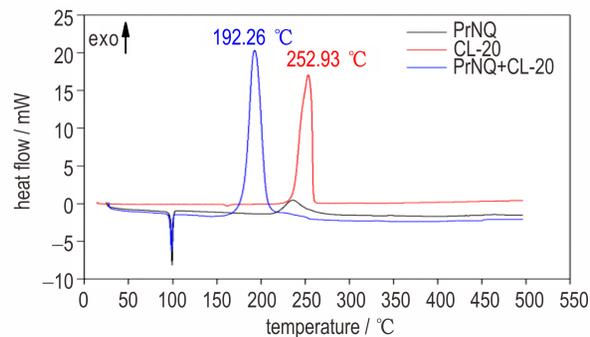
a. RDX



b. HMX



c. TKX-50



d. CL-20

Fig.5 DSC curves describing the compatibility of PrNQ with existing high explosives.

is exactly same with TKX-50 and a little higher than PrNQ while the other major exothermic peak of

the mixture is higher than both of TKX-50 and PrNQ. The higher exothermic peak value of the mixture shows an ideal compatibility of PrNQ with TKX-50. The experiment data are summarized in Table 1. In conclusion, PrNQ is compatible to HMX and TKX-50 from a heat standpoint, while not compatible with RDX and CL-20, of which the compatibility with CL-20 is the worst.

Table 1 Compatibility data of PrNQ with commonly used explosives

sample	T_p / K	$\Delta T_p / K$	evaluation
RDX	241.74		
PrNQ	236.10	-4.58	incompatible
PrNQ+RDX	231.52		
HMX	283.63		
PrNQ	236.10	-0.30	compatible
PrNQ+HMX	235.80		
TKX-50	237.46		
PrNQ	236.10	1.36	compatible
PrNQ+TKX-50	237.46		
CL-20	252.93		
PrNQ	236.10	-43.84	incompatible
PrNQ+CL-20	192.26		

4 Conclusions

Thermal behaviors and decomposition process of PrNQ were studied with DSC-TG and *in-situ* FTIR spectroscopy methods. Conclusions are obtained as follows:

(1) According to the DSC-TG analysis, PrNQ is melted around 99.39 °C, which has an ideal melting point as the potential formula carrier for melt-cast explosives.

(2) The major exothermic decomposition peak of PrNQ is near 236.10 °C and the discrepancy between melting temperature and decomposition temperature is about 136 °C, which is large enough to guarantee the safety of the melt-cast process.

(3) Studies on kinetics and decomposition mechanism of PrNQ show that this energetic molecule has excellent thermostability. Furthermore, from studies of compatibilities of PrNQ with other

high explosives, PrNQ is proved to be compatible to HMX and TKX-50 from a heat standpoint, while not compatible with RDX and CL-20, of which the compatibility of PrNQ with CL-20 is the worst.

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丙基硝基胍(PrNQ)热化学特性及分解机理

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摘 要: 采用差示扫描量热法(DSC)和热重分析(TGA)法研究了丙基硝基胍(PrNQ)的热分解行为和非等温分解反应动力学,利用原位红外技术研究了PrNQ分子的分解机理,利用DSC实验研究了PrNQ与黑索今(RDX),奥克托今(HMX),六硝基六氮杂异伍兹烷(CL-20),5,5'-联四唑-1,1'-二氧二羟铵(TKX-50)的相容性。结果表明,PrNQ的熔点约为99℃,可应用于熔铸炸药体系。PrNQ的热稳定性良好,PrNQ的熔融和分解温度相差约137℃,可保证熔铸工艺的安全性。根据DSC实验,PrNQ与HMX及TKX-50的 ΔT_p 分别为-0.3 K和1.36 K,表明其与HMX及TKX-50相容性良好。

关键词: 含能材料;热分解;相容性;熔铸;丙基硝基胍(PrNQ)

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