

Synthesis, characterization and computational study of novel highly heat-resistant nitrogen-rich polymers based on 1H-tetrazole rings

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Abstract: The purpose of this paper was the expansion of new nitrogen-rich, energetic polymers based on tetrazoles. The requirement to the polymers was the suitability as energetic binders. So, the polymers should relieve high thermal and physical stabilities, in order to stabilize the energetic explosive, along with mild to well eruptive characteristics. These nitrogen-rich polymers, obtained by radical homopolymerization of 4-chloromethylstyrene and radical copolymerization of acrylonitrile and 4-chloromethyl styrene with different ratios followed by replacement of all the chlorine atoms of 4-chloromethyl styrene with cyanide ions and formation of tetrazole rings from cyanide groups in dimethylformamide at elevated temperatures. These polymers, obtained in good yields, were characterized by FT-IR and ¹H-NMR spectroscopy; differential scanning calorimeter (DSC) and GPC studies. The advantage of these polymers is that the tetrazole rings are stabilized by the formation of hydrogen bridges of NH-protons. Energy of all nitrogen-rich polymers was calculated by Materials Studio program.

Keywords: Acrylonitrile, 4-Chloromethyl styrene, Nitrogen-rich polymers, Energetic polymers, Heat-resistant energetic polymer.

Introduction

Explosions can be caused by different sources. One type of explosions is chemical explosion [1]. The chemical explosion is a result of the decomposition of molecules evolving gases and heat [2]. In recent years, the growth of the tetrazole chemistry has been significant [3, 4], mainly as a result of the central roles played by tetrazoles in high energetic materials as nitrogen-containing heterocyclic polymers [5]. The tetrazole moiety exhibits a wide and growing number of applications. This nitrogen-rich ring system is used in propellants [6], explosives [7], and pharmaceuticals [8]. Although tetrazoles are a well-investigated group of heterocycles, the number of polymers containing these heterocycles is small. The first polymer based on tetrazoles was 1-poly (vinyltetrazole) and 1-poly

(vinyl-5-amino-1H-tetrazole) [9]. Today, there is a noticeable fondness in polyvinyltetrazoles because of their powerful energetics [10]. The drawback of these polymers is their extremely low solubility in common solvents, holding up them from any usage. Therefore, they are used as copolymers with polystyrene [11]. Despite their high sensitivity towards physical stress, their thermal stability operates these compounds into interesting building blocks for nitrogen-rich polymers [12].

This paper deals with an effective preparation and characterization of the polyvinyltetrazole by the tetrazolation of the cyano groups in the copolymers. In this work, we first synthesized the copolymer of 4-chloromethyl styrene with acrylonitrile by radical polymerization with different ratios followed by replacement of all the chlorine atoms of 4-chloromethyl styrene with cyanide ions. Reaction of

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azide ion with copolymers simultaneously causes the nitrile groups are entirely converted to tetrazole in dimethylformamide at elevated temperatures. Thermal properties nitrogen-rich copolymers were characterized by differential scanning calorimeter (DSC) studies.

Results and discussion

The PTMS homopolymer, PTNSA1 copolymer and the PTNSA2 copolymer are black solid, brown solid powder and sticky black solid respectively. These copolymers are soluble only in dimethylsulfoxide solvent. Replacement of all chlorine atoms of 4-chloromethyl styrene moiety of all polymers in step 2 with cyanide groups was obtained easily in dimethylformamide at elevated temperatures. Stretching vibrational peak of nitrile groups was revealed at 2238 cm^{-1} in FT-IR spectrum. The $^1\text{H-NMR}$ analysis of the copolymers in step 2 wasn't recorded because these polymers were insoluble in DMSO-d_6 and CDCl_3 solvents. Cycloaddition of $\text{C}\equiv\text{N}$ bond of nitriles with sodium azide in the presence of ammonium chloride occurs in step 3 and results in tetrazole derivatives. To increase the yield of reaction and complete conversion, excess sodium azide was used in this work. Analysis of the IR spectra shows that with reaction azide ion with copolymers the band at 2238 cm^{-1} (the stretching vibrations of the nitrile group) disappears. The copolymer compositions were calculated from the $^1\text{H-NMR}$ spectra data. In the past few decades $^1\text{H-NMR}$ spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [13, 14]. The study of composition of polymers shows that monomers reactivity ratios are different and 4-chloromethyl styrene is more reactive than acrylonitrile toward propagating species. Therefore, there is a larger proportion of the more reactive monomer (CMS) in random placement in the copolymers. DSC study was showed the copolymer PTNSA1 was stable under heat because in this nitrogen-rich polymer intra-molecular hydrogen bonds are more.

