



## Synthesis and characterization of novel micro-sized tetrazole-based high energetic nitrogen-rich polymers

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### Abstract

Energetic materials are a class of material with high amount of stored chemical energy that can be released. Typical classes of energetic materials are e.g. explosives, pyrotechnic compositions, propellants (e.g. smokeless gun powders and rocket fuels), and fuels (e.g. diesel fuel and gasoline). The novel functionality of aromatic tetrazole derivatives with high nitrogen content predetermines a great interest to tetrazole-containing polymers. The tetrazole-based nitrogen-rich polymers were well investigated. The tetrazole rings play an important role in development of energetic polymers. The high thermal stability of these rings causes the polymers as good candidates as energetic applications. The aim of the present work is to synthesize novel nano-sized high energy density polymers based on tetrazole rings. The resulted polymer was characterized by SEM, <sup>1</sup>H NMR and <sup>13</sup>C NMR.

**Keywords:** Nano-size; Tetrazole; Nitrogen-rich polymers; Explosives; Energetic materials.

## Introduction

High energetic materials can be classified as three types of nuclear, physical and chemical explosives. The decomposition of compounds with production of heat and gases is the deduction of detonation process of explosives. The important groups of energetic compounds are related to the primary and secondary explosives, propellants and pyrotechnics [1-2]. From a structural point of view, the explosives can be classified as nitro compounds, nitric esters, nitramines, chloric and perchloric acid derivatives, azides [3-4] and various molecules capable of preparing a detonation (acetylides, fulminates, ozonides, peroxides and polynitrogen compounds (PNCs) such as tetrazole-, triazole-,triazine- and tetrazine-based compounds). Nitrogen-rich polymers point to the polymer structures including a high content of nitrogen atoms, frequently over 50 percent [5-6]. This high nitrogen content can be gained by the aza-based aromatic rings. Nowadays, the several high energetic nitrogen-rich polymers were developed and reported in scientific papers. Common high energetic polymers have nitro or azide groups [7]. From the most known energetic polymers, nitrocellulose (NC) [8-9], glycidylazide polymer (GAP) [10], poly[3,3-bis(azidomethyl)oxetane] (polyBAMO), poly(azido methyl methyloxetane) (polyAMMO), poly(nitroto methyl methyloxetane) (polyNMMO/polyNIMMO) [11], polyglycidyl nitrate (polyGLYN) [12] and polyvinyl nitrate (PVN) [13] can be noted. In recent years, a number of researchers work on aza-heteroaromatic ring based polymers. The tetrazole-based nitrogen-rich polymers were

well investigated. The tetrazole rings play an important role in development of energetic polymers [14]. The high thermal stability of these rings causes the polymers as good candidates as energetic applications. Recently we reported some nitrogen-rich polymers: PAST1, PAST2, (PTMS), PTNSA1, PTNSA2, (PTS) and PDATS polymers. The aim of the present work is to synthesize novel nano-sized high energy density polymers based on tetrazole rings.

## Experimental

### Materials

The acrylonitrile, azobisisobutyronitrile (AIBN), ammonium chloride, hydrochloric acid (37%), ammonia (25%), hydrazinium hydroxide (95%), hydroxylamine (50%), aminoguanidine bicarbonate (97%), sodium azide and all solvents were purchased from Sigma-Aldrich Company. All the solvents were distilled and stored over a drying agent.

### Measurements

Infrared spectra were recorded with a 4600 Unicam FT-IR spectrophotometer as KBr pellets. Nuclear magnetic resonance (NMR) spectra were run on a Bruker 400 MHz spectrometer at room temperature using deuterated solvents. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/min under N<sub>2</sub>.

### Polymerization of acrylonitrile: PAN

For preparing of polyacrylonitrile (PAN), the acrylonitrile (10 ml) was dissolved in 100 mL of toluene and was mixed with AIBN (1%

molar) as a radical initiator, in a pyrex glass ampoule. The ampoule was degassed under argon gas, sealed under vacuum, and maintained at  $80 \pm 1$  °C in a water bath, with stirring for about 24 h. The polymerization temperature was well controlled in a water bath. After reacting for 24 h, the ampoule was cooled rapidly. Then the solutions were poured into cooled methanol. The light yellow precipitates were collected and washed with methanol three times and dried under vacuum to yield (approximately 95%) of PAN (Scheme 1).