Conclusion

The energetic polymers were synthesized in 3 steps. The molar compositions showed that 4-chloromethyl styrene is more reactive than acrylonitrile in the copolymers. These polymers showed an explosive thermal degradation together with a release of huge heat and magnitude of heat increased by increases of amount of nitrogen atoms in tetrazole rings of

copolymers, but the copolymer PTNSA1 was stable under heat because of more intra-molecular hydrogen bonds. This nitrogen-rich copolymer can be used as rocket fuel due to its thermal stability.

Experimental

Materials:

The 4-chloromethyl styrene (Aldrich, 90%) and acrylonitrile (Merck) were distilled under reduced pressure to remove inhibitors, before use. The initiator α , α -azobis (isobutyronitrile) (AIBN) (Merck) was purified by crystallization from methanol. The solvents and other reagents were obtained from Merck. All the solvents were distilled and stored over a drying agent.

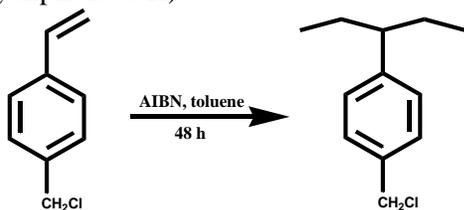
Measurements:

IR spectra were recorded with a Shimadzu FT-IR-408 spectrophotometer as KBr pells. $^1\text{H-NMR}$ spectra were recorded on a Bruker 250 AC spectrometer in CDCl_3 and dimethyl sulfoxide (d_6) as solvents at room temperature. The molecular weights (M_w and M_n) were determined using a Waters 501-gel permeation chromatograph (GPC) fitted with 102 and 103 nm Waters styragel columns. THF was used as an elution solvent at a flow rate of 1 mL/min, and polystyrene standard was employed for calibration. The differential scanning calorimetry (DSC) curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 .

Homopolymerization of 4-chloromethylstyrene: PCMS:

For preparing of homopolymer (PCMS), 2 mL of 4-chloromethylstyrene was dissolved in 10 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 $80 \pm 1\text{ }^\circ\text{C}$ in a water bath, with stirring for about 48 h. To ensure an inert atmosphere and to prevent inhibition effect from oxygen, the ampoule was swept with a continuous flow of argon at least 15 minutes before and during the course of the reaction. The polymerization temperature was well controlled in a water bath. After reacting for 48 h, the ampoule was cooled rapidly to room temperature. Then the solutions were poured from ampoules into cooled methanol. The precipitates were collected and washed with methanol and dried under vacuum to yield (approximately 95%) of homopolymer (Scheme 1). For PCMS: $^1\text{H NMR}$ (DMSO-d_6 , ppm) 1–1.7 ($\text{CH}_2\text{-CH}$), 4.7 ($\text{CH}_2\text{-Cl}$), 5.3–7.5 (Ar-H). FT-IR (KBr, cm^{-1}): 3024–3072 (stretching aromatic C-H), 2850–2923 (stretching aliphatic C-H),

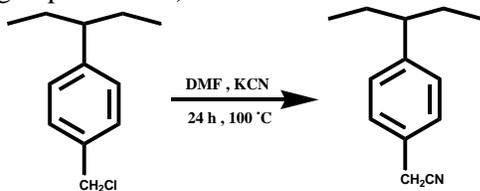
1610-1675 (stretching aromatic C=C), 1420-1509 (bending aliphatic C-H).



Scheme 1: Homopolymerization of 4-chloromethylstyrene.