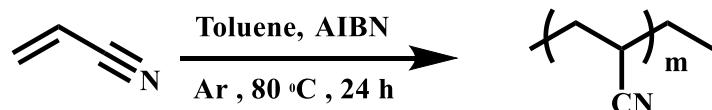
#### Synthesis of poly(5-vinyltetrazole): PVT

The reaction of PAN polymer with sodium azide and ammonium chloride (Scheme 2) were done in a conical bottle equipped with stirrer and reflux condenser. About 1.4 g (26.4 mmol) of PAN powder and 30 mL of DMF were added to a conical bottle with stirring at room temperature. Then to the solution, 1.68 g (25.8 mmol) of  $\text{NaN}_3$  and 1.4 g (26.2 mmol) of  $\text{NH}_4\text{Cl}$  were added with stirring. The bottle was immediately placed

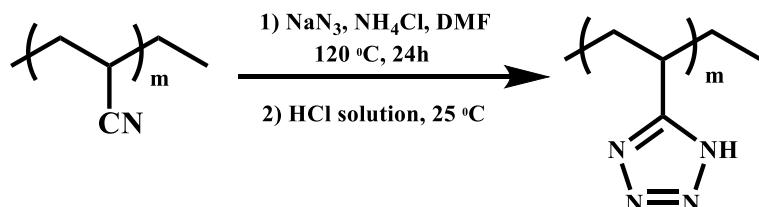
into an oil bath and heated to 120 °C and maintained the temperature with stirring for 24 h. After reacting, the ampoule was cooled rapidly to room temperature. The final reaction mixture was added into distilled water for precipitate and also an elimination of DMF. The products obtained were treated in 300 mL of 0.5 M HCl and repeatedly washed with distilled water for a complete removal of  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{H}^+$ . The brown precipitates were left to dry at room temperature in air for several days (yield around 95%).

#### Synthesis of ammonium salt of poly(5-vinyltetrazole): APVT

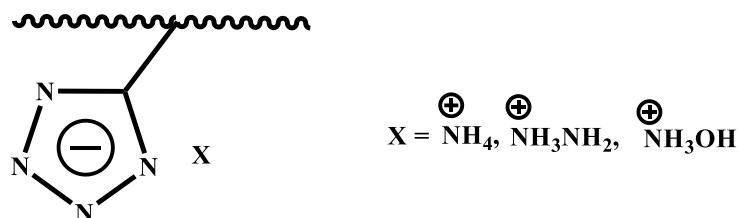
1 g (10.4 mmol) of PVT powder, 10 mL of distilled water and 1 mL of ammonia 25% were poured in an ampoule and stirred at 35 °C for 48 h. After this period of time, the reaction mixture was heated into the oven at 50 °C for 24 h. The yellow precipitates (Scheme 3) were obtained. The yield of this reaction was 42%.



Scheme 1. Preparation of PAN.



Scheme 2. Preparation of PVT.



Scheme 3. Structure of PVT salts.

### Synthesis of hydrazinium salt of poly (5-vinyltetrazole): HPVT

For preparation of HPVT, 1 g (10.4 mmol) of PVT powder was poured in a pyrex ampoule containing 10 mL distilled water. Then 0.51 mL of hydrazinium hydroxide was added to the mixture. All reactants were stirred together at 35 °C for 48 h. After the reaction time, the reaction mixture was heated in the oven at 40 °C for 24 h. The yellow precipitates (Scheme 3) were collected and weighted (approximately 70%).

### Synthesis of hydroxyl ammonium salt of poly(5-vinyltetrazole): HAPVT

The nitrogen-rich HAPVT salt (Scheme 3) was obtained by the reaction of PVT powder (1 g, 10.4 mmol), distilled water (10 mL) and hydroxylamine solution (0.6 mL). All reactants were reacted at 35 °C for 48 h with hard stirring. Then, the reaction mixture was heated into the oven at 45 °C for 24 h. The yield of this yellow nitrogen-rich polymer was approximately 75%.

### Synthesis of aminoguanidinium salt of poly(5-vinyltetrazole): AGPVT

In a two-necked pyrex glass ampoule, 1 g (10.4 mmol) of PVT powder was stirred with 40 mL of distilled water under argon gas. After the degassing of the ampoule, 0.7 g (9.4 mmol) of aminoguanidine bicarbonate was added to the reaction mixture and stirred

hardly with them. After 24 h, the yellow precipitates (Scheme 4) were dried under vacuum. The yield of this reaction was approximately 70%.

### Synthesis of nano-sized nitrogen-rich polymers

For preparing of nano-sized energetic polymers, the synthesized polymers (APVT, HPVT, HAPVT and AGPVT) were dissolved in distilled water and cooled in freeze-drying machine at -80 °C for 2 h. Then, the compounds were dried in freeze-drying equipment for 24 h.