Reaction of potassium cyanide with homopolymer: PNMS:

The reaction of PCMS with KCN was carried out in a conical bottle equipped with stirrer and reflux condenser. About 5 g of polymer powder and 100 mL of DMF were added to a 250 mL conical bottle with stirring at ambient temperature. Then to the solution, 3 g of KCN was added with stirring. The bottle was immediately placed into an oil bath and heated to 100 °C and maintained the temperature with stirring. After reacting for 24 h, the ampoule was cooled rapidly to room temperature. Then the solutions were poured from ampoules into cooled distilled water for a complete precipitate. The precipitates were collected and washed with diethylether and dried under vacuum to yield (approximately 95%) of PNMS (Scheme 2). For PNMS: ¹H NMR (DMSO-d₆, ppm) 2.5–2.8 (CH₂-CH), 4.7-4.8 (CH₂-Cl), 6.3–7.2 (Ar-H). FT-IR (KBr, cm⁻¹): 3013-3146 (stretching aromatic C-H), 2784-2926 (stretching aliphatic C-H), 2097 (stretching CN), 1655-1687 (stretching aromatic C=C), 1438-1560 (bending aliphatic C-H).

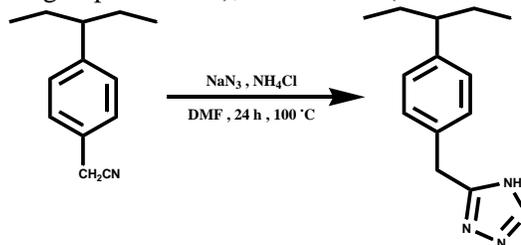


Scheme 2: Replacement of all the chlorine atoms of 4-chloromethyl styrene with cyanide ions.

Formation of tetrazole rings from nitrile groups: PTMS:

The reactions of PNMS polymer with sodium azide and ammonium chloride were carried out in a conical bottle equipped with stirrer and reflux condenser. About 4 g of polymer powder and 80 mL of DMF were added to a 250 mL conical bottle with stirring at ambient temperature. Then to the solution, 2.4 g of NaN₃ and 2.4 g of NH₄Cl were added with stirring. The bottle was immediately placed into an oil bath and

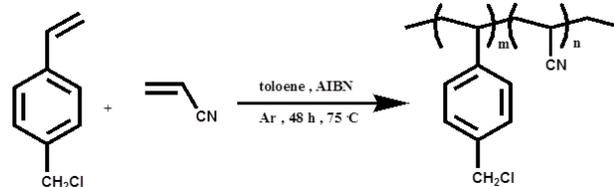
heated to 100 °C and maintained the temperature with stirring for 24 h. After reacting, the ampoule was cooled rapidly to room temperature. The final reaction mixture was added into distilled water for precipitate and also an elimination of DMF. The products obtained were treated in 300 mL of 0.5 M HCl and repeatedly washed with distilled water for a complete removal of Cl⁻, Na⁺ and H⁺. The desired polymer was left to dry in air for several days to constant weight (yield around 95%) (Scheme 3). ¹H NMR (DMSO-d₆, ppm): 1.4–1.7 (CH₂-CH), 4.4 (CH₂-tetrazole), 2.7-3.4 (N-H of tetrazole rings), 6.5–7.4 (Ar-H). FT-IR (KBr, cm⁻¹): 3442 (aromatic C-H and tetrazole N-H), 2924 (stretching aliphatic C-H), 1560–1718 (aromatic C=C).



Scheme 3: Synthesis nitrogen-rich homopolymer.

Copolymerization of 4-chloromethylstyrene with acrylonitrile: PCSA:

For preparing of copolymers (PCSA1 and PCSA2), a mixture of 4-chloromethylstyrene with different amounts of acrylonitrile with molar ratios of 1:1 and 1:2, respectively, was dissolved in 10 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 ± 1 °C in a water bath, with stirring for about 48 h. To ensure an inert atmosphere and to prevent inhibition effect from oxygen, the ampoule was swept with a continuous follow of argon at least 15 minutes before and during the course of the reaction. The polymerization temperature was well controlled in a water bath. After reacting for 48 h, the ampoule was cooled rapidly to room temperature. Then the solutions were poured from ampoules into cooled methanol. The precipitates were collected and washed with methanol and dried under vacuum to yield (approximately 85%) of copolymers (Scheme 4). For PCSA1 and PCSA2: ¹H NMR (DMSO-d₆, ppm) 0.88–2 (CH₂-CH), 4.85 (CH₂-Cl), 6.9–7.7 (Ar-H) (Figure 1). FT-IR (KBr, cm⁻¹): 3085-3026 (stretching aromatic C-H), 2926-2860 (stretching aliphatic C-H), 2239 (stretching CN), 1600-1490 (stretching aromatic C=C).



Scheme 4: Copolymerization of 4-chloromethylstyrene with acrylonitrile.

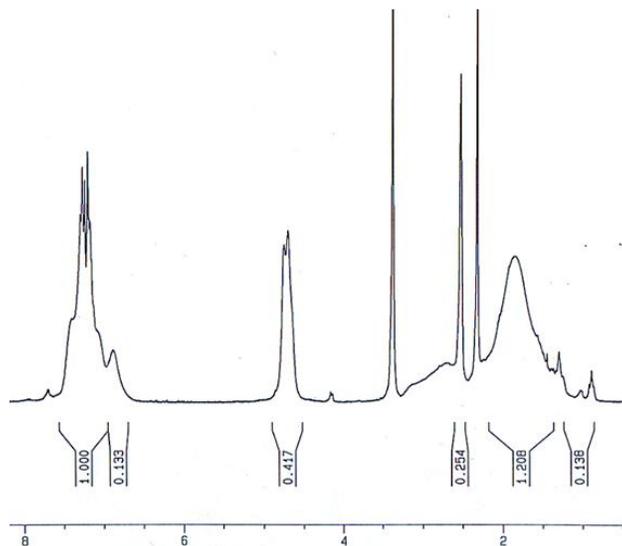
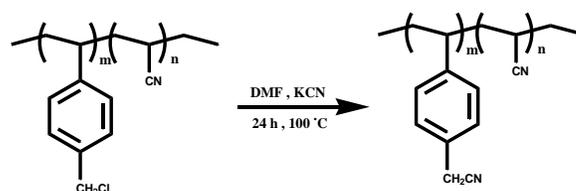


Figure 1: ^1H NMR spectrum of PCSA2 in DMSO-d_6 .

Reaction of potassium cyanide with copolymers: PNSA:

The reactions of copolymers (PCSA1 and PCSA2) with potassium cyanide were carried out in a conical bottle equipped with stirrer and reflux condenser. About 5 g of polymers powder and 100 mL of DMF were added to a 250 mL conical bottle with stirring at ambient temperature. Then to the solution, 1.50 g of KCN was added with stirring. The bottle was immediately placed into an oil bath and heated to 100 °C and maintained the temperature with stirring. After reacting for 24 h, the ampoule was cooled rapidly to room temperature. Then the solutions were poured from ampoules into cooled distilled water for a complete precipitate. The precipitates were collected and washed with distilled water and dried under vacuum to yield (approximately 95%) of copolymers (Scheme 5). The ^1H -NMR analysis of these polymers wasn't recorded because the copolymers (PNSA1 and PNSA2) were insoluble in $\text{DMSO (d}^6\text{)}$ and CDCl_3 solvents. FT-IR (KBr, cm^{-1}): 3421 (stretching aromatic C-H), 2925 (stretching aliphatic C-H), 2238 (stretching CN), 1424–1638 (stretching aromatic C=C).



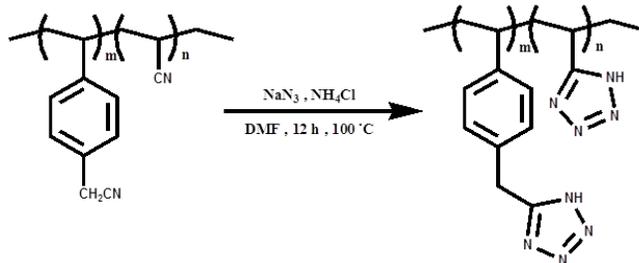
Scheme 5: Replacement of all the chlorine atoms of 4-chloromethyl styrene with cyanide ions.