### Results and discussion

The structures of the salts of poly(5-vinyltetrazole) were characterized by FT-IR spectroscopy technique. The nitrogen-rich salts were not soluble in NMR solvent. Then, the NMR analysis of the compounds was not performed. The characterizations of all synthesized compounds are drawn in below: PAN:  $^1\text{H}$  NMR (DMSO-d<sup>6</sup>, ppm): 2.05–2.09 (CH<sub>2</sub>), 3.15–3.19 (C-H) (Figure 1). FT-IR (KBr, cm<sup>-1</sup>): 2938 (aliphatic C-H), 2243 (CN), 1454 (bending C-H).

PVT:  $^1\text{H}$  NMR (DMSO-d<sub>6</sub>, ppm): 2.1 (2H, t, CH<sub>2</sub>), 3.1 (1H, m, CH) and 7.2–7.3 (1H, s, NH) (Figure 2).  $^{13}\text{C}$  NMR (DMSO-d<sub>6</sub>, ppm): 30 (CH<sub>2</sub> and CH) and 160 (C<sub>tetrazole</sub>) (Figure 3). FT-IR (KBr, cm<sup>-1</sup>): 3300–3500 (stretching N-H), 2850–3000 (stretching C-H), 1557–

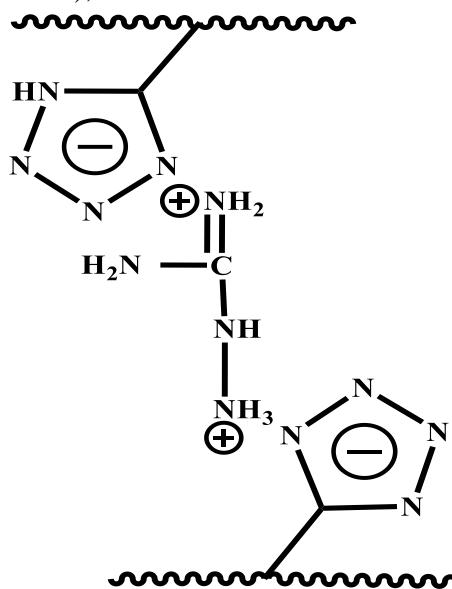
1636 (stretching C=N), 1456 (bending C-H and N-H) and 1056-1355 (bending C=N).

APVT: FT-IR (KBr,  $\text{cm}^{-1}$ ): 3423 (stretching N-H), 2853, 2925 and 3070 (stretching C-H), 1561-1624 (stretching C=N), 1410-1460 (bending C-H and N-H) and 1030-1245 (bending C=N).

HPVT: FT-IR (KBr,  $\text{cm}^{-1}$ ): 3421 (stretching N-H), 2853 and 2925 (stretching C-H), 1543-1637 (stretching C=N), 1409-1473 (bending C-H and N-H) and 1029-1245 (bending C=N). HAPVT: FT-IR (KBr,  $\text{cm}^{-1}$ ): 3421 (stretching N-H and O-H), 2925 (stretching C-H), 1542-1636 (stretching C=N), 1409-

1473 (bending C-H and N-H) and 1033-1206 (bending C=N).

AGPVT: FT-IR (KBr,  $\text{cm}^{-1}$ ): 3423 (stretching N-H), 2853 and 2924 (stretching C-H), 1638-1719 (stretching C=N), 1384-1459 (bending C-H and N-H) and 1099 (bending C=N).



Scheme 4. Structure of aminoguanidinium salt of PVT.

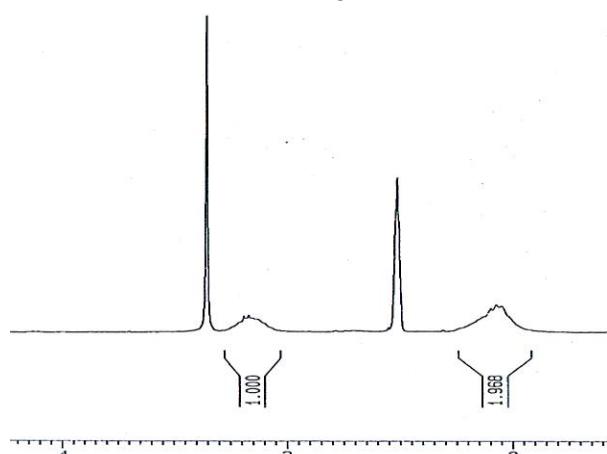


Figure 1.  $^1\text{H}$  NMR spectrum of PAN in DMSO-d6.