Formation of tetrazole rings from nitrile groups (PTNSA):

The reactions of PNSA copolymers with sodium azide and ammonium chloride were carried out in a conical bottle equipped with stirrer and reflux condenser. About 4 g of polymers powder and 80 mL of DMF were added to a 250 mL conical bottle with stirring at ambient temperature. Then to the solution, 5.50 g of NaN_3 and 4.50 g of NH_4Cl were added with stirring. The bottle was immediately placed into an oil bath and heated to 100 °C and maintained the temperature with stirring for 12 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 Cl^- , Na^+ and H^+ . The desired polymer was left to dry in air for several days to constant weight (yield around 95%) (Scheme 6). These copolymers (PTNSA1 and PTNSA2) were soluble in

DMSO solvent and ^1H -NMR analysis was recorded. ^1H NMR (DMSO- d_6 , ppm): 1.3–2.3 ($\text{CH}_2\text{-CH}$), 4.1 ($\text{CH}_2\text{-tetrazole}$), 2.7–2.9 (N-H of tetrazole rings), 6.9–8.0 (Ar-H). FT-IR (KBr, cm^{-1}): 3423 (stretching aromatic C-H), 2925 (stretching aliphatic C-H), 2242 (stretching CN), 15190–1686 (stretching aromatic C=C).



Scheme 6: Synthesis nitrogen-rich copolymers.

Molar composition of copolymers:

Tetrazole rings formation in step 3 was obtained by cycloaddition of $\text{C}\equiv\text{N}$ bond of nitriles with sodium azide in the presence of ammonium chloride. To increase the yield of reaction and complete conversion, excess sodium azide was used in this work. In ^1H NMR spectra, tetrazole ring formation by reaction of nitrile groups with azide group, and the peak around 4.1 ppm corresponding to two methylene protons attached to tetrazole ring appeared. In analysis of the IR spectra the band at 2238 cm^{-1} (the stretching vibrations of the nitrile group) disappears.

The copolymer compositions were calculated from the ^1H -NMR spectra data. The ^1H -NMR spectroscopic analysis is a powerful tool for the designation of copolymer compositions. ^1H -NMR spectrum of PCSA2 in DMSO- d_6 is shown in Figure 1. The molar percent of 4-chloromethyl styrene and acrylonitrile in PCSA2

were calculated from the ratio integrated intensities of the peaks around 4.85 ppm, corresponding to two methylene protons of benzyl chloride and the total area between 0.88–2 ppm, corresponding to six protons as to 4-chloromethyl styrene and acrylonitrile. The molar percent of structural units in these copolymers were calculated from Eqs. (1) and (2) where m and n were the mole fractions of 4-chloromethyl styrene and acrylonitrile, respectively.

$$m + n = 100 \quad (\text{Eq. 1})$$

$$\frac{\text{Area at 4.85}}{\text{Area at 0.88-2}} = \frac{2m}{3m + 3n} \quad (\text{Eq. 2})$$

The molar percent of structural units in PCSA1 was calculated by similar method. The compositions of copolymers are demonstrated in Table 1.

The study of composition of copolymers shows that 4-chloromethyl styrene is more reactive than acrylonitrile.

Table 1: Molar composition and GPC data of copolymers.

Copolymer	Molar composition of monomers in the feed (%)	Calculated from the ^1H -NMR (% mole)		Mw	Mn	Mw/Mn
		m	n			
PCSA1 (CMS) $_m$ (acrylonitrile) $_n$	50 : 50	69.2	30.7	22816	10045	2.27
PCSA2 (CMS) $_m$ (acrylonitrile) $_n$	33 : 66	46.4	53.5	18836	9125	2.06

Thermal Behaviour:

In Differential scanning calorimetry (DSC) study of copolymers, as can be seen from Figures 2 and 3, PCSA1 and PCSA2 are completely stable until $320\text{ }^\circ\text{C}$ and $280\text{ }^\circ\text{C}$ respectively, and the decomposition nitrogen-rich copolymer PTNSA2 occurred about $160\text{ }^\circ\text{C}$ which that is due to the fact that tetrazol-rings are

destroyed in this stage, while the copolymer PTNSA1 was stable (Figure 4). With comparing the two copolymers, PTNSA1 and PTNSA2, it is observed that in PTNSA2 with decrease of the benzyl unit percentage, increasing the amount of energy released. The thermal properties of the polymers were

summarized in Table 2, including the initial decomposition temperature of the polymer (IDT), temperature of 20% weight loss of the polymer (PDT) and the temperature at which the maximum decomposition rate occurred for the polymer

(PDTmax). Comparing the polymers shows that the PTNSA1 copolymer is more stable than other polymers. All polymers decompose completely by 900 °C leaving no residue at 950 °C.

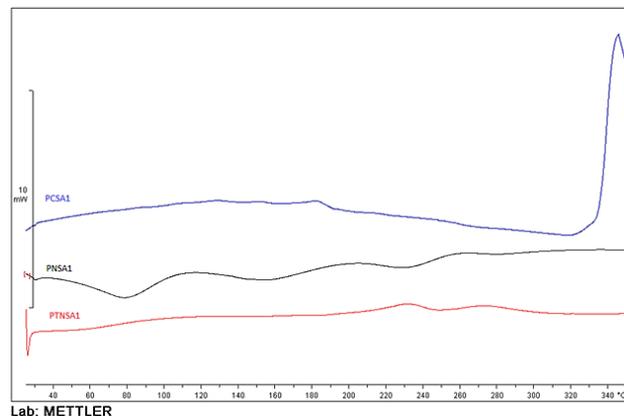


Figure 2: Comparing thermal behavior (DSC analysis) of PCSA1, PNSA1 and PTNSA1.

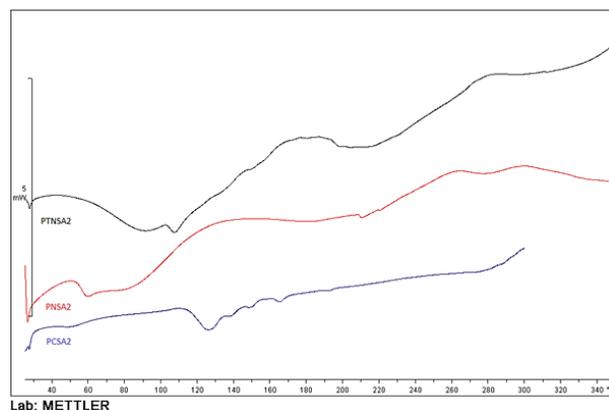


Figure 3: Comparing thermal behavior (DSC analysis) of PCSA2, PNSA2 and PTNSA2.

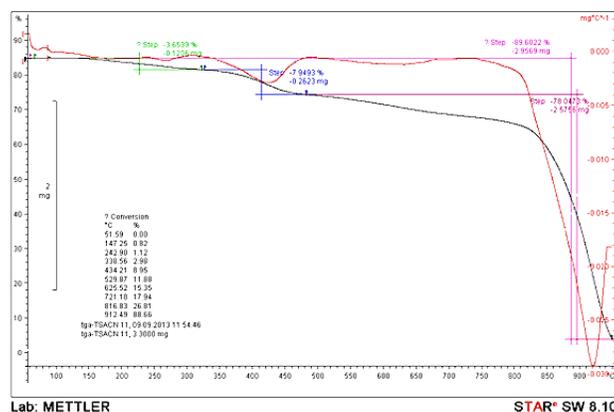


Figure 4: TGA analysis of PTNSA1.

Table 2: Thermal properties of polymers.

Polymer	IDT(° C)	PDT(° C)	PDT _{max} (° C)
PCMS	147	338	910
PNMS	145	337	909
PTMS	148	243	814
PCSA1	146	337	913
PNSA1	146	338	817
PTNSA1	242	817	913
PCSA2	146	337	914
PNSA2	146	336	914
PTNSA2	145	241	913