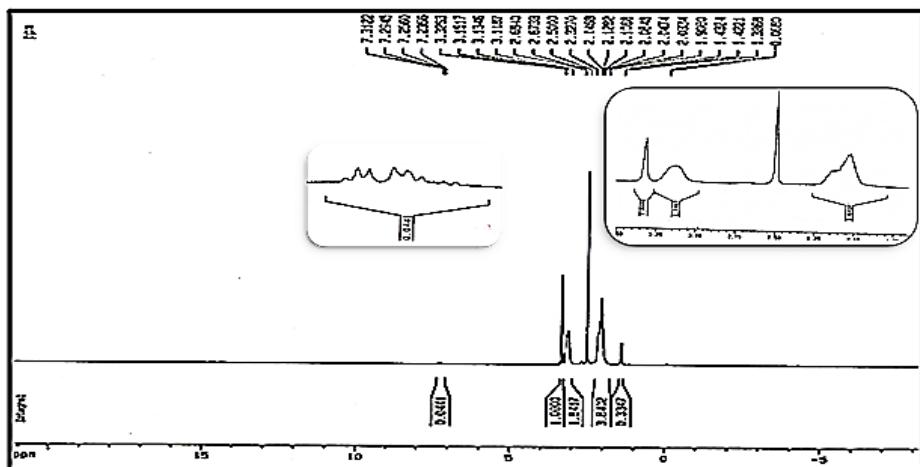


Figure 2.  $^1\text{H}$  NMR spectrum of PVT in DMSO-d6.

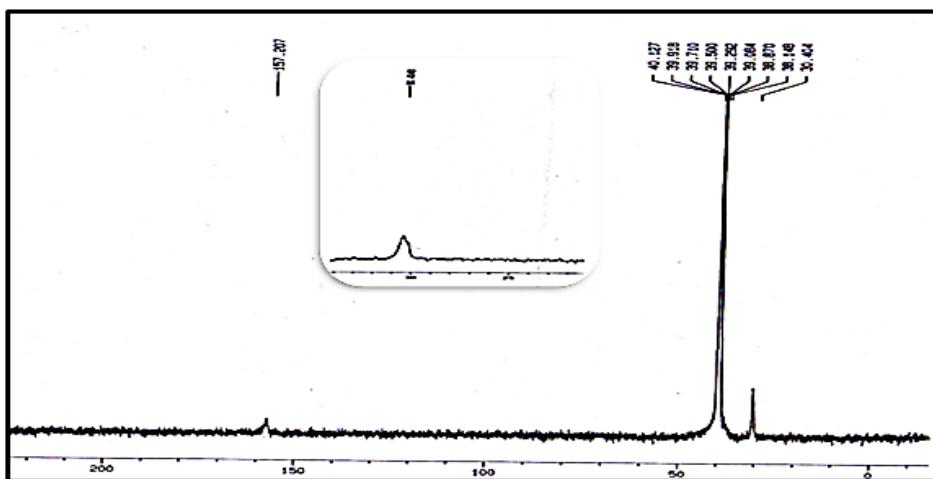


Figure 3.  $^{13}\text{C}$  NMR spectrum of PVT in  $\text{DMSO-d}_6$ .

Figures 4-7 show the SEM micrographs of the nitrogen-rich salts of the PVT. The particles sizes were 30  $\mu\text{m}$ , 300 nm, 30  $\mu\text{m}$  and 1  $\mu\text{m}$  for APVT, HPVT, HAPVT and AGPVT salts, respectively.

Thermal properties of polymers were studied by TGA technique and were listed in Table 1. The IDT, PDT and PDT<sub>max</sub> are related to the initial decomposition temperature of the polymer, temperature of 20% weight loss of the polymer and the temperature at which the maximum decomposition rate occurred for

the polymer, respectively. We can see the PVT polymer losses 20% weight of its structure at 323 °C. On other hand, the PDT of nitrogen-rich salts of PVT polymer and their nanoparticles is in range of 235-245 °C. It can be deduced from the data, the PVT polymer is more stable than its nitrogen-rich salts. Also, it is shown that the size of polymers is not important on stability of compound.