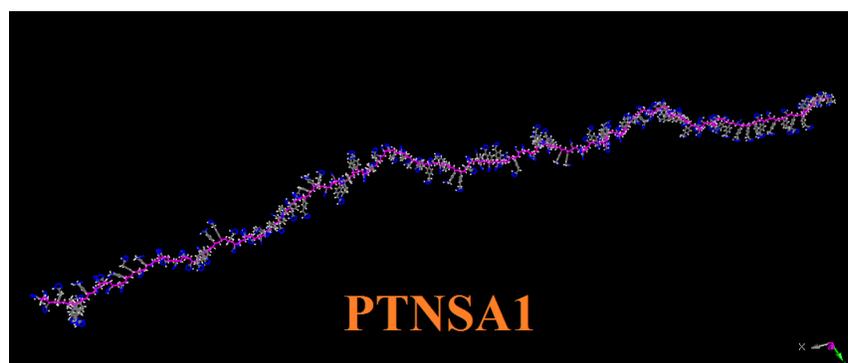
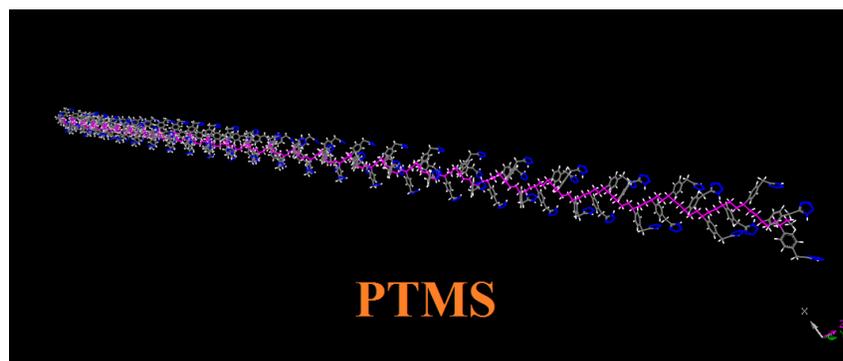
Energy of nitrogen-rich polymers:

All calculations were performed using the Materials Studio 6.0.0 program package [15]. In order to achieve reliable optimized structures for the construction of the amorphous cells, the preliminary molecular mechanical optimizations were carried out on the homopolymer and random copolymers using Forcite module [16-18] and COMPASS force field. The COMPASS is an ab-initio force field which is applicable to both gas and condensed phase and the pertinent parameters within the force field have been validated through dynamical simulations on liquids, condensed phases and polymers [19-21].

For calculation of nitrogen-rich polymers energy, first we considered both linear and non-linear structure of PTNSA1 copolymer (intra-molecular hydrogen bonds are more likely to be more stable). After both structures optimization with Dreiding force field, the linear structure showed greater stability to the non-linear structure (34073.761 kcal/mol). Molecular mechanics calculations on isolated molecules using COMPASS force field indicate the following stability:

PTNSA1>PTNSA2>PTMS

Optimized structures of nitrogen-rich polymers are showed in Figure 5.



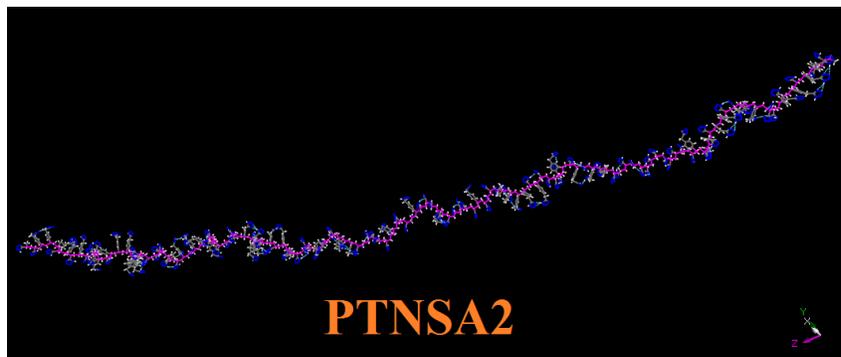


Figure 5: Optimized structures of nitrogen-rich polymers.

The resulting optimized structures were considered as inputs for the Monte Carlo global optimization algorithm of the Amorphous Cell module [22-25] to

produce the germane amorphous cells. Optimized structures of polymers in the solid state are showed in Figure 6.