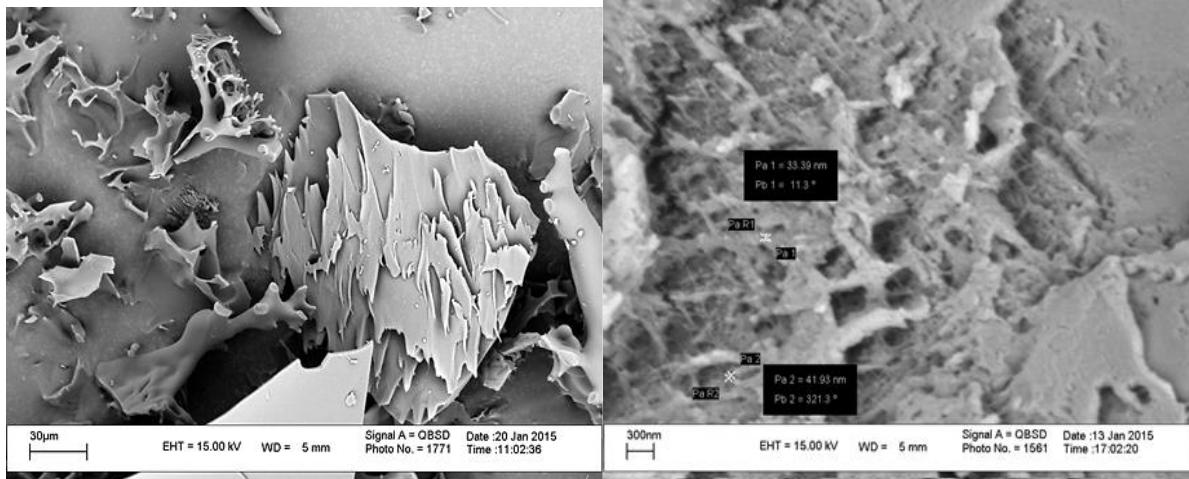


Figure 4. SEM image of APVT. Figure 5. SEM image of HPVT.

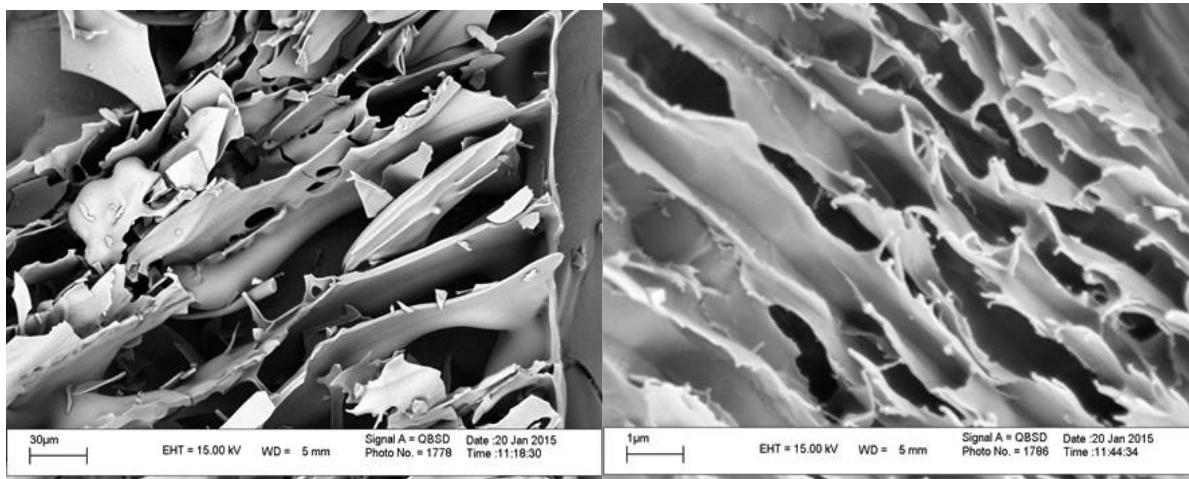


Figure 7. SEM image of AGPVT.

Figure 6. SEM image of HAPVT.

## Conclusions

The present work studies four nitrogen-rich polymer salts based on poly (5-vinyltetrazole) polymer. The compounds were synthesized in three steps. Firstly, the polyacrylonitrile (PAN) polymer was synthesized by free radical polymerization (FRP) approach. In second step, the tetrazole rings were prepared by reaction of nitrile groups and sodium azide. Then, the polynitrogen salts (APVT, HPVT, HAPVT and AGPVT) were prepared by reaction of PVT with ammonia, hydrazinium hydroxide,

hydroxylamine and aminoguanidine bicarbonate, respectively. For make small the size of the mentioned four polymer salts, the polymers were frizzed and dried by the freeze-drying machine. The nitrogen-rich polymer salts indicate a detonation thermal degradation with a release of huge heat.

## Acknowledgments

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Table 1. Thermal behavior of compounds.

Compound	IDT (°C)	PDT (°C)	PDT <sub>max</sub> (°C)
PAN	147	720	912
PVT	141	323	870
APVT	142	233	690
HPVT	146	243	918
HAPVT	146	243	918
AGPVT	143	235	874
m-APVT*	146	242	919
n-HPVT*	147	243	919
m-HAPVT*	148	244	919
m-AGPVT*	146	245	920

\* m and n present the size (micro and nano) of compounds.

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