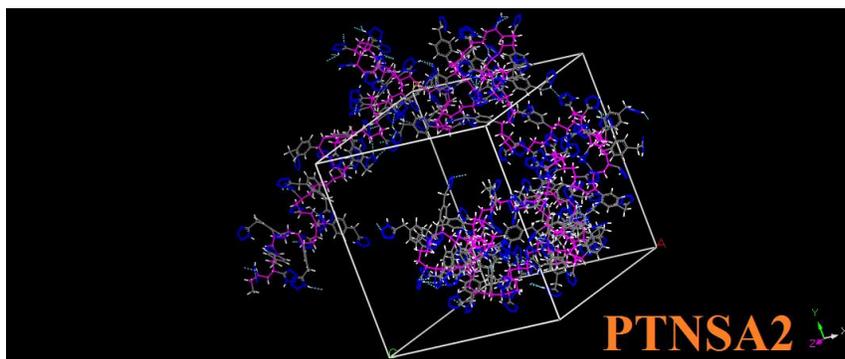
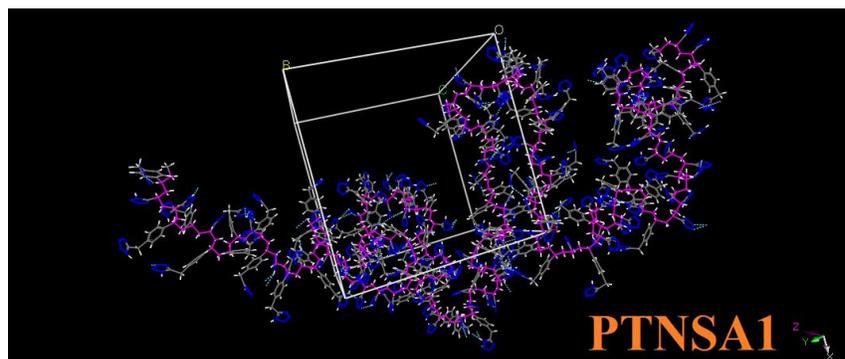
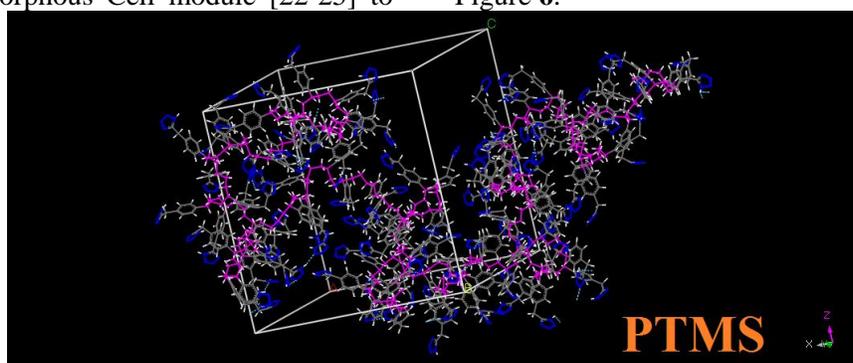


Figure 6: The amorphous cell of the nitrogen-rich polymers.

Sustainable energy in the solid state is also expected to follow the trend:



Energy numerical values obtained from the optimization calculations for both phases using the COMPASS force field were summarized in Table 3. As can be seen, the stability difference in the solid-

state (due to stronger electrostatic interactions) is more than in the gaseous state. It should be noted that the stable structure of the energetic structure is the most negative energy.

The amorphous cell properties of the polymers were summarized in Table 4.

Table 3: Energy numerical values of nitrogen-rich polymers.

Compound phase	Energy (kcal/mol)		
	PTMS	PTNSA1	PTNSA2
Gas state	-3673.4	-5283.9	-4373.6
Energy difference from stable structure in gas state	1610.5	0.0	910.3
Solid state	-6565.0	-8490.1	-6850.2
Energy difference from stable structure in solid state	1925.1	0.0	1639.9

Table 4: The amorphous cell properties of the nitrogen-rich polymers.

Compound	Cell Symmetry	α (degrees)	β (degrees)	γ (degrees)	a (Å)	b (Å)	c (Å)
PTMS	Triclinic	89.9953	90.3278	89.9568	32.2779	32.3157	32.3934
PTNSA1	Triclinic	90.3716	89.7476	90.0551	34.2226	34.4053	34.0621
PTNSA2	Triclinic	88.9887	89.2256	90.1877	31.8739	32.2166	31.9484

